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APR 14 1995

Lindsay A. Lovejoy, Jr.
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P.O. Drawer 1508
Santa Fe, N.M. 87504-1508

Dear Mr. Lovejoy:

Thank you for your comments on the Hazardous Constituent Source Term Position Paper. Your interest and participation in the Systems Prioritization Method (SPM) is greatly appreciated. Enclosed is the Carlsbad Area Office's response to the questions you have expressed regarding this paper.

(12/14/94)

If you have any questions regarding these responses, please contact George T. Basabilvazo of my staff at (505) 234-7488.

Sincerely,

Michael H. McFadden
Assistant Manager
Office of Regulatory Compliance

Enclosure

cc w/o enclosure:
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Hazardous Constituent Source Term Paper Responses and Questions

1. *The position paper does not state a position. DOE must choose between the vapor pressure limited model and the headspace concentration limited model (or some other model) as a defensible model for SPM purposes and must state its defense of that model.*

Response. Revision 3 of the System Prioritization Methodology Hazardous Constituent Source Term Position Paper selects the headspace concentration limited model and discusses the basis for it's selection.

2. *The vapor pressure limited model specifies that each hazardous constituent is present in quantities sufficient to saturate the gas or brine in the waste region (draft at 2-3). Is this model therefore the more conservative (i.e., releases-enhancing) of two proposed?*

Response. Yes. In fact, the fundamental rationale for selecting the use of headspace measurements over the saturation vapor pressure model is because the vapor-pressure -limited model was overly conservative. The vapor pressure limited concept assumed VOC vapors in equilibrium with an infinite pool of liquid phase VOC source material. Measured headspace concentrations of VOCs are at least two orders of magnitude lower than saturated vapor concentrations indicating that such a concept is unrealistic. Bounding headspace concentrations, calculated based on regulatory limits, are expected to be orders of magnitude higher than weighted VOC concentrations (by TRUCON [Transuranic Package Transporter Model II] code) measured in headspace gas sampling and analysis programs.

3. *Is it correct that the validity of the vapor pressure limited model depends upon the accuracy of characterization data which establishes the inventory of hazardous constituents? How will such inventory be established, given that the presence of hazardous constituents in waste is indicated only qualitatively through process knowledge in the BIR (draft at 5, lines 6-8)?*

Response. The validity of the vapor pressure limited model depends on thermodynamic principles. Please note that characterization of data does

not, by itself, establish the inventory of hazardous constituents. The inventory is established by process knowledge augmented by other aspects of waste characterization.

4. *The vapor pressure limited model has the rationale, inter alia, that headspace measurements do not represent the total mass of hazardous constituents in a waste container (at 3). Given such rationale, can the headspace concentration limited model be defended?*

Response. The Revision 3 paper explains that headspace gas analytical data will be used to define the gas phase source term only. The paper also discusses a number of conservative assumptions made to bound uncertainties about the total mass.

Preliminary calculations show that headspace gas concentrations, from the DOE waste characterization program sampling and analysis, are as much as two orders of magnitude below the saturated concentrations. The difference between measured concentrations and saturated concentrations (calculated) indicates a significant margin of safety that bounds any uncertainty that could be posed by VOCs and semi-volatile organics that could be physically bound to sorptive waste forms.

The only mechanisms which could result in release of additional quantities are post-closure release mechanisms, and the actual impact of these mechanisms on the post-closure source term are uncertain. For example, anoxic corrosion of iron and aluminum based metal alloys will result in corrosion products that will also act as substrates for VOC adsorption. The same is true for degradation products for cement and gypsum based waste materials. Lastly, controlling processes for many release mechanisms in the post-closure time frame are dependent on an assumption that sufficient brine inflow will occur to initiate such mechanisms. It is important to note that performance assessment (PA) modeling will, by design, predict varying degrees of brine inflow. Some realizations will include high values and some will include low values for brine inflow.

5. *The headspace concentration limited model is said to be bounded by measured drum headspace concentrations weighted by waste types (at 3). Is it then correct that the validity of this model depends upon the representativeness of available headspace concentration data and the validity of projections of waste types? Please state the waste types to be used in weighting; at the meeting it was said to be TRUCON codes. Please explain why projections of waste types can be viewed as defensible.*

Response. The Revision 3 paper addresses this concern through the addition of weighting factors for VOC constituents by TRUCON code. The relative defensibility of projections of waste types will appropriately be addressed in other forums through assessing data and information produced by the DOE waste characterization program efforts.

6. *What is the rationale for the conceptual model provision that liquid VOC's and semi-volatiles do not go into solution with brine (draft at 3, lines 45-46)?*

Response. The Revision 3 paper addresses three physical states (liquid, solid, and vapor forms). These forms are still conservatively assumed to exist in sorbed forms relative to cellulose and other potentially sorptive physical forms of waste. Although likely insignificant, the headspace model described in Revision 3 does account for VOCs and semi-volatiles that go into solution with brine as a liquid phase source term parameter.

7. *The draft asserts as a rationale for the headspace concentration limited model that measured drum headspace concentrations in INEL and RFP waste, which is believed to be the most contaminated of all generator sites, are at least two orders of magnitude lower than saturated vapor concentrations (at 4, lines 5-7). Please provide data underlying such statements. Without supporting data the statements cannot be accepted.*

Response. A Table in Revision 3 compares average weighted headspace concentrations to saturated vapor concentrations. The data on the INEL and RFP drum headspace analyses are included in the response letter to your September 8, 1994 letter. These data will also be included in the Disposal Phase No Migration Variance Petition (NMVP).

8. *What "post-closure driving mechanisms" (draft at 4, line 8) have been considered in evaluating whether any such mechanism may elevate VOC concentrations above headspace levels?*

Response. Driving mechanisms expected to occur in the post closure time frame are described in the gas generation and disposal room papers. The actual impacts of processes like corrosion, decomposition/compression of sludges, and microbial degradation on the source term are uncertain. Conservative assumptions defined in the headspace model preclude the need for detailed evaluation.

9. *Please provide the data underlying the statement that VOC's volatilize easily through most waste forms and achieve steady-state rapidly within the drum (draft at 4, lines 10-11).*

Response. The report due from DOE diffusion studies conducted at the Idaho National Engineering Laboratories (INEL) on transuranic (TRU) mixed wastes will be provided to you when final. This report will contain the information you are requesting. Based on preliminary results, steady-state conditions in vented waste containers are observed after periods of from 100 to 200 days. Existing unvented containers have been determined to be at steady-state conditions.

10. *Please justify the statement that VOC data obtained from INEL and RFP waste, while not necessarily representative of the entire waste inventory, are believed to be conservative based on process knowledge (draft at 6, lines 8-10).*

Response. This statement is deleted in Revision 3. This statement is defended by process knowledge documentation in the NMVP.

11. *It is said that headspace data for VOC concentrations exist for nearly 500 drums from RFP and INEL (at 6 line 12). Please identify and provide the data. Without publication of such data it cannot be accepted as factual.*

Response. See response to question # 7. These data will be included in the Disposal NMVP.

12. *Please explain in what way "use of existing headspace data would result in establishing a bounding criteria against which future sampling data would have to be compared." (draft at 6, lines 17-18).*

Response The sentence in quotations above (draft at 6, lines 17-18) refers to the concept of the Performance Based Waste Acceptance Criteria (PBWAC). The conceptual discussion of PBWAC in Revision 3 of the paper also addresses this concern.

13. *It is said that EG&G is conducting a study to establish a relationship between headspace VOC measurements and localized variations in VOC concentrations that may occur in a typical drum of waste (draft at 6, lines 41-43). Please state when the results of the study will be published. Without such study the headspace concentration limited model is not defensible.*

Response The results of the diffusion study at INEL are not yet final. When the results are final a report will be generated and a report will be forwarded to you.

14. *When will the future BIR referred to at draft 7, lines 8-10, be available? Please provide a copy of this document when it is available.*

Response The Baseline Inventory Report (BIR) was completed in mid-March 1995 and will be available for stakeholder distribution in mid April. The DOE will ensure that the Attorney General's Office is on the distribution list.

15. *What studies are planned of potential dewatering through waste compaction (draft at 7, lines 37-38)? Without such data a limitation on free liquids cannot be assumed.*

Response. There are no studies planned to address dewatering through compaction of waste. The Revision 3 paper reasonably dismisses such a phenomena based on consequence and probability for significance, as the number of conservative assumptions in the Revision 3 paper reasonably account for any consequence such a scenario would present. This assumption is also consistent with assumptions in the disposal room paper. Specifically, the DOE reasonably assumes that the process would be one of coupled diffusion/vaporization and would be very slow, and therefore of little consequence.

16. *What studies are planned of degradation of cement-based materials as it may affect VOC concentrations (draft at 7, lines 39-40)? Again, without such studies a limitation of VOC's cannot be assumed.*

Response. Studies related to degradation of cement based materials are not planned. The headspace limited conceptual model and the associated reasonable and conservative assumptions account for any potential impact such a degradation process could have on the overall system.

17. *What studies are planned to quantify hazardous constituents released as polymers and cellulose degrade and metals corrode (draft at 7, lines 43-47)? No limit on hazardous constituents can be assumed without such data.*

Response. Studies to quantify the net release of hazardous constituents from degraded substrates are not planned. The conceptual model accounts for this postulated phenomenon with conservative assumptions.

18. *Will further studies be done of VOC production by radiolysis (draft at 7, lines 48-57)? What studies are planned, and when will they be completed?*

Response. Studies of VOC production through waste constituent radiolysis are not planned. The process is screened on the basis that formation of complex organic molecules are highly unlikely to be a by-product of degradation of relatively simple chains of organic compounds.

19. *Will studies be done to identify the solubilities of liquid and solid hazardous constituents in brine (draft at 8, lines 39-52)? If not, how does the project plan to deal with these factors? In the absence of a project position, the models cannot be accepted.*

Response. The Revision 3 paper details methods the DOE will use to predict the solubilities of hazardous constituents in brine. Concentrations of VOC's and semi-volatiles in brine are governed by the laws of thermodynamic equilibrium between the gas and liquid phases. Henry's Law will be used to calculate the liquid phase concentrations given the gas phase concentrations. Chemical specific parameters for fugacity, Henry's Law constants, etc., are readily available in the literature. Metal constituent concentrations are conservatively assumed to be equal to their maximum solubilities in brine. These concentrations will be estimated using the EQ3/6 geochemical code, or an equivalent.

20. *It does not seem that the project has developed a position as to the means to estimate concentrations of hazardous chemicals in the brine phase in the headspace concentration limited model (draft at 10-12). This position needs to be developed before the model can be endorsed.*

Response. The Revision 3 paper describes the DOE position that will be used to estimate concentrations of hazardous constituents in brine. See response to question # 19.

21. *The draft asserts that credit should be taken for post-closure administrative controls to exclude sealed containers and free liquids (draft at 12, lines 41-42). This position is not acceptable without a demonstration of the effectiveness of such controls. Moreover, there will always be some uncertainty, which must be accounted for in the calculations.*

Response. The effectiveness of DOE's administrative controls implemented through the WIPP WAC have been, and will continue to be demonstrated. Experience at INEL indicates a miscertification rate of 2% for all the WAC criteria (including operational safety and transportation related limits). Free

liquids are not a controlling parameter. The DOE will include an uncertainty analysis in its final NMVP for disposal operations.

22. *Since decomposition and/or compression and degradation processes may elevate VOC's above headspace concentrations, the headspace concentration limited model is not defensible (see draft at 12, lines 44-47).*

Response. As stated previously, the occurrence of, and any impacts that could be attributed to such post closure mechanisms is uncertain. If such mechanisms were to occur, the DOE has reasonably concluded that the potential for significance is minimal, and the other reasonable and conservative assumptions associated with the concept described in Revision 3 of the paper more than account for any potential consequence. See response at AG-4.

DOE used guidance from our regulator to simplify the model using reasonable assumptions. There is precedent for this approach throughout the history of RCRA rulemaking and related legislation. The extent to which any remaining uncertainties affect the outcome of compliance will be identified, and addressed in the long term compliance analysis in the final NMVP for disposal operations.