



**Department of Energy**

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August 20, 1999

ENTRUSTED

Mr. Greg Lewis  
Water and Waste Management Division  
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P. O. Box 26110  
Santa Fe, NM 87502-6110



Dear Mr. Lewis

Please find enclosed our responses to the July 1, 1999 NMED comments on the RFETS Waste Determination for RF005.01.

If you have any questions, please contact me at (505) 234-7456 or Butch Stroud of my staff at (505) 234-7483.

Sincerely,

E. Kent Hunter, Assistant Manager  
Office of National TRU Waste Program

Enclosure

cc w/enclosure:  
S. Zappe, NMED

cc w/o enclosure:  
P. Maggiore, NMED  
R. Mertz, NMED  
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I. Triay, CAO

Reference: CAO:ONTP:RAS 99-1303 / UFC 5822



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**DOE/CAO**  
**Responses to NMED Preliminary Review**  
**Comments**

**On**

**RFETS Non-Mixed Waste Determination**  
**for TRU Stabilized Pyrochemical Salts –**  
**Profile No. RF005.01**

## A. General Completeness Analysis

The following information is being provided per the request of the New Mexico Environment Department to facilitate the review of the document.  
(Attachments A.1 – A.10):

1. Flow charts for the pyroredox and vacuum melt processes, including Building(s) where the processes were performed.
2. "Waste Stream and Residue Identification and Characterization, Building 707," Version 6.0, Process 39.
3. Reference P053: "Reconstruction of Historical Rocky Flats Operations and Identification of Release Points"
4. "LDR Assessment for Transuranic Waste Streams, Rocky Flats Environmental Technology Site," WASTREN, Inc., August 27, 1997.
5. "Assessment of RCRA Metal Contaminating Plutonium," Letter from Kevin Peters to Pam Edrich, January 29, 1998.
6. Visual verification of Waste Summary Category Group and absence of prohibited items for IDC 454X was recorded on the Visual Examination Forms included with the supporting documentation forwarded to NMED earlier (SS-DP data, Appendix 8, for each can of salt waste. Appendix 1 provides the data review and verification at the data generation level and the PAQO review of the visual verification record is provided on the summary form). There are no associated video/audio tapes because this is visual verification of Acceptable Knowledge using the VE technique for newly generated waste.
7. "Presence of Chromium in Pyrochemical Salts at Rocky Flats Environmental Technology Site," prepared by KMI Services and Lamb Associates, EG&G, 1993.
8. "Environmental Technologies Internal Technical Report," Analysis of Volatile Organic Compounds on Specific Waste Forms, Scott Brendecke, et. Al., 94-039, October 19, 1994.
9. "Statistical Evaluation of Toluene Analysis Results in the Headspace Gas of Transuranic (TRU) Waste Drums – ELD-012-97," memorandum from E.L. D'Amico to D.K. Sullivan, August 12, 1997, and related memoranda/documentation.
10. Visual Examination Procedure 4-W84-RS-0114.

B. Technical Comments on the Non-Mixed Determination for TRU Stabilized Pyrochemical Salts – Profile No. RF005.01.

1) The Document does not include sufficient acceptable knowledge information to completely confirm the validity of RFETS' non-hazardous waste determination. Missing information could be in the above references, but additional information must be provided concerning the pyroredox and vacuum melt processes including flow diagrams and assessments performed to evaluate hazardous constituents present in waste. Specific references documenting the presence or absence of VOCs/SVOCs in each of the waste streams (i.e. IDCs 365, 404, 412, 414, and 416 comprising IDC 454X) and in all materials placed in the IDC 454X waste drums should be provided. In addition, the attached acceptable knowledge summary does not provide sufficient information regarding the IDCs that comprise the IDC 454 waste stream with respect to the wide range of chromium results (including 2 samples well over the regulatory threshold). The chromium results indicate a significant level of heterogeneity of chromium in the waste. This heterogeneity could be attributed to:

- Inadequate control of the processes that originally were used to generate the salt wastes to allow for fluctuating levels of chromium;
- Significant differences in the composition of waste in IDCs 365, 404, 412, 414, and 416 that are not adequately explained in the acceptable knowledge documentation;
- Introduction of chromium contamination that was not otherwise identified in the acceptable knowledge documentation; or
- The method of sampling may not be representative due to liquid stratification of certain wastes. The acceptable knowledge does not address the homogeneity of each of the IDCs that comprise waste stream IDC 454X.

Provide more detailed acceptable knowledge to include information about IDCs 365, 404, 412, 414, and 416 that would explain the elevated levels and wide concentration range of chromium in some of the metals samples. In addition, metals analyses of all waste samples should be clearly traceable to the precedent IDC.

**Response:**

The pyrochemical salts are byproducts of the pyrochemical plutonium metal purification and production processes conducted in the past at RFETS, including direct oxide reduction (DOR), pyroredox, and vacuum melt processes. IDCs 365 and 414 are from the DOR process. DOR used calcium metal to reduce relatively pure plutonium oxide to plutonium metal.  $\text{CaCl}_2$  was used as the molten salt medium for the reaction. The pyroredox process generated IDCs 404, 412, and 416. In addition the vacuum melt research and development program generated a small quantity of IDC 416. For all pyrochemical salt IDCs, these processes did not involve the use of solvents that could have resulted in the presence of volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs) (see attachments A.1, A.2,

A.8, and A.9). In each of these processes, which produced this salt waste, the salt was heated until it was molten (about 800° to 900° C) and stirred at 300 rpm for two hours. At these temperatures any VOCs or SVOCs, if they had been present, would have been volatilized. Additionally, each of the pyrochemical salt IDCs introduced into the pyrochemical stabilization process were again heated until molten (about 800° to 900° C), with stirring, resulting in IDC 454X. The DOR, pyroredox, and vacuum melt processes are described in the Backlog Waste Reassessment Baseline Book, Waste Form 34, "Pyrochemical Salts" (Attachment B.1).

The purpose of the pyrochemical salt process was to purify the plutonium metal by removing metal impurities. The plutonium metal that provided the feed material for the pyrochemical salt treatment did not meet the DOE requirements for purity due to the presence of metal impurities, including chromium. The concentrations of these impurities varied dependent upon the source of the plutonium. Thus, chromium will be present in varying concentrations in the salt waste. Process controls were established to produce or purify plutonium metal, not to control chromium or other metal impurities removed from the plutonium. (see also attachments A.4 and A.7)

Confirmation of characterization is accomplished on a waste stream basis and not on an individual waste container basis through statistical evaluation of random sampling/analysis of the waste stream (refer to Section 5.4.1 of the Transuranic Waste Characterization Quality Assurance Program Plan, Revision 0). Specifically, random samples are collected and analyzed, and the results are used to statistically estimate the average population (i.e., waste stream) concentration for each analyte. If the random sample results are normally distributed then one is 90 percent confident that the population average is less than or equal to the calculated upper 90 percent confidence limit. Calculation of the upper 90 percent confidence limit incorporates all the variability (and thus "heterogeneity") associated with the sample results (i.e., variability associated with sampling, analysis and waste stream heterogeneity). Therefore, the more heterogeneity in the waste stream then the higher the upper 90 percent confidence limit and the more likely that the upper 90 percent confidence limit will exceed the regulatory threshold.

Source container(s) identification (including IDC, container net weight, and plutonium content) for each outbound container is part of the information recorded on the furnace run sheets for pyrochemical stabilization activities (see attachment A.10-Appendix 4, Furnace Run Sheets, 4-W84-RS-0114). Laboratory analyses and furnace runs are traceable to the outbound container number. Thus traceability of metals analyses of waste samples back to the precedent IDC or IDCs, if more than one IDC was added to an outbound container, is possible by accessing these furnace run sheets data packages and laboratory analyses packages in Waste Records storage.

Over 96% of the inbound containers were IDC 414 so the random selection of cans of 454X for RCRA metals resulted in final cans made up of inbound IDC 414 being selected, sampled and analyzed for metals.

- 2) The Document indicates that the salt stabilization treatment would sufficiently degrade any VOCs or SVOCs present in waste, but analytical/technical justification for this assertion is not provided.

**Response:**

The pyrochemical salts are byproducts of the pyrochemical plutonium metal purification and production processes conducted in the past at RFETS, including direct oxide reduction (DOR), pyroredox, and vacuum melt processes. These processes did not involve the use of solvents that could have resulted in the presence of volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs). In each of these processes, which produced this salt waste, the salt was heated until it was molten (about 800° C), with stirring. At these temperatures any VOCs or SVOCs, if they had been present, would have been volatilized. These processes are described the Backlog Waste Reassessment Baseline Book, Waste Form 34, "Pyrochemical Salts" (Attachment B.1).

Section 5.2.1 of the QAPP, Revision 0, states:

"With the exception of salt waste (matrix parameter category S3140), each of the waste streams must be sampled and analyzed for total RCRA-regulated VOCs, SVOCs, and metals in accordance with the requirements of Sections 8.0, 13.0, 14.0, and 15.0. Knowledge of the electrorefining processes that generate salt waste indicates high-temperature molten salt extraction is involved. This knowledge is adequate to demonstrate that organic constituents are not present in salt waste."

- 3) Specific waste mixing and management activities should be clarified with regard to salt stabilization. Supplemental information infer that sampling was performed on an individual IDC basis (i.e. containers of IDC 365, 404, 412, 414, or 416 waste), but the IDCs associated with each can number are not provided. A listing of IDCs/can number should be provided.

**Response:**

The samples for confirmation of acceptable knowledge were taken on the outbound containers of IDC 454X waste salt. The IDC for the cans is 454X. Supplemental information may refer to sampling for other purposes and may have been cited to support specific topics in the acceptable knowledge. No sampling of inbound containers was done for WIPP characterization. The sampling referred to in the Profile is for the IDC 454X portion of the TRU stabilized pyrochemical salts waste stream.

Source container(s) identification (including IDC, container net weight, and plutonium content) for each outbound container is part of the information recorded on the furnace run sheets for pyrochemical stabilization activities (Attachment A.10 – Appendix, Furnace Run Sheets, 4-W84-RS-0114). Laboratory analyses and furnace

runs are traceable to the outbound container number. Thus traceability of metals analyses of waste samples back to the precedent IDC is possible by accessing these furnace run sheets data packages and laboratory analyses packages in Waste Records storage.

Over 96% of the inbound containers were IDC414 so the random selection of cans of 454X for RCRA metals analysis resulted in final cans made up of inbound IDC 414 being selected, sampled and analyzed for metals.

Inbound cans were identified by IDC and container number. Below is a listing of inbound container identifiers and IDCs and final can number of IDC 454X.

Inbound Container Identifiers	IDC	Final Can # (IDC 454X)
DOR 191 192 193A	414	Z07608
639,641,642,RS	414	
DOR BS-1	414	
DOR1,DOR 3B	414	
DOR4A	414	Z07251
DOR4B	414	
D06675-3	414	Z07262
D06675-5	414	
771159C	414	Z07348
771159A	414	
770060	414	Z07514
947A	414	
936A	414	
930A	414	
RCS-001	414	Z07572
COLD SALT #1	*454X	
DOR 369-2842,397-2617, DORER-6	414	
770030-A	414	
770030	414	
ST DOR5A-RS	414	
524146010	414	Z07651
521416034	414	
524146027	414	
DOR86	414	
D94711	414	Z07713
D95773	414	Z07979

\* Note: A single stabilized can of IDC 454X (IDC 414 prior to stabilization) was blended with untreated IDC 414 waste. The blended waste was then treated in the pyrochemical stabilization process

resulting in final can Z07572. This was done to affect plutonium content, not to affect RCRA regulation.

- 4) Provide additional justification for combining IDC 365, 404, 412, 414, and 416 into a single waste stream IDC. Analytical data and other RFETS documentation imply that there may be significant chemical differences with respect to metals and process differences between these IDCs which bring this combination into question.

**Response:**

The initial processes producing the IDCs in question used  $\text{CaCl}_2$  as the basic matrix salt. Metals concentrations in the salt are not controlled parameters. They reflect the variations in the feed material.

IDCs 365 and 414 are from the Direct Oxide Reduction (DOR) process. This process used calcium metal to reduce relative pure plutonium oxide to plutonium metal.  $\text{CaCl}_2$  was used as the molten salt medium for the reaction. The pyroredox process generated IDCs 404, 412, and 416. In addition the vacuum melt research and development program generated a small quantity of IDC 416. The pyrochemical processes that generated these five IDCs were used to produce or purify plutonium metal. All used  $\text{CaCl}_2$  and Ca metal at some stage in the processing.

Due to the same salt ( $\text{CaCl}_2$ ) being used in all the processes and the need to use the same process parameters for pyrochemical stabilization of  $\text{CaCl}_2$  based salts, the decision was made to combine these five inbound IDCs into the single stabilized outbound IDC 454X. (see also attachment A.5)

- 5) The discussion(s) pertaining to radiolysis is incomplete. Stakeholders have questioned the generation of reactive, corrosive, and ignitable waste, as well as TC wastes due to radiolysis. Sections of the Document should be revised to specifically indicate the effects of radiolysis with respect to generation of these wastes. In addition, the Document indicates that the waste configuration/contents specifically preclude radiolytic gas generation, but do not provide any additional information pertaining to this assertion including visual examination results, radiolytic decay products/particles and the impact these might have on radiolytic gas generation, etc.

**Response:**

Hazards associated with radiolysis have been evaluated and presented in the Safety Analysis Report for the TRUPACT-II Shipping Package (specifically refer to Appendix 3.6.8). Radiolysis is primarily attributed to the interaction of alpha radiation on certain waste and packaging materials. Alpha radiation can not penetrate through a piece of paper and is easily shielded. To generate hydrogen gas by radiolysis, a hydrogen source (e.g., water or organic material) must be present and in intimate contact with the radioactive material. The salt waste is an inorganic material, which is visually inspected as part of the process and placed

directly into metal cans. Because the material is contained within a metal can through which alpha radiation can not penetrate to interact with plastic/organic packaging material, the potential for radiolysis to occur is basically eliminated.

- 6) The Document states, on page 5, that “only contents of the same IDC are allowed in one payload container. “Does this mean that containers include only IDC 365 (for example), or that payload containers are a mix of IDCs 365, 404, 412, 414, and 416 as part of IDC 454X? See comment number B.3 above.

**Response:**

The statement means that each payload container contains waste material consistent with only one IDC as identified on the associated payload container documentation. IDC 454X is assigned to the contents of each payload container containing the subject waste material described in document GAO-029-99. IDC 454X is a process output IDC from the salt stabilization treatment process. IDC 454X consists of one or a combination of feed IDCs (i.e., feed IDCs 365, 404, 412, 414, and 416). Therefore, each payload container contains IDC 454X, but IDC 454X may have been processed from a combination of feed IDCs. See response to comment B.3 for additional information.

- 7) Metals data were inappropriately evaluated on a log-normalized basis by RFETS. RFETS did not adequately investigate the possibility that the lognormal fit of the data was due to differences in the concentration means of the precedent IDCs that comprise the IDC 454 waste stream, and combining these IDCs may therefore be inappropriate. EPA guidance indicates that the occurrence of lognormal distributions of data are attributed to random and multiplicative dilution and mixing of contaminants with uncontaminated air or water (EPA 1992, pg. 2). Log-normally distributed data is expected when the contaminants are in an uncontained and uncontrolled environment, such as that associated with a spill or a release to the environment. However, the acceptable knowledge for the IDC 454X waste indicates that the pyrochemical salts were derived from well-defined processes that used materials meeting specified composition requirements. The waste were not released to the environment or subject to uncontrolled or undefined mixing or dilution. The salts were also subject to thermal treatment that functioned to thoroughly mix and homogenize the waste. Based on the acceptable knowledge provided, the contaminants in this waste should have been thoroughly mixed and normally distributed. The lognormal distribution of the data indicates a source of variability that is not indicated in the acceptable knowledge documentation. RFETS should further examine the waste to determine if the demonstrated variability of the waste is due to differences in the precedent IDCs or if the process and process components are not as well controlled as indicated in the acceptable knowledge documentation. Evaluation of the data for chromium indicates that two of the nine sample results were significantly higher than the regulatory threshold for chromium. Evaluation of the data assuming a normal distribution indicated that the waste was hazardous for chromium. Evaluation of the data on a lognormal basis resulted in a determination

that the chromium levels were elevated but below the regulatory threshold. Log normalization of the data reduced the impact of the two results that were significantly above the regulatory threshold. However, RFETS did not adequately correlate the variable chromium concentration levels to precedent IDCs nor address the possibility that the precedent IDCs should be segregated into separate waste streams based on the chromium levels in the waste.

**Response:**

The statement that “the waste was thoroughly mixed,” applies only on a can basis. The entire waste stream was not homogenated in a single batch. Variability between cans is therefore expected.

Total Metals analyses were originally to be evaluated on IDC 454X samples collected from the first twenty pyrochemical stabilization process runs. From this data, control charts were to be constructed and a sampling frequency determined for the remainder of the production runs. A decision was made to continue sampling each run until confirmation was received from RFETS TRU Waste Projects that the method of determining the random sampling and the determined sampling frequency was appropriate. Confirmation was received on April 21, 1998 (see attachment B.2). At this time, in excess of two hundred process runs had been made and in excess of two hundred samples had been taken. The original control charts were constructed from the first 37 samples taken. The control charts were updated with the analysis results from the next 29 samples taken. Analysis for these 66 samples resulted in data that were not normally distributed, as was expected.

The plutonium metal that provided the feed material for the pyrochemical salt treatment did not meet the DOE requirements for purity due to the presence of metal impurities, including chromium. Feed material is processed in batches. The concentrations of these impurities varied dependent upon the source of the plutonium (this would be the same for the input IDCs as well). The purpose of the pyrochemical salt process was to purify the plutonium metal by removing metal impurities. Thus, chromium will be present in varying concentrations for each salt sample. Since the metals concentrations in the salt were not controlled, the control charts showed the expected variations. Control charting proved an unacceptable method for tracking the metals concentrations and assigning sampling frequencies. Salts are therefore characterized in process batches.

The waste stream population for waste stream 454X was initially estimated at 900 containers (cans) and based on EPA SW-846 and the initial samples, the calculated sampling frequency is five. It was recommended to take more samples than required in case the comparison of the results of the random samples to the original mean and standard deviation yielded a requirement to do additional sampling. The random number generator capability of Excel software was utilized to produce 10 random numbers between 1 and 900 (see attachment B.3).

Statistical analysis of the laboratory reported results from nine random samples collected for the first lot of the stabilized pyrochemical salts (IDC 454X) was conducted. A summary of the laboratory reported Total Metals analysis results are shown in attachment B.4. SW-846 requires normally distributed data for calculation validity with small sample sizes (less than about 30). Analysis showed that the data were not normally distributed. Transformation of the data was required per the guidance of SW-846 to achieve normality. The statistical analysis supported the conclusion that a sufficient number of samples were taken to characterize the waste stream lot per the criteria of SW-846 and no analyte exhibits a toxicity characteristic per United States Environmental Protection Agency (EPA) criteria.

Highly right-skewed analyte concentration data is common within all input IDC waste and is, therefore, not unexpected in the output waste stream. Right-skewness can often be compensated and normality in distribution achieved by using the log transformation (Gilbert, 1987). This practice is not only recommended but also required for unbiasedness in the statistical calculations when small sample sizes are involved.

Other references indicating the need for normality and/or appropriateness of transformation to achieve a normal distribution include but are not limited to the following:

- 1) Statistical Methods for Environmental Pollution Monitoring, Richard O. Gilbert, 1987, Van Nostrand Reinhold, Inc., New York. (pp.148-149)
  - 2) Statistics for Environmental Engineers, Paul Mae Berthonex and Linfield C. Brown, eds.,1994, CRC Press, Inc., Boca Raton, F. L.. (pp. 17, 57-63, 108)
  - 3) Introduction to Mathematical Statistics, Robert V. Hogg and Allen T. Craig, 1978, Macmillan Publishing Co., New York. (p. 215)
  - 4) Encyclopedia of Statistical Sciences, Samuel Kotz and Norman L. Johnson, eds., 1998, John Wiley & Sons, New York. (Vol. 9, pp. 162-163, 312-317) and (Vol. 5 p.114)
  - 5) Sampling Techniques, third edition, William G. Cochran, 1997, John Wiley & Sons, New York. (pp. 39-44, 77-78)
- 8) The reason for using SW-846 method 7742 (Selenium by Atomic Absorption and borohydride reduction) is not fully explained. The laboratory was unable to achieve an adequate level of detection using the ICP methodology. However, the underlying cause was not identified and there was no discussion regarding the potential impact on other analytical parameters. Specifically, there was no discussion regarding the potential impact of interference due to high salt concentrations in the waste on selenium as well as the other analytical parameters.

In addition, RFETS did not adequately explain the selenium concentration difference in sample 98H1474-005 when the ICP results are compared to the Atomic Absorption

results. The Atomic Absorption result for the sample is 3.0U mg/kg, where U signifies that the result is a non-detect. The ICP result for the sample is 40 mg/kg, which is twice that regulatory threshold. RFETS did not provide any evidence regarding spectral or chemical interferences that would result in such a significant difference in selenium results.

**Response:**

RFETS' Building 559 Laboratory uses a JY-48 ICP spectrometer for metals analyses. This is an older instrument that, despite its age, continues to meet or exceed the manufacturer's original design specifications. However, this instrument can not achieve WIPP's Program Required Detection Limit (PRDL) for selenium. As a result, RFETS uses hydride generator atomic absorption (HAA), taking advantage of this technique's lower selenium detection limit.

Higher selenium detection limits do not diminish the JY-48's capabilities for other analytes. Selenium's emission line is below 200 nm, and newer instruments outperform the JY-48 in the shorter wavelength regime. At longer wavelengths, the JY-48 performance exceeds WIPP's detection limit requirements.

The QAPP Section 15.1 states, "IDLs must be less than or equal to the PRDL for the method used to quantitate a specific analyte. Any method listed in Table 15-2 may be used if the IDL meets this criteria." This instruction makes HAA a permissible choice, regardless of ICP performance.

The NMED also commented on interference arising from high salt concentrations. Methods found in SW-846 incorporate matrix interference tests with each analytical batch. Pre-digestion spikes, post digestion spikes, duplicates, and serial dilutions serve this purpose. Each data package presents these results in Forms 5A, 5B, 6, and 9. Also, Form 1 displays a "Z" flag for analytes that do not achieve interference test tolerances.

As required by QAPP Section 15, metals analyses use an instrument detection limit (IDL) rather than a method detection limit (MDL). High salt concentrations could affect MDLs but have no effect on IDLs. Sometimes, these analyses display elevated detection limits due to matrix interference and ICP selenium results are susceptible to this.

Partially to compensate for matrix interference, data quality objectives in the QAPP, Table 15-1, set the PRDL a thousand times lower than the Program Required Quantitation Limit (PRQL). For selenium, the RFETS ICP could not achieve this factor-of-a-thousand difference between the PRDL and PRQL. Therefore, data users may not make RCRA decisions using the ICP selenium results.

In the range of an instrument's detection limit, false positives are common. For sample 98H1474-005, the ICP selenium concentration exceeds the IDL by a factor of 1.7. WIPP's data quality objectives allow blank concentrations to exceed the IDL by a factor of three. Under this directive, the ICP selenium result for sample 98H1474-005 qualifies as a legitimate blank.

However, the RFETS ICP failed to achieve the QAPP data quality objective for PRDL, causing the false positive to exceed the regulatory threshold. RFETS did not use the ICP selenium results for RCRA determinations.

The HAA selenium results for sample 98H1474-005 exhibited successful spike recoveries and duplicate comparison. For this analysis, the observed concentration was less than twenty-five times the IDL, so a serial dilution was not performed. These tests, along with a selenium determination below the HAA detection limit, show negligible matrix interference. Therefore, when making RCRA determinations, RFETS used the HAA selenium results.

- 9) The acceptable knowledge documentation indicated that mercury was not expected in any of the waste streams and that the subsequent pyrochemical treatment would have volatilized any residual mercury in the waste. However, mercury was found at a concentration of 1.1 mg/kg in sample 99H3511-003. This value is 5-10 times the detection limit for the remaining samples. RFETS does not explain the presence of mercury in the waste stream when RFETS indicates that the acceptable knowledge shows the waste composition and treatment would result in an absence of mercury in the waste.

**Response:**

Even though the mercury was not expected to be present, it was detected in only two out of more than 200 samples and at concentrations below the RTL. These results support the original AK nonhazardous determination for mercury.

RFETS' certification program does not assess trace level contaminants or disparities in sets of analysis points, as long as the RTL is not exceeded. As part of DQO reconciliation, the QAPP requires the sites to track and document changes to waste determinations. The QAPP does not require any action to be taken unless the RTL is exceeded for a given contaminant for streams that were not previously assigned the EPA hazardous waste number using AK. This is consistent with the requirements for application of TC waste codes listed in Section B-3a(2) of Attachment B to the November revised draft permit.

- 10) The reason for the wide disparity of lead values in the samples was not adequately explained. Lead was found in the samples at values ranging from 14.0U mg/kg to 120 mg/kg. The regulatory threshold for lead, as indicated by RFETS, is 100 mg/kg.

**Response:**

As discussed in the response to B - 1, analyte heterogeneity, including lead, is expected in the salts due to the variability of the plutonium feed streams (feed source and contaminants).

Confirmation of characterization is accomplished on a waste stream basis and not on an individual waste container basis through statistical evaluation of random sampling/analysis of the waste stream (refer to Section 5.4.1 of the Transuranic Waste Characterization Quality Assurance Program Plan, Revision 0).

Specifically, random samples are collected and analyzed, and the results are used to statistically estimate the average population (i.e., waste stream) concentration for each analyte. If the random sample results are normally distributed then one is 90 percent confident that the population average is less than or equal to the calculated upper 90 percent confidence limit. Calculation of the upper 90 percent confidence limit incorporates all the variability (and thus "heterogeneity") associated with the sample results (i.e., variability associated with sampling, analysis and waste stream heterogeneity). Therefore, the more heterogeneity in the waste stream then the higher will be the upper 90 percent confidence limit and the more likely that the upper 90 percent confidence limit will exceed the regulatory threshold. This is consistent with the requirements for application of TC waste codes listed in Section B-3a(2) of Attachment B to the November revised draft permit.

C. Waste Analysis Plan Compliance with respect to the Non-Mixed Determination for TRU Stabilized Pyrochemical Salts-Profile No. RF005.01

- 1) The metals data associated with IDC 454X were log-normalized but Attachment B2 of the revised draft permit does not allow for the log-normalization of data. According to the formula provided in Attachment B2 in Equation B2-7, the site would be required to collect 56 metals samples based on the normal chromium results that are provided; using log-normalized data, a total of 4 samples would have been required. Although a total of 9 samples were collected, which is greater than the required number calculated using log-normal data, this still falls short of the 56 samples required using formula in Attachment B2.

**Response:**

Attachment B2 of the revised draft permit does not prohibit log-normalization of data. The equations provided in EPA SW-846 Chapter 9 require normally distributed data and EPA SW-846 does allow the use of log-linearly-transformed data. The results of the nine random samples are not normally distributed; therefore, they must be transformed to a normal distribution before the EPA SW-846 equations can be applied. The transformation involves multiplying by 20 and taking the natural log of that value. See Sampling Techniques, third edition, William G. Cochran, 1997 for discussion of the statistical rationale. After the

transformation of the data shows a normal distribution, the EPA SW-846 equation can then be applied.

Attachment B2 of the Final Draft Permit requires the use of EPA SW-846 statistical treatment of the data. As stated above, in order to use EPA SW-846 equations, the data had to be transformed. Attachment B2 does not prohibit data transformation; moreover, by requiring the use of data with a normal distribution it appears that Attachment B2 is requiring transformation when necessary.

- 2) The UCL<sub>90</sub> based on the *normal* data for chromium is 130.42 mg/kg which is over the RTL of 100 indicated for chromium. As such, this waste would be hazardous for chromium if calculated using the revised draft permit equations and requirements. The *log-normalized* UCL<sub>90</sub> for chromium in the Document is 4.25, which is less than the log-normalized Regulatory Threshold of 4.61. That is, if normalized data were used as mandated in the revised draft permit, the waste would not be adequately characterized as non-hazardous for chromium.

**Response:**

Per standard statistical practices and as discussed in EPA SW-846, statistics derived from equations utilizing t-distribution values and relatively small samples require that the data demonstrate at least an approximately normal (Gaussian) probability distribution in order to be valid. The UCL<sub>90</sub> is one such statistic. The raw non-transformed data from Cr analyses fail the commonly accepted mathematical distribution tests for normality, with probabilities on the order of 0.001. Thus, any UCL<sub>90</sub> value calculated from the non-transformed data would not be valid. The log-transformed data with fitted non-detects easily passes all tests for normality and is the appropriate choice for calculating the UCL<sub>90</sub> value per the guidance of EPA SW-846.

- 3) Headspace gas analyses are required for every waste container as specified in Module II.C and Section B-3(a)(1) of Attachment B of the revised draft permit. However, Section 3.4.1 of the Non-Mixed Waste Determination for TRU Stabilized Pyrochemical Salts indicates that headspace gas sampling and data were not performed on IDC 454X containers. RFETS justifies this exception based on visual examination results, acceptable knowledge information regarding the presence of VOCs/SVOCs, and lack of radiolytic gas generation. However, several questions remain concerning this justification (refer to comments above).

**Response:**

The processes that originally generated the feed IDCs currently undergoing stabilization to produce output IDC 454X neither used, generated, nor contacted organic materials (see RFETS Backlog Waste Reassessment Baseline Book, Waste Form 34, "Pyrochemical Salts" (Attachment B.1)). Also, these materials

were generated from processes operated at high temperatures, generally above 800 °C.

Salt stabilization is performed on the feed IDCs by placing the salt waste directly into metal cans, heating to a molten state at temperatures between 800 to 900 °C (1472 to 1652 °F) and stirring for approximately two hours. This process destroys and/or volatilizes any water or organic material in the waste and acts to stabilize/oxidize the waste material itself into an inert form. EPA guidance (*ARCS Remediation Guidance Document*, Chapter 7, Treatment Technologies) shows that these temperatures are sufficient to volatilize and/or oxidize any organic material that could have inadvertently been introduced into the process.

The RCRA regulations authorize hazardous waste determinations to be made either using approved sampling and analysis methods or by applying knowledge of the waste in light of the materials or process used. Based upon documented acceptable knowledge, application of RCRA implementing regulations, and determining that additional sampling would pose unnecessary risk to workers with no corresponding benefit, CAO approved an exemption from headspace gas sampling and analysis (see E. K. Hunter letter to J. Legare, *Residue TRU Waste Characterization Methods Evaluation*, CAO:NTP:RAS 98-0617-UFC-5822, February 12, 1998. See also, related responses to issues B.1 regarding Acceptable Knowledge, B.2 regarding degradation of VOCs and SVOCs and B.5 regarding radiolytic gas generation.

- 4) Solids sample analysis for SVOCs and VOCs is required in the revised draft Permit, Attachment B, Waste Analysis Plan (WAP). The WAP does not exclude confirmatory sampling of SVOCs and VOC totals analyses based on process knowledge. However, SVOC and VOC analysis of salt samples was not performed for IDC 454, as RFETS indicates that the thermal stabilization process would volatilize or destroy all potential VOC and SVOC compounds in the waste. Refer to comment number B.2, above.

**Response:**

As provided in our response to comment B.2, the processes that produced these salts did not involve the use of solvents that could have resulted in the presence of volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs). In each of the processes the salt was heated until it was molten (about 800° C), with stirring. This process destroys and/or volatilizes any water or organic material in the waste and acts to stabilize/oxidize the waste material itself into an inert form. EPA guidance (*ARCS Remediation Guidance Document*, Chapter 7, Treatment Technologies) shows that these temperatures are sufficient to volatilize and/or oxidize any organic material that could have inadvertently been introduced into the process.

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- 5) Visual examination data forms and videotapes were not provided for the waste containers. Section B1-3 of Attachment B1 of the revised draft permit specifies the requirement that all visual examination activities will be video/audio taped and documented on a visual examination data form. Documentation of visual examination activities must be provided.

**Response:**

Visual verification of Waste Summary Category Group and absence of prohibited items for IDC 454X was recorded on the Visual Examination Forms included with the supporting documentation forwarded to NMED earlier (SS-DP data, Appendix 8, for each can of salt waste. Appendix 1 provides the data review and verification at the data generation level and the PAQO review of the visual verification record is provided on the summary form). There are no associated video/audio tapes because this is visual verification of Acceptable Knowledge using the VE technique for newly generated waste. Section B-3d(1) of the Waste Analysis Plan specifies in part that this process consists of the operator confirming that the waste is assigned to a waste stream that has the correct Summary Category Group for the waste being packaged. A second operator, who is equally trained to the requirements stipulated in permit attachment B1, will provide additional verification by reviewing the contents of the waste container to ensure correct reporting.

- 6) There was no discussion of the data quality objectives (DQOs) for this waste stream. The Document did not indicate DQOs levels as specified in sections B3-1 And B3-8 of Attachment B3 of the WAP, not did it indicate how DQOs were evaluated or whether the DQOs were met for IDC 454X.

**Response:**

Reconciliation with DQOs is documented on Form A of Waste Stream Profile Form RF005.01. Quality assurance objectives (QAOs) – such things as precision and accuracy – are reviewed for each batch report produced as part of the data

validation, usability and reporting process. Data that fail to achieve QAOs are either identified and evaluated by a nonconformance report or by being appropriately flagged in accordance with the requirements of the Interim Change to Revision 0 of document CAO-94-1010, Transuranic Waste Characterization Quality Assurance Program Plan. The following table summarizes the deviations to QAOs associated with the nine confirmatory samples collected and analyzed for IDC 454X.

Summary of QAO Deviations

Drum Number	WIPP Sample Number	Description of QAO Deviation
D93976	RF98H0983005	None
D90824	RF98H0983013	PRE-DIGESTION SPIKE SAMPLE AND DUPLICATE RECOVERIES FOR MERCURY WERE 131.5% AND 126.7%, RESPECTIVELY. MERCURY RESULT IS ASSIGNED A "Z" FLAG.  DUPLICATE PRE-DIGESTION SPIKE SAMPLE RECOVERY FOR CHROMIUM WAS 77.8%. CHROMIUM RESULT ASSIGNED A "Z" FLAG.  DUPLICATE PRE-DIGESTION SPIKE SAMPLE RECOVERY FOR THALLIUM WAS 69.8%. THALLIUM RESULT IS ASSIGNED A "Z" FLAG.
D93051	RF98H0792009	None.
D92236	RF98H1474005	BLANK RESULTS FOR SILVER WERE SLIGHTLY ABOVE THE IDL BUT BELOW 3 X IDL. SILVER IS ASSIGNED A "B" FLAG.  SERIAL DILUTION FOR ZINC HAS A PERCENT DIFFERENCE OF 14.1 % (ABOVE 10%). ZINC RESULT IS ASSIGNED A "Z" FLAG.
D92621	RF98H1904004	PRE-DIGESTION SPIKE RECOVERY FOR ZINC WAS 130.7%. ZINC RESULT IS ASSIGNED A "Z" FLAG.
D94304	RF98H2383003	None.
D93951	RF98H2727006	PRE-DIGESTION SPIKE AND DUPLICATE RECOVERIES FOR CHROMIUM WERE 68.4% AND 57.5%, RESPECTIVELY. CHROMIUM RESULT IS ASSIGNED A "Z" FLAG.  PRE-DIGESTION SPIKE AND DUPLICATE RECOVERIES FOR NICKEL WERE 201% AND 248.8%, RESPECTIVELY. NICKEL RESULT IS ASSIGNED A "Z" FLAG.
D94711	RF98H2727026	PRE-DIGESTION SPIKE RECOVERY FOR NICKEL WAS 77.3%. NICKEL RESULT IS ASSIGNED A "Z" FLAG.
D95773	RF99H3511003	None.

- 7) There is no indication that the facility collected co-located samples (field duplicates), equipment blanks (or used certified clean disposable sampling equipment), and

demonstrated adequate decontamination procedures as specified in section B1-2b of the WAP.

**Response:**

The site did not collect co-located samples because of the sampling method used did not require it. Co-located samples are used to assess the degree of variability introduced by the sampling method. The stabilized salt samples were gathered in a liquid state after being rapidly stirred for approximately two hours. This sampling method assures that the material being sampled was homogenous at the time of sample collection. This sampling method was submitted to CAO for review and approval on November 27, 1997 in accordance with the requirements in the WIPP Methods manual (Attachment B.5). Clarification that duplicate samples were not required was given by CAO on February 25, 1999 (Attachment B.6).

The carbon steel sample cups used to collect the molten salt samples were analyzed to ensure that they did not pose a threat to contaminate the samples. Report RDT-99-051 (Attachment B.7) shows that only trace amounts of RCRA regulated metals were found in rinsate samples taken from unused sampling cups, posing no detrimental impact to data quality. Also, since the results of the salts samples show that the stabilized salt waste stream is not hazardous, there could be no significant contamination introduced by the sampling cups. If the cups had contaminated the samples, it would have been reflected in the sampling data.

- 8) The site used the retrievably stored sampling number collection calculations, but collected the samples using newly generated sampling techniques. Whether the waste would actually be considered newly generated (because it was repackaged) or retrievably stored (because it was generated prior to issuance of a final permit) is somewhat ambiguous. If the permit had been issued, the waste would be newly generated/repackaged. The proposed final permit has been modified to allow use of the retrievably stored sample number calculation for newly generated waste *if this* results in more samples being collected, but as indicated in comment number C.1 above and in the site's own documentation, use of the newly generated process would result in *many more* samples being collected due to sample inhomogeneity. (This is probably why the site sought – and was granted by CAO – and allowance to use the retrievably stored calculation). Since this activity has transpired pre-permit, the waste would be considered retrievably stored, and the appropriate sample number collection methodology (i.e., retrievably stored) was used. However, the revised draft permit does not allow scoop sampling of retrievably stored waste, and therefore the waste was not sampled in accordance with the WAP.

**Response:**

Section B2-4 of Attachment B2 of the revised draft permit discusses sampling newly generated waste from continuous processes. It states that the “underlying

assumption for control charting are that the data are independent and normally distributed with constant mean  $\mu$  and constant variance  $\sigma^2$ ." As shown previously, the stabilized salt residues do not meet these criteria and can not be characterized as a continuously generated waste stream.

The Salt Residues Stabilization Process samples were collected with the product (approximately 2 liters) in the molten state at temperatures between 800 to 900 °C (1472 to 1652 °F) immediately after stirring at 300 rpm for a minimum of two hours. The sample cup is lowered into the molten salt immediately after the stirrer control is placed in the off position to ensure homogeneity. At the process temperature range the molten salts have a viscosity near that of water and are therefore homogeneous liquid when sampled. Solidification occurs after sampling. This method provides the collection of a homogeneous sample with significantly less investigation-derived waste than would be generated by coring. This method also reduces risk to workers.

A more representative sample is collected using this method, it meets the requirements of EPA SW-846, and is therefore equivalent to the sample collection requirement of the WAP.