rec'd 9am - 1-11-83

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

JAN 10 1983

WM Record File 101.1
WM Dir.
WM Dep. Dir.
WMHL
WMUR
Others

MEMORANDUM FOR: Robert Cook, WMHL/NMSS

THRU: Jared J. Davis, Chief, WMB/DHSWM/RES

FROM: Michael B. McNeil, WMB/DHSWM/RES

SUBJECT: SOLUBILITY CONSTRAINTS ON TRU RELEASE IN THE BWIP ENVIRONMENT

The BWIP SCR (Chapter 6, pp 6.4-3ff) asserts that solubility constraints will restrict the maximum possible release rates for Np, Pu, and Am so severely that the 10^{-5} restriction in 10 CFR 60 is satisfied irrespective of waste package failure.

The solubilities of various TRU ions must be consistent with the Pourbaix diagrams for the appropriate elements (since they are based on the same thermochemistry) and so I have given some thought to this question. While at BWIP I examined Pourbaix diagrams for Np and Pu which were being used by Rockwell. These were extremely simple and, even considering that they were for pure water without any ions such as Cl^-, CO_3^{--}, etc., seemed remarkably uncomplex for elements with such a wealth of valence states as TRU's generally show. A brief review of the aqueous chemistry of Pu, for example, reveals that there are four species--Pu^{+3}, Pu^{+4}, PuO_2^+, PuO_2^{++}--on which significant thermochemical data exist, and hydroxyl complexes as well. I could not find data on Pu hydroxyl complexes, but one would assume that they are rather similar to Th hydroxyl complexes, which are quite stable (see National Bureau of Standards Special Publication 270-8, Table 90). While at Hanford I asked that I be supplied with documentation on how these diagrams were developed. This has not been supplied, so I cannot say how these diagrams were prepared, but in no document I have seen does Rockwell describe how they make use of the data from the IAEA/NBS project on Pu Chemistry (the obvious source of critically evaluated data), so I cannot regard their diagrams as convincing. They may have been worked up quite hastily and without adequate consideration of possible complexities.

But even if one believes the basic framework of Rockwell's diagrams, there are further problems. The TRU Pourbaix diagrams are, as I said, for solutions in water where all other ions can be ignored from the point of view of TRU thermochemistry. Now TRU solution complex chemistry is a subject on which I have access to no data at all (the data are probably very sparse), but both U and Th show quite extensive complexing with such ions as Cl^- and SO_4^{--}, so it is reasonable to suppose that the TRU's do as well. Examination of the Pourbaix diagrams for such much-studied elements as Fe and Cu reveals that the introduction of anions which shown a significant tendency to complex will

WM Record File 101.1
WM Project WM-10
Docket No.
PDR ✓
LPDR ✓
Distribution:
(Return to WM, 623-SS)

00154

produce really radical changes in these diagrams, changing solubilities by orders of magnitude. Furthermore, examination of these familiar diagrams shows that small changes in pH and Eh (especially Eh) can often make huge changes in solubility. Rockwell's failure to analyze the sensitivity of their diagrams to such changes is puzzling, considering the doubts about what the Eh and pH of the groundwater are.

I suggest that in our response to the SCR we advise that we do not find the documentation of the statement that solubility limitations on movement of TRU's will satisfy 10 CFR 60 irrespective of waste package and container performance to be entirely convincing, and request that they obtain access to the best available critically reviewed data on TRU thermochemistry (probably through NBS), including complex chemistry, and re-evaluate this claim in the light of these data. It might be suggested that in the case of complex species where data on the TRU's are not available. some effort might be made to estimate the needed data from avaiable data on Th and U (Professor Leo Brewer of LBL/UCBerkely is very good at this sort of thing).

Incidentally (and quite independently of the purely thermodynamic issues addressed above), we should point out that the extreme chemical and thermal inhomogeneity of the system may offer prospects for additional TRU transport by supersaturation and colloid transport. I believe that Rockwell would be well advised to look into this type of transport problem as well.

MBMcNeil

Michael B. McNeil
Waste Managment Branch
Division of Health, Siting,
and Waste Management

cc: R. Wright, NMSS
P. Justus, NMSS
D. Alexander, RES