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Juliet – copy to Steve, [redacted] original to my file

via fax 505-827-4440, 8 pages

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July 7, 1998

Review of Documents Relating to the Proposed Shipments of LANL TA-55-43 Wastes to the Waste Isolation Pilot Plant

Dear Mr. Fettus;

On June 5, I provided you with the above referenced report, which I co-authored with Hisham Zerriffi, as well as with my declaration in this matter. Over the last few weeks, we received more documents that you obtained from the Department of Energy (DOE). I have also received the initial review of the New Mexico Department of the Environment (NMED) that appears to have been based on the same set of data that was made available to IEER during the preparation of our report.

In a June 17, 1998 letter by NMED Secretary Mark E. Weidler to Governor Johnson, NMED concerns were summarized as follows:

> "NMED staff concluded that the LANL waste stream was inadequately characterized on numerous grounds including the following:
> (1) the "process" for characterization was incomplete and substantially deviated from AK requirements;
> (2) there was no validation of acceptable knowledge, a minimal requirement for use of the AK process; and
> (3) there was no chemical analysis of any constituents."

I note that the NMED's determination concurs with our finding that the waste stream labeled for shipment to WIPP is insufficiently characterized to allow it to be treated as non-hazardous under RCRA. Our analysis showed that it is more likely than not that part of the waste would be considered hazardous under RCRA regulation because it exhibits the following characteristics of hazardous waste: corrosivity, toxicity and

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reactivity. In addition, we found flaws in the documentation of the waste Los Alamos National Laboratory (LANL) proposes to ship that are substantial enough to invalidate LANL's claim that it has "Acceptable Knowledge" that the wastes are not hazardous. Our report pointed out that only a chemical analysis could provide conclusive data that allows evaluation of the corrosivity, toxicity and reactivity of the waste stream.

You asked us to review our determination in light of the additional information received. Assisted by Hisham Zerriffi, I have conducted such a review. We have organized our comments according to the Flow Chart entitled "Process for Characterization and Certification of Waste Stream TA-55-43, Lot No. 01". Our comments are attached.

We conclude that the additional documents do not contain information that would change our original conclusions. We actually found further flaws in the documentation of the waste LANL proposes to ship as well as further evidence that it is more likely than not that part of the waste would be considered hazardous under RCRA regulation because it exhibits the following characteristics of hazardous waste: corrosivity, toxicity, reactivity and ignitability. In addition, the new documents suggest the following:

- Based on calculations by Kosiewicz (TWCP-1211), the waste stream is likely to fulfill the RCRA criterion for ignitability because the acetone concentration in void volume, at least in part of the waste, could exceed the lower flammability limit of 2.5%.
- TWCP-1211 also contains a review of data on radiolysis that is in general agreement of IEER's use of the data; thus indirectly corroborating the findings on radiolysis expressed in our June 5, 1998 report.
- The visual inspection of several drums resulted in a finding of corrosion (interior of drum #55683, inner cans in drum #55431 rusted through, unknown rust colored powder found in drum #55476), supporting our finding in our June 5, 1998 report.
- Given the number of differences between the Visual Examination (VE) and the Real-Time Radiography (RTR) as evidenced by the number of Nonconformance Reports (NCRs) issued, it would seem prudent for LANL to conduct further VE of other drums. This is especially important since the visual examination conducted during repackaging of drums indicated numerous significant problems including the presence of sealed containers that are greater than four liters (which are not accepted under the WIPP WAC). For example, drum 55403 contained sealed six liter containers.
- We find the documentation still incomplete. Updated waste drum packages with complete information have not been provided to address our concern over missing documents and incomplete information. As noted in our original report, in addition to improper documentation, the procedure for testing pH of rags was not followed.

You will find further details of our review in the enclosed attachment. Please do not hesitate to contact me if you have any questions or comments.

Sincerely,

Bernd Franke
Executive Director

Encl.

Comments on Documents for Process for Characterization and Certification of Waste Stream TA-55-43, Lot No.01

By Bernd Franke and Hisham Zerriffi

Pu-238 Analysis at SRS (TWCP-1044): We have no comment on the determination of the Pu-238 initial feedlot as being non-RCRA.

Pu-238 re-Analysis at LANL (TWCP-1025,26,30): We have no comment on the determination of the Pu-238 initial feedlot as being non-RCRA.

Separation of Pu-238 processing (TWCP-1042, 934): We have no comment on the assertion that Pu-238 processing was kept separate from other TA-55 activities even though this may have been difficult at times.

LANL Waste Profile Form (WPF) approval to generate waste: The WPF is supposed to be in the generator's drum package. As noted in our previous report a number of WPFs were missing the second page. The recent documents provided by LANL do not appear to address the missing information. Furthermore, the original waste profile forms for repackaged drums have not been provided by LANL.

Pu-238 waste generated and packaged according to TA-55 procedures (TWCP-700 and other waste management procedures referenced therein): Many of the documentation problems outlined in our original report indicate that procedures were not followed completely. Examples include missing documentation and improperly completed forms (e.g. many of the Waste Origination and Disposition Forms). Updated waste drum packages with complete information have not been provided. As noted in our original report, in addition to improper documentation, the procedure for testing pH of rags was not followed.

Pu-238 waste stored in Area G and retrieved for further characterization:
No comment at this time.

Acceptable Knowledge Summarized for 5 waste streams (TWCP-1042): Our June 5, 1998 report contains a detailed discussion of problems related to the use of Acceptable Knowledge, particularly on the issue of radiolysis.

TA-55-43 Lot No.1 selected for certification and shipment to WIPP (TWCP-597): This lot supposedly contains 36 drums. As noted in our previous report, five of these drums are filled with filters and should thus not be not be included in the TA-55-43 waste stream. They are, by LANL's definition in their Acceptable Knowledge Summary Report (TWCP-1042) part of the TA-55-47 waste stream. This issue continues to remain unaddressed.

RTR performed on every drum to confirm material content of drum (LA98-3.2.1-014 and 015, TWCP-1109 and 1110): According to the Process flow diagram the RTR confirmed the absence of lead and other prohibited items. It should be noted that the RTR actually resulted in a number of NCRs being issued. For example, TWCP 1110 covers the RTR for eighteen drums (plus a second RTR on each of two drums). Ten NCRs were issued as part of TWCP-1110, nine of which were for the presence of sealed containers greater than four liters. The RTR did not detect these prohibited items. As a result a CAO Corrective Action Report was issued and the RTR operators were re-trained. See below for more discussion on the issue of sealed containers and the WIPP Waste Acceptance Criteria.

Reconcillation of RTR results with AK information (TWCP-1217): RTR results were not corroborated by visual examination (see below). Thus, even if RTR results were reconciled with AK information, this would be of little merit.

Visual Examination (VE) performed for QA of RTR Activities for five drums (LA98-3.4.1-001, TWCP-1205): Various discrepancies were discovered by LANL between the Visual Examination and the RTR. For example, only two of the five drums were assigned the same Waste Matrix Parameters (Sheet 5, p.1). A second example is assignment of TRUCON sub-codes. A comparison of TRUCON sub-codes assigned by Visual Examination, RTR and AK showed none of the five drums were assigned the same code by all three methods. The RTR assigned code never matched the AK and the VE assigned code only matched the AK on two of the five drums. Another problem identified was poor agreement on the volume. This was apparently due to the voltage settings during RTR.

Another issue discovered by the VE is that sealed containers greater than 4 liters were being identified in the RTR as ≤ 4 L (see NCR 98-077). The WIPP Waste Acceptance Criteria do not allow these containers. According to the Nonconformance Report a temporary measure of removing the tape from the cans was undertaken since no guidance on how to deal with this issue was given from CAO or WIPP to the TWCP and then to the generator. It should be noted that we have not been given the opportunity to review the videotapes of the VE. These videos would be useful in assessing the effectiveness of the VE procedure (despite the fact that a number of problems exist with the videotapes; such as being off subject and the taping over of some videotapes by subsequent Visual Examinations).

Given the number of differences between the VE and the RTR as evidenced by the number of NCRs issued, it would seem prudent for LANL to conduct further VE of other drums. This is especially important since the visual examination conducted during repackaging of drums indicated numerous significant problems, including the presence of sealed containers that are greater than four liters (which are not accepted under the WIPP WAC). For example, drum 55403 contained sealed six liter containers. There is therefore direct evidence that drums not included in the VE for purposes of RTR comparison might not meet the WIPP WAC.[1]

[1] It should be noted that the original logbook (#VE-197) for both the VE and the repackaging is the same and the work appears to have been conducted by the same personnel. The information gained from repackaging, however, was not used in comparing VE with RTR.

The VE data also shows evidence found of corrosion on both individual metal cans and on the drum interior:

- Drum #55431: "Some inner cans rusted through w/small pits" (VE 197, p. 31)
- Drum #55683: "Light corrosion all over" noted for the interior of drum (VE 197, p. 34)
- Drum #55476: Item#8: "unknown rust colored powder ~30cc looks like rust or sand (very fine like silt)" (VE 197, p. 55)

Head Space Gas analysis performed on each of the 36 drums (TWCP 1108 and TWCP-1211):

TWCP-1211 is a nine-page document entitled "Analysis of Literature Review on Radiolytically Generated Volatile Organic Compounds" by Stanley T. Kosiewicz, dated June 8, 1998. It is the only document in the entire new set of documents that specifically addresses the question of radiolysis that IEER reviewed in detail. The document by Kosiewicz reviews, among others, two publications that IEER relied on in its numerical determination of the amount of radiolytical degradation products:

- Reed D.T. and Molecke M.A. (1994). Generation of Volatile Organic Compounds by Alpha Particle Degradation of WIPP Plastic and Rubber Material. Mat. Res. Soc. Symp. Proc. Vol. 333, pp. 233-240 (Kosiewicz reference No. 12, quoted as Reed D.T. without mentioning the co-author)
- Arakawa K., Seguchi T., Yoshida K. (1986). Radiation-induced gas evolution in chlorine-containing polymer. Poly(Vinyl chloride), chloroprene rubber, and chlorosulfonated-polyethylene, Radiat. Phys. Chem. Vol. 27, No.2, pp.157-163 (Kosiewicz reference No. 11)

Kosiewicz stresses the particular importance of the paper by Reed and Molecke "because it focused on the potential for alpha radiolysis to generate VOCs." On page 3 of his report, Kosiewicz correctly points out that

> "calculations were not done to estimate the mass balance between gaseous phase and solid materials. In addition, the test chambers were not checked for surface adsorption of evolved VOCs. Since this artifact would reduce the concentration of VOCs in the gas phase, it is speculated that the concentration of VOCs measured in these experiments are probably lower than what was really generated."

The limitation of the Reed and Molecke data to gaseous VOCs, thus neglecting solid phase VOCs was also observed on page 7 of IEER's analysis of their paper. IEER estimated the G value for benzene (number of benzene molecules per 100 eV of absorbed radiation) to be ~0.00062. We did this on the basis of reported G values for hydrogen and the relative concentrations of hydrogen and benzene in the gas phase. In preparation of the report, Bernd Franke had an e-mail exchange with Drs. Reed and Molecke in which some background information about the paper was requested. Taking hydrogen formation from polyethylene in N_2 as an example, the discrepancy by the reported hydrogen concentration (0.005 mg) and the one calculated using the G-value (0.14 mg), had to be resolved – a factor of 28 difference. The question, posed to the authors, was whether the volume in the experimental vessel of gas was diluted before analysis. In his reply on June 1, 1998, Reed promised to look into this matter but has

not provided any information to date. From Appendix A in the paper by Koslewicz (based reference 21, a June 1998 personal communication of Kosiewicz with Reed), it appears that the puzzle can be solved easily: the irradiation cell with a volume of ~10 cm^3 was placed into a reactor vessel of ~300 cm^3. Therefore, the gaseous concentration had to be multiplied with a total volume of ~300 cm^3. Despite the limited information in the paper by Reed and Molecke, the G value for benzene was correctly calculated by IEER by using the reported G value for H_2 and the reported concentrations of H_2 and benzene.

Kosiewicz did not provide a quantitative analysis of the amount of benzene produced by radiolysis even though this could be easily done using the data from Reed and Molecke's paper. Using the assumptions in Kosiewicz's scenario and a G value for benzene of ~0.0006, the amount of benzene in a TRU waste drum in 6 years is calculated to be ~43 mg per kg of waste[2]. This concentration exceeds the RCRA TCLP criterion for benzene of 10 mg/kg of waste material.

Kosiewicz focused on the calculation of the amount of acetone produced[3] and concluded that an acetone concentration in a waste drum after 6 years is estimated to be in the range of 12,000 ppmv (1.2%) to 620,000 ppmv (62%). The lower and upper flammability limits of acetone at atmospheric pressure and room temperature are 2.5% and 12.8%, respectively.[4] It therefore appears likely that at least part of the waste would exhibit the RCRA characteristic of the ignitability which is defined as follows in 40CFR261.21:[5]

(a) A solid waste exhibits the characteristic of ignitability if a representative sample of the waste has any of the following properties:
(...)
(2) It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.

Headspace analysis of the TA-55-43 waste drums indicates the presence of acetone (above the minimum detection limit of 21 ppmv) in 25 out of 36 drums for which data was supplied. The concentrations found in the headspace range from 26 to 150 ppmv. The maximum concentration found of 150 ppmv (0.015%) is below the lower flammability limit. Given the multiple types of packaging (many sealed with tape), it is reasonable to assume that only a fraction of the acetone generated by radiolysis would actually make its way into the headspace. On the basis of the calculations provided by Kosiewicz, it is likely that the acetone concentration in at least part of the waste is in the flammability range. It is therefore likely that at least part of the waste exhibits the

[2] In Appendix B to TWCP-1211, Kosiewicz uses a scenario in which a drum is filled with 10 kg of combustible material and contains 1 g of heat source grade Pu-238. In 6 years the energy deposited in the waste is 5.5×10^{26} eV. If a G value for benzene of 0.0006 (molecules per 100 eV) were used, the total production of benzene is calculated to be 0.0055 mole (430 mg).
[3] TWCP-1211, Appendix B
[4] Quick Guide - a computerized version of the NIOSH Pocket Guide to Chemical Hazards, DHHS (NIOSH) Publication No. 90-117, version 3.0, 1994
[5] 45 FR 33119, May 19, 1980, as amended at 46FR 35247, July 7, 1981; 55 FR 22684, June 1, 1990

characteristic of ignitability. Only a careful, complete waste analysis can provide a conclusive answer.

Kosiewicz also reviewed the paper by Arakawa et al. (1986) that IEER used to infer the amount of HCl produced by radiolysis. Kosiewicz did not use the data provided by Arakawa et al. to perform a quantitative analysis of the amount of HCl formed.

Comparison of Gas Analysis with PRQL and reconciliation with AK information (TWCP-1108): The AK does not provide numerical estimates on radiolytic degradation products such as benzene, acetone, and HCl. Gas analysis demonstrates the presence of acetone and benzene.

Repackage Drums in TA-55-43 Lot No. 1 to meet thermal limits (LA98-RPK-001, TWCP-1215): LANL has provided new information about the repackaging of drums from the TA-55-43 waste stream. These documents concern the repackaging of drums in order to meet the thermal limits in the WIPP Waste Acceptance Criteria. However, the documentation does not address the concerns raised in our report of June 8, which concerned a different repackaging operation, so far as we can determine. Table 1 shows the repackaging of drums as determined from the waste drum data packages used to prepare our original report.

Table 1

Original Drum Number	Re-packaged Drum Number in drum data packages
LA24007	LA55400
LA24077	LA55401
LA24297	LA55403
LA24536	LA55406
LA25738	LA56019

Table 2 is reprinted from LANL repackaging report of either 5/26/98 or 6/10/98 (both dates are on the document) and are the drums recently repackaged to meet the WIPP WAC and which have been packed in Standard Waste Boxes (SWB).

Table 2

Repackaged SWB Number	Repackaged Drum Number	Original Drum Number
	57032	55403
57033	57033	55403
	57035	55403
	57022	55476
57023	57023	55476
	57051	55695
57200	57200	55695
	57201	55695
	57202	55695
	57028	56053
57029	57029	56053
57030	57030	56053
	57031	56053

Comparing these two tables it is easy to see that the questions about repackaging operations we raised in our report have not been resolved. Table 2 concerns a different repackaging and renumbering operation. Note however that Drum 24297 was repackaged as drum 55403, which was then split into three separate drums (57032, 57033, and 57035).

Assign new TRUCON codes based on repackaging and confirm other information (TWCP-1216): The repackaged drums have been assigned TRUCON code LA-125A which corresponds to the TA-54 Size Reduction Facility. No documentation has been provided concerning the TRUCON code issues discussed in our original report. These issues remain to be resolved for those drums not being repackaged.

However, it is not clear that LA-125A is the appropriate TRUCON code for this waste. The LA-125A TRUCON code is associated with metal waste (and associated combustibles) from the TA-54 Size Reduction Facility (SRF) which dismantles and packages "mostly gloveboxes, process equipment, and ductwork from decommissioning operations."[6] There is no indication that this TRUCON code can be used simply because drums may have been repackaged at the SRF.[7]

The issue of TRUCON codes appears even more confused than before. The use of the TRUCON code LA-125A appears to be inconsistent with its definition. It is not clear that the TRUCON code assigned to waste should be changed for repackaging. LA-125A appears to be intended for the creation of waste during dismantlement operations.

[6] DOE/WIPP 89-004, p. 14-28.

[7] It is unclear at the moment that the drums were even repackaged at the SRF. Documentation in the repackaging data report (TWCP-1215) indicates that the repackaging was done in TA-50 Building 69.

Furthermore, LA-125A is defined for a very specific LANL facility that may not have been used for repackaging operations.

Radioassay of each repackaged drum to determine Pu-238 content (LA98-PAN-001, TWCP-1213): No specific comments at this time.

Reconciliation of Gamma Spectroscopy and PAN data with AK information and calculation of Cr content in each repackaged drum (TWCP-1218): No specific comments at this time.

Drums loaded into standard waste boxes to meet TRUCON code LA125A: No specific comments at this time.

SWB characterization and certification information entered into WWIS for approval by DOE/CAO (TWCP-1214): No specific comments at this time. The waste characterization is incomplete with regard to RCRA characteristics of corrosivity, toxicity, reactivity and ignitability.

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Comments:

Benito -

FYI. Please pass on to John K. et al, as appropriate.

Thanks,
John

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