



Attorney General of New Mexico



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Mr. Steve Zappe
New Mexico Environment Department
Hazardous Waste Bureau
2905 Rodeo Park Drive, Building E
Santa Fe, NM 87505



Dear Mr. Zappe:

The following comments are submitted by the New Mexico Attorney General's Office in response to the notice issued by the permittees U.S. Department of Energy and Westinghouse TRU Solutions LLC (collectively, "DOE") concerning three proposed Class 2 modifications to the Hazardous Waste Act permit issued by the New Mexico Environment Department ("NMED") for the Waste Isolation Pilot Plant ("WIPP"), dated September 28, 2001. The proposed modifications would change certain waste sampling and analysis procedures and quality control procedures in connection with waste characterization.

The Attorney General's Office ("AGO") has reviewed the proposals and requests that NMED deny the modifications in the form submitted for the reasons set forth herein. It should be noted that DOE has stated that it plans to submit several Class 3 modification proposals in December 2001, requesting changes in data management, elimination of solids sampling and analysis, elimination of headspace gas sampling, changes in estimation of material parameter weights, and adoption of digital radiography/computed

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tomography for quality control purposes. Such modifications, if adopted, might render the current proposals moot. In any case, it would make more sense to present and consider the current proposals along with other requests to modify characterization procedures in a combined Class 3 procedure.

1. Item 1: Using composite headspace gas data and compositing up to 20 samples.

The proposal asks to amend the permit to allow use of composite sampling, wherein aliquot portions of a sample are taken from up to 20 waste containers, combined, and analyzed as a unit. Analyses address two needs: The upper 90% confidence level for mean values (“UCL₉₀”) for volatile organic compound (“VOC”) hazardous constituents are compared with a Program Required Quantitation Limit (“PRQL”) to determine whether certain anticipated constituents are present at relevant levels. In addition, hazardous constituents detected by gas chromatography/mass spectrometry methods that are not on the list of target analytes are to be reported as tentatively identified compounds (“TICs”). Further, if such compounds are listed on Appendix VIII of 40 CFR Part 261 and they are detected in 25% of the samples from a given waste stream, they are to be added to the target analyte list for that waste stream.

Addressing the fundamentals of the workability of compositing, DOE asserts that “mean concentrations are equivalent at a 90% confidence level on the mean for up to 20 to 1 composite samples.” (A-5). Further, it is pointed out that the concentrations found in composite analyses are assigned to each individual container used in the composite sample and entered into the WIPP Waste Information System (“WWIS”).

In the existing permit the Waste Analysis Plan requires as follows concerning headspace gas sampling and analysis:

“Headspace-gas samples are used to determine the types and concentrations of VOCs in the void volume of waste containers. Measured headspace VOC concentrations in waste containers received at the WIPP facility will be compared routinely and in accordance with requirements of Permit Attachment N to ensure that, on an annual basis, there are no associated adverse worker or public-health impacts. In addition, VOC constituents will be compared to those assigned by acceptable knowledge, and the Permittees will assign hazardous waste codes, as warranted. This comparison may include an analysis of radiolytically derived VOCs. The Permittees may also consider radiolysis when assessing the presence of listed waste, and whether radiolysis would generate wastes which exhibit the toxicity characteristic. Refer to Permit Attachment B4 for additional clarification regarding hazardous waste code assignment and headspace gas results.” (Att. B at B-10).

The Waste Analysis Plan further explains the purpose of headspace-gas sampling and analysis:

“To satisfy the RCRA regulatory compliance requirements, the following DQOs are established by this WAP:

Headspace-gas sampling and analysis

-To identify VOCs and quantify the concentrations of VOC constituents in the total waste inventory to ensure compliance with the environmental performance standards of 20 NMAC 4.1.500 (incorporating 40 CFR § 264.601(c)), and to confirm hazardous waste identification by acceptable knowledge.” (Att. B at B-19).

It should be noted that waste is characterized by waste steam. See Att. B at B-26, B-29.

Thus, the presence of a given hazardous constituent is determined and reported as to all containers in a given waste stream.

In further detail, Attachment B4, TRU Mixed Waste Characterization Using Acceptable Knowledge, states as follows:

“The Permittees shall require sites to use acceptable knowledge to identify spent solvents associated with each TRU mixed waste stream or waste stream lot. Headspace-gas data will then be used to confirm acceptable knowledge concerning the presence or absence of F-listed solvents and concentration of applicable toxicity characteristic solvents. Sites shall confirm the assignment of F-listed hazardous waste codes (20 NMAC 4.1.200, incorporating 40 CFR § 261.31) by evaluating the average concentrations of each VOC detected in

container headspace gas for each waste stream or waste stream lot using the upper 90 percent confidence limit (UCL₉₀). The UCL₉₀ for the mean concentration shall be compared to the program required quantitation limit (PRQL) for the constituent. If the UCL₉₀ for the mean concentration exceeds the PRQL, sites shall reevaluate their acceptable knowledge information and determine the potential source of the constituent. Sites shall provide documentation to support any determination that F-listed organic constituents are associated with packaging materials, radiolysis, or other uses not consistent with solvent use. If the source of the detected F-listed solvents cannot be identified, the appropriate spent solvent hazardous waste code will be conservatively applied to the waste stream. In the case of applicable toxicity characteristic VOCs and non-toxic F003 constituents, generator/storage sites may assess whether the headspace gas concentration would render the waste non-hazardous for those characteristics and change the initial acceptable knowledge determination accordingly.” (Att. B4 at B4-10, B4-11).

Thus, the relevant data for determination in characterization are mean values as to individual hazardous constituents, determined on a waste stream basis.

It should also be noted that the definition of a waste stream is not rigorously constrained in the permit and may be done on a fairly arbitrary basis. Further, if one or more hazardous constituents, not previously identified, are found in certain containers, those containers may be reclassified as a separate waste stream.

DOE asserts that its technical analysis shows that the “use of compositing results in calculating the UCL₉₀ result in a value that is equivalent to or more conservative than the UCL₉₀ that would have been calculated from individual drum results.” (A-6). To be sure, the proposed procedures specify that all containers assessed in a composite sample shall be from the same waste stream. (A-6).

The question remains whether it is possible that, under the existing system of analyzing separately the headspace gas of each container, different characterization results might be reached. The DOE technical analysis shows the example of cyclohexane, whose UCL₉₀ has a notably higher value in individual sampling than in sampling of a five-container composite. The technical analysis explains that

“a single large value among the remaining very small values (i.e., one half of the detection limit) in the individual container data skews the final results. However, this phenomenon is not significant because it only occurs in cases where there are primarily non-detectable concentrations resulting in UCL₉₀ values that are well below the PRQL, as in this case. Had both of the sets of physical containers that were sampled contained similar concentration ranges in the headspace, the composite and individual container UCL₉₀ values would have been equivalent.” (at 19).

This explanation is unsatisfactory. It seems that a single large value can still lead to a UCL₉₀ value that might in some cases exceed the PRQL, thus requiring that the hazardous constituent be assigned to the waste stream or that a new waste stream be identified for that and similar containers. Nevertheless, under composite sampling, the value for the individual container would be submerged in the average value. In other words, composite sampling would not achieve the same substantive result as the current system.

It must be kept in mind that headspace gas sampling is to be used here to confirm the results of characterization based upon acceptable knowledge. The assumption is that the acceptable knowledge is basically reliable but can usefully be confirmed. In such situation, the effectiveness of the confirmation methods should not be compromised, as would the suggested compositing procedure. The proposal should be rejected.

Headspace gas analysis is also used to identify TICs. The identification of TICs is not done on a waste-stream basis but by individual container. Permit requirements as to TICs are as follows. The Waste Analysis Plan requires:

“Sampling protocols, equipment, and QA/QC methods for headspace-gas sampling are provided in Permit Attachment B-1. In accordance with EPA convention, identification of hazardous constituents detected by gas chromatography/mass spectrometry methods that are not on the list of target analytes shall be reported. These compounds are reported as tentatively identified compounds (TICs) in the analytical batch data report and shall be added to the target analyte list if detected in a given waste stream, if they appear in the 20

NMAC 4.1.200 (incorporating 40 CFR § 261) Appendix VIII, and if they are detected in 25% of the samples from a given waste stream. The headspace gas analysis method Quality Assurance Objectives (QAOs) are specified in Permit Attachment B3.” (Att. B at B-10).

Attachment B3 specifies as follows:

“In accordance with SW-846 convention, identification of compounds detected by gas chromatography/mass spectrometry methods that are not on the list of target analytes shall be reported. Headspace gas, volatile analysis (TCLP/Totals), and semi-volatile (TCLP/Totals) shall be subject to tentatively identified compound (TIC) reporting. These TICs for GC/MS Methods are identified in accordance with the following SW-846 criteria:

* * *

TICs that meet the SW-846 identification criteria, are detected in 25 percent of all samples from a given waste stream, and that appear in the 20 NMAC 4.1.200 (incorporating 40 CFR § 261) Appendix VIII list, will be compared to acceptable knowledge data to determine if the TIC is a listed waste in the waste stream. TICs identified through headspace gas analyses that meet the Appendix VIII list criteria and the 25 percent identification criteria for a waste stream will be added to the headspace gas waste stream target list regardless of the hazardous waste listing associated with the waste stream. TICs reported from the Total VOC or SVOC analyses may be excluded from the target analyte list for a waste stream if the TIC is a constituent in an F-listed waste whose presence is attributable to waste packaging materials or radiolytic degradation from acceptable knowledge documentation. If a listed waste constituent TIC cannot be attributed to waste packaging materials, radiolysis, or other origins, the constituent will be added to the target analyte list and new hazardous waste codes will be assigned, if appropriate. TICs subject to inclusion on the target analyte list that are toxicity characteristic parameters shall be added to the target analyte list regardless of origin because the hazardous waste designation for these codes is not based on source. However, for toxicity characteristic and non-toxic F003 constituents, the site may take concentration into account when assessing whether to add a hazardous waste code. If a target analyte list for a waste stream is expanded due to the presence of TICs, all samples collected from that waste stream will be analyzed for constituents on the expanded list.” (Att. B3, at B3-5, B3-6).

The proposed modification seeks to qualify the identification of TICs—imposing the limitation that the TIC have a response that is a minimum of 10% of the area of the nearest internal standard. (A-8). This condition has not previously been a part of the

permit (although it is asserted that it was contained in a “Clarification” issued by the Carlsbad Field Office; A-6, A-8).

Further, in support of the proposal to use composite samples, DOE proposes that at various levels of dilution of individual samples the percentage level be ratably reduced; thus, 2% for up to five samples, 1% for up to ten samples, and 0.5% for up to 20 samples. (A-8, A-9). DOE states that the detection standards proposed for identification of TICs in composite samples are achievable:

“The automated software in use at generator/storage sites was evaluated to ensure that the reporting levels proposed below are achievable. The software allows a minimum value of 0.1% to be entered for the area of the TIC relative to the nearest internal standard. The minimum value proposed for any reporting level is 0.5%; therefore, all of the proposed reporting levels are achievable.” (A-8).

However, these assertions are not supported by data. The assertion of the capability of software addresses a complex question of detectability of highly diluted constituents. The Technical Evaluation of Headspace Gas Compositing (Aug. 2001) supplied with the proposal states that a TIC would be detectable at the lowest level required by the program (referring to Table B3-2), if present in 25% of samples composited. (at 30). However, detection of TICs present in 25% or more of the containers is not the only requirement of the Waste Analysis Plan. TICs present in any one container and identified (based on the test of 10% of the nearest internal standard or a similar test) are required to be reported even if not present in 25% of containers. The compositing of samples has not been shown to permit such reporting.

It should be recalled that the system of identifying TICs found in the existing permit was adopted over DOE’s different and lesser proposal, the Hearing Officer stating that a more stringent identification process was required by law:

“32. Permit conditions II.C.3.k and II.C.4, and associated language regarding TICs, are conditions necessary to protect human health and the environment by requiring identification and characterization of hazardous waste, such as headspace gas components, volatile organic compounds, and semi-volatile organic compounds, that could be emitted to the air during management, storage, or disposal of waste at WIPP. 20 NMAC 4.1.900.A.8 and NMSA 1978 § 74-4-4.2(c)(Repl. Pamp. 1993).

33. The TIC process proposed by Applicants in the Part B permit application was deficient because it failed to ensure that all applicable waste codes would be applied to a hazardous waste, as required by 20 NMAC 4.1.200 (incorporating 40 CFR §§ 261.20(b) and 261.30(c)).

34. The TIC process proposed by Applicants in the Part B permit application was deficient because it might allow Applicants to manage, store, or dispose improperly characterized hazardous waste, as prohibited by 20 NMAC 4.1.500 (incorporating 40 CFR § 264.13(a)).

35. The TIC process proposed by applicants in the Part B permit application was deficient because it did not provide data necessary to monitor and prevent releases to the air, as required by 20 NMAC 4.1.500 (incorporating 40 CFR § 264.601(c)).

36. Permit Conditions II.C.3.k and II.C.4, and associated language regarding TICs, are conditions necessary to ensure the Applicants do not dispose hazardous waste without identifying all applicable hazardous waste codes, as required by 20 NMAC 4.1.200 (incorporating 40 CFR §§ 261.20(b), 261.30(c)).

37. Permit Conditions II.C.3.k and II.C.4, and associated language regarding TICs, are conditions necessary to ensure the Applicants obtain a detailed chemical analysis of the waste, as required by 20 NMAC 4.1.500 (incorporating 40 CFR § 264.13(a)(1)).

38. Permit Conditions II.C.3.k and II.C.4, and associated language regarding TICs, are conditions necessary to ensure that Applicants develop and follow a written waste analysis plan which describes the waste analysis procedures, including the parameters for analysis of each hazardous waste; the test methods that will be used to test for these parameters; and the sampling method that will be used to obtain a representative sample of the waste to be analyzed, as required by 20 NMAC 4.1.500 (incorporating 40 CFR § 264.13(b)(1), (2), (3)).

39. Permit Conditions II.C.3.k and II.C.4, and associated language regarding TICs, are conditions necessary to achieve compliance with the hazardous waste act and regulations specified at 20 NMAC 4.1.200 & 500 (incorporating §§ 261.20(b), 261.30(c), 264.13(a)(1), (b)(1), (2) & (3), 264.601(c) & 264.602), as required by 20 NMAC 4.1.900 (incorporating 40 CFR § 270.32(b)(1)).

40. No Party or commentor has met their burden in challenging NMED's determination to impose permit conditions regarding TICs by presenting substantial evidence that this condition is unreasonable or inconsistent with the HWA. *See* 20 NMAC 4.1.901.E.6; 20 NMAC 1.4.401.A." (Hearing Officer's Report at 95-96 (Sept. 10, 1998).

With this record, NMED cannot authorize modification of the permit to impose a lesser standard, based on unsupported assertions as to complex scientific and engineering issues. The use of composite samples cannot be allowed until its compatibility with procedures for reporting of TICs is established.

2. Item 2: Establishing Safety Conditions for Visual Examination (VE) of Waste Containers.

Permittees also request a modification to allow generator/storage sites to establish conditions upon the selection of waste containers for visual examination ("VE") based upon the asserted safety hazards presented by certain containers. VE is used to confirm the results (*i.e.*, waste matrix code and waste material parameter weights) of radiography examination of the contents of waste containers. The proposal does not specify the safety criteria and simply states that they must be based on "characteristics of the waste and the site-specific operational safety requirements for VE." (A-22).

This proposal should be rejected. The purpose of VE here is to verify the effectiveness of radiography in determining waste matrix code and waste material parameter weights. The method selected is the sampling of a certain percentage of "randomly" (Att. B2 at B2-2) selected containers. Clearly, once new conditions are placed upon the selection of containers, the containers subject to VE are no longer "randomly selected." (A-22). The established system of determination of a historical error rate and derivation of a number of containers to be sampled based on that rate

assumes that the containers examined will be *randomly* selected. Once that assumption is negated, the verification system is no longer valid.

The proposal fails to state what new grounds of selection will be employed. It places no real restriction upon sites' decisions to adopt new selection criteria. It is clearly possible that criteria adopted by some sites may bias the selection of containers so as to invalidate the confirmation process. Certain conditions might be deemed to present a safety hazard, which also tend to make radiography more difficult, so that the containers presenting a particular risk of mischaracterization would not be subject to VE. One may not speculate as to such situations, but certain debris waste of high opacity might also have sharp edges and be excluded from VE. Or a site might deem its procedures unsuited to visual examination of containers with Pu238 waste, which might also need special examination for liquids or sealed containers. There is no showing that the new—indeed, essentially unstated—conditions to be put upon VE will not affect the validity of the confirmation process, and in the absence of such a showing the modification should be denied.

3. Item 3: Taking Samples of Headspace Gas through Existing Filter Vent Holes.

Permittees also seek to modify the permit to allow sampling of headspace gas through existing filter vent holes or through a self-tapping screw with a septum, rather than through the filter vent itself or through a hole punched in the drum lid. The currently authorized methods provide that during sampling the filter shall be sealed to prevent outside air from entering the drum and diluting or contaminating the sample and that an airtight seal shall be maintained. (B1-7). The proposed modification, as to replacing the filter, would permit the filter body to be removed and “replaced as quickly

as is practicable with the airtight sampling apparatus.” (A-30). Thus, the proposal would allow the container to stand unsealed without a filter for the length of time needed to install the sampling apparatus. That time is not quantified by the language of the proposal.

Discussion at the public meeting in Santa Fe indicated that the sampling problem essentially involves pipe overpack containers, which have a thicker-walled construction than 55 gallon waste drums. The 55 gallon drums can effectively be tapped using a self-tapping screw with a septum under another provision in the proposal, which does not allow the container to stand unsealed. Thus, the AGO proposes that the allowed modifications be limited to (a) use of a self-tapping screw to penetrate a 55 gallon drum and (b) use of a gas tap affixed to the filter vent fixture in the case of pipe overpacks. Further modification seems unnecessary.

Accordingly, this Office respectfully suggests that NMED deny the proposed modifications, except as stated with regard to Item 3. Further, NMED should advise DOE that, should items 1 and 2 of the proposal be submitted with additional data support, they shall be considered under Class 3 procedures along with other forthcoming proposals for modification of characterization procedures.

Very truly yours,



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