U-006-305.17

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DISAPPROVAL OF TREATABILITY STUDY WORK PLAN FOR OU #4

09-03-91

USEPA/DOE-FSO

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LETTER

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
230 SOUTH DEARBORN ST.
CHICAGO, ILLINOIS 60604

SEP 03 1991

Mr. Jack R. Craig
United States Department of Energy
Feed Materials Production Center
P.O. Box 398705
Cincinnati, Ohio 45239-8705

REPLY TO ATTENTION OF:

RE: Disapproval of Treatability Study Work Plan for OU #4

Dear Mr. Craig:

The United States Environmental Protection Agency (U.S. EPA) has completed its review of the Treatability Study Work Plan for Operable Unit #4. 4-006-303.2

U.S. EPA hereby disapproves the Work Plan. The deficiencies are attached.

Please contact me at (312/FTS) 886-0992 if you have any questions.

Sincerely,

James A. Saric
Remedial Project Manager

Enclosure

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cc: Graham Mitchell, OEPA-SWDO
Pat Whitfield, U.S. DOE-HDQ

bcc: David Ullrich->William Muno->Kevin Pierard, WMD
Mary Butler, ORC
Sandra Lee, ORC
David Kee, ARD
Jim Benetti, ARD
Dan O'Riordan, OPA
Ed Schuessler, PRC

GENERAL COMMENTS

1. The methodology for conducting stabilization treatability studies does not clearly address several issues which are common to stabilization/solidification (S/S) technologies. The following observations on the work plan experimental design outline the issues not adequately addressed.

   a) The work plan does not propose pH measurements of stabilization mixtures. The solubility of heavy metals is strongly influenced by the pH of the leaching solution. For each metal the optimum pH for minimum solubility is unique. Most metals, particularly lead, exhibit amphotericity, which means they have high solubility at both high and low pH. Because each metal has a different solubility curve, the combination of metals to be stabilized is critical in selecting the optimum pH of a stabilization mixture in order to minimize the leachability of the metals of concern.

      Furthermore, during the leaching procedure (as proposed to be simulated in the work plan using toxicity characteristic leaching procedures (TCLP)), chemical changes continue to occur in the stabilized matrix. For example, an acidic leach will achieve some neutralization of the basicity common in cementatious materials. If a metal is soluble at a high pH, the acidic leach may offset its solubility. However, if in reality a stabilized material would be exposed on site to fairly neutral leaching (such as being exposed to non-acidic rainwater), no neutralization will occur as the leaching occurs, and the metal in question will in fact leach out of the matrix at a much higher rate than observed in a bench scale demonstration with an acidic leach.

   b) Advanced screening of the stabilization formulations does not address site-specific aspects of the alternatives proposed in the feasibility study. For example, as described in comment 1a above, site specific conditions a stabilized waste would experience under the proposed FS alternatives should be simulated. Unconfined compressive strength (UCS) measurements do not provide much useful information for stabilized wastes that will not be disposed of as monoliths. Consideration should be given to advanced testing with a prepared leach that simulates the carbon dioxide concentration (carbonic acid content) and pH of leachate filtering through on-site soils, a cap, or through local ambient air. Site-specific testing should include modification of the TCLP test protocol to address realistic waste-to-leaching solution ratios and exposed surface areas for the various remedial alternatives. Additional leaching tests, such as American Nuclear Society (ANS) 16.1, should be considered.

   c) Preliminary screening of stabilization mixtures appears to be based solely on physical parameter measurements (such as UCS) and penetration resistance) and reagent usage. It is important to note that both physical and chemical phenomena occur in conventional S/S processes. For a specific waste stream, the effectiveness of the chemical fixation cannot be determined by measuring the physical properties. The most important aspect of the treatability testing relative to protection of human health and the environmental is the ability of the selected S/S formulation to

chemically fixate the constituents of concern. The physical properties are not unrelated to this process but are of particular interest primarily in the implementation of the remedial alternative design. The primary screening criteria for the preliminary phase should be the ability of a stabilization formulation to chemically fix the heavy metal constituents.

d) TCLP is proposed to be performed on the treated waste mixtures only and is not proposed for the untreated samples. The efficiency and quantifiable effectiveness a mixture to fix heavy metal constituents cannot be exactly determined without measuring TCLP before and after treatment. It should be noted that after treatment TCLP measurements must be corrected for the dilution of additives.

e) The organic analysis of the samples collected from the first silo contents sampling event did not detect significant organic contamination; however the holding times were excessively exceeded. The second silo contents sampling event may find that organic contaminates are a significant factor and the potential of organic constituents to inhibit S/S process effectiveness should be addressed in the work plan.

2. The objectives of the treatability study are not stated up front in the work plan, and they conflict with the performance and screening criteria of the test design. As stated in section 1.0, page 10, line 13, the purpose of treatability studies performed during the remedy selection phase should be to gather data. The data will assist in screening remedial alternatives by assessing the ability of the treatment technology to meet the cleanup criteria (action levels) and assess costs. However, the performance criteria for stabilization testing described in the test objectives, section 3.0, page 2, line 13, [UCS greater than 500 psi and TCLP less than characteristic listing criteria] are not necessarily consistent with the study objectives. For example, for alternative 1B (Silos 1 and 2), successful stabilization to the TCLP criteria is relatively meaningless. Since action levels have not been established specifically for all the wastes in question, the performance objectives for the stabilization testing should be revised to conform to quantitative criteria that are related or consistent with the ground-water action levels and should take into consideration the variety of remedial alternatives being considered. For example, for alternative 1B, a ground-water model can be used to predict allowable constituent leachability to meet the ground-water action levels.

Qualitative criteria should be considered as performance criteria, especially during the preliminary screening tests. For example, stabilization formulations can be screened by choosing those that demonstrate the highest reduction in constituent leachability on a percentage basis (when corrected for additive dilution). None of the formulations in the proposed stabilization matrix (Table 4-3) may be able to treat lead to the TCLP criteria without extremely high volume increases, which essentially would be treatment by dilution. Secondary screening criteria should include selection of formulations that result in the lowest volume increases and require the least amount of chemical additives. The UCS should be used as a secondary screening criteria because only some of the remedial alternatives require a treated waste with certain physical properties.

Finally, the work plan should clearly provide a framework for screening formulations based on both the primary and secondary criteria. For example, must a formulation meet all of the criteria in order to be included in the advance testing?

3. The test plan does not clearly identify the constituents of concern that will be used to measure the success of the testing at each phase of the treatability testing. For example, if during preliminary screening of stabilization formulations, a particular test mixture shows the best fixation for lead but the worst for thorium, what criteria will be used to screen the formulations for the next phase.

4. A description of the waste characteristics from all three silos should be presented in section 1.0 of the work plan. This description should be a short summary of the chemical and physical properties of the wastes in each silo.

5. The work plan has many decision points in the test design defined by ambiguous terms such as "if necessary," "if warranted," "the most promising formulation," and so forth. The work plan should replace all such terms with concrete decision criteria if possible. When providing specific decision criteria is not possible, the test should explain the process by which a decision is to be made.

SPECIFIC COMMENTS

1. Subsection 1.3.1, page 6, line 12: The purpose of treatment is not to render the waste materials noncharacteristic but to treat them so that the remedy will attain the action levels. Treatment to below the TCLP limits that define toxic characteristic wastes may or may not result in attainment of action levels, depending on which remedial alternative is considered. This statement should be deleted from the justification section and/or rewritten.

2. Subsection 1.3.1, page 6, lines 14-18: This paragraph appears to conflict with the statement made in section 2.1, page 1, lines 28 and 29. The paragraph cited or other appropriate text should clearly state that while in situ vitrification is not considered feasible, vitrification treatability studies are proposed to address the ex situ alternatives.

3. Subsection 1.3.4, page 11, lines 23 and 24: Provide a brief justification for selection of the additives proposed in the stabilization. For example, Type II Portland cement is designed to be used in the presence of moderate sulfate levels. The test plan should describe how the selection of additives relates to the expected characteristics of the wastes and constituents of concern.

4. Page 12, Figure 1-2: The figure does not make clear whether the solvent extraction procedure is a single-step process or multiple step process to render the remaining solid residue a nonhazardous waste. A single step process with any chemical may fail to meet TCLP and radioactive substances criteria for the treated residues. This point should be clarified. Similarly, the supernatant (liquid) from the precipitation step is shown as discharging into the wastewater collection system. The supernatant should meet the industrial wastewater pretreatment standards before it is discharged to the publicly owned treatment works (POTW). The treatability study should include a treatment step for the supernatant resulting from precipitation. TCLP and radioactive substances criteria for the stabilized waste and for the solid waste treated by solvent extraction should be listed in a

table of potential contaminants of concern. The acronyms MTCLP and PCT should be defined, and the criteria for MTCLP and PCT should be included.

5. Subsection 1.3.5, page 13, lines 1-11: Identify the various acids proposed for metals extraction testing and provide a brief justification for the selection of each.

6. Subsection 1.3.5, page 13,lines 1-11: Clarify whether the preliminary or remedy screening study will include all the steps shown in Figure 1-4 or if they will include only the metals extraction step with various chemicals. The text should clearly indicate the various steps to be used separately in the preliminary screening and in the advanced screening treatability studies. Whether or not additional studies such as "leaching kinetics . . ." will be conducted in the preliminary screening should also be specified.

   The text states that the most effective stabilization reagents used in the preliminary screening for stabilization of untreated silo material will be used to stabilize the precipitated material. Because the precipitated material will vary in composition due to the presence of organic compounds compared to untreated silo materials, a preliminary screening test should be conducted to select the effective stabilization reagents and best formulation for the advanced treatability studies. The procedures to be used for vitrification of the liquid from the solvent extraction step are not provided. Another viable option for volume reduction and treatment of liquid from solvent extraction is evaporation followed by stabilization of concentrated material from the evaporator. This process option should also be considered during the preliminary screening study.

7. Subsection 2.1, pages 1 and 2: Alternatives 3 through 5 are not described. If these alternatives have been previously eliminated, provide a brief explanation of the rationale for their elimination.

8. Subsection 2.1, page 2, line 16: The references Mound Laboratories (1951) and Battelle (1981) are not listed in the Work Plan References section.

9. Subsection 3.0, page 1, line 10-30: The specific objectives of the laboratory treatability testing program should be expanded to clearly state if they pertain to both the preliminary and advanced screening programs. If they do, the objectives should be given separately for preliminary screening and advanced screening.

   The text on the fifth bullet is not applicable for laboratory treatability testing program during preliminary screening. The preliminary screening test does not provide cost and design data (EPA, 1989).

   The following objectives should also be included:

   - Establish the validity of the selected stabilization technology.
   - Screen a large number of parameters and identify those that will be critical for later bench-scale studies.

10. Subsection 3.1, page 1, lines 16-17: Rewrite this test objective to more accurately reflect the type of leaching results desired in the treatability testing as described in general comment 2 above.

11. Subsection 3.1, page 1, lines 18-20: Provide justification for selection of 500 psi as an appropriate physical property performance criteria. What type of field conditions would necessitate the treated material to withstand 500 psi?

12. Subsection 3.1, page 1, lines 27-29: As described in the general comments section above, pH measurement of the formulated waste mixture should be added to the process parameters.

13. Subsection 3.1, page 1, lines 27-29: The potential evolution of gases and vapors during stabilization should be identified as a phenomena to be observed and recorded during testing. Such occurrences can affect remedy selection, influence the testing protocol in future studies, and require specific address in the remedy design.

14. Subsection 3.1, page 2, line 31 and Section 3.0 general: Explanation should be provided as to how the measurement of the temperature rise after stabilization treatment will be accomplished in a controlled manner to be of value in this phase of treatability testing. Temperature rise could theoretically be calculated and will be strongly affected in practice and in testing by the rate of chemical addition, by the adequacy of mixing, by sample size, by the ambient conditions in the laboratory or field, by physical occurrences such as wind, air conditioning, temperature of the containment vessel, and by factors such as thermometer placement in the mixture. What is the justification for selection of the 10 minute reaction time? Is this based on the proposed sample size and a predicted peak of heat release? The work plan does not adequately address these potential influences on the measurement, and therefore, such measurements will be of non quantitative value.

15. Table 3-2, page 4: The procedures for pocket penetrometer compressive strength, shear strength, 5-day static leach, permeability, waste-form temperature, and full TCLP tests, including sample volume and sample preparation, should be included in this work plan. In addition, the rationale (or a reference) for using the 5-day static leach test should be provided.

16. Subsection 3.2.2, page 6, general: The general design of the advanced testing phase is confused by the statements made on lines 14 through 16. These statements describing the advanced screening are not clear but seem to state that the formulations which are successful on strata samples will be rerun to confirm the first trial results. The statement implies that the criteria for success will be low reagent usage and volume increase. The measurement of formulation success of strata is inadequate, because it considers physical properties only. Furthermore, the next sentence is ambiguous in its purpose and intent to provide further study direction. What is considered "adequate waste form" and what types of "additional formulations" will be attempted?

17. Subsection 3.3, page 7, lines 22, 23, 28, and 29: The performance criteria for the extraction treatability testing should be reassessed with respect to general comment 2 above.

18. Subsection 3.3, page 7, lines 24 and 25: The work plan should clarify whether the proposed performance goals are total concentrations or leachable concentrations and should provide a justification for these levels.

19. Subsection 3.3, page 7, line 31: Provide justification for selection of 500 psi UCS as a performance criteria.

20. Subsection 3.3, page 8, lines 7-9: Reference specific comments 12, 13, and 14 above.

21. Subsection 3.3, page 8, line 10: Consideration should be given to evaluating a temperature matrix during vitrification studies.

22. Subsection 3.4 general: The data quality objectives (DQO) for the metal extraction/precipitation aspect of this phase of treatability testing appear weak with respect to evaluation of all the parameters that can potentially affect extraction effectiveness. This section does not address important process parameters such as pH, leaching time, temperature, and waste-to-leach solution ratios. The DQOs for this testing should be more comprehensive.

23. Section 4.0, page 1, line 4: Provide a justification for the selection of the 3/8-inch screen. The DQOs should be revised to include a record of the maximum particle size treated.

24. Subsection 4.1.2.2, page 2, general: This section should be rewritten to describe the procedures to be followed in performing the ethylenediaminetetraacetic acid (EDTA) extractions.

25. Subsection 4.1.2.3, page 2, line 17: The test plan should clearly identify the precipitation reagents that will be used.

26. Subsection 4.2, page 3, lines 6-9: Additional physical characterization, such as viscosity measurements, should be considered.

    TCLP analysis on the raw waste composites should be added to the chemical characterization. The text should provide a justification for the selection of the chemical parameters in Table 4-2.

    Specific analytical procedures should also be referenced in Table 4-2.

    Sample analysis of the stabilization additives, especially Portland cement and fly ash, should be performed as part of the treatability studies. Both additives contain some quantity of heavy metal constituents. Alternatively, a reagent mix blank samples can be prepared by using pure quartz sand in place of the waste materials. The sand should also be tested to confirm that it is free of any contamination.

27. Subsection 4.3, Figure 4-1: The stabilization treatability flowsheet indicates that Stage 1 preliminary screening will be based strictly on UCS testing. This test approach should be revised in accordance with general comment 1c above.

28. Subsection 4.3.2, page 10, lines 27-31: The text should justify the selection of the bentonite-silo material mixture ratios.

29. Subsection 4.4.1.1, page 13, line 6: Provide an explanation for performance of certain run numbers before others.

30. Subsection 4.4.1.1, page 13, line 7 and 8: What criteria will be used to determine when and if hydrogen peroxide and ferric chloride are to be added?

31. Subsection 4.4.1.1, page 13, lines 8 and 9: How will a determination be made if additional experiments (other run numbers) are "warranted"?

32. Subsection 4.4.1.3, page 13, line 16-25: The text in this section does not clearly indicate the purpose of stage 3 preliminary screening. Analytical procedures are detailed rather than presenting the objectives and steps to be used for stage 3 preliminary screening. The risk-based limits for uranium should be included in the work plan.

33. Table 4-4, page 15: Provide the rationale for the selection of hydrochloric acid (HCl) and the weak acetic acid (HOAc) for the extraction procedure. The residues in the silos include untreated uranium ore and other impurities from treating uranium-rich ore with nitric acid. With the use of HCl and HOAc, additional impurities such as chlorides and acetates will be increased in the leachate. The presence of these compounds will make the subsequent treatment steps more complex.

    The actual volume in milliliters (ml) of a particular normality of an acid and the weight in grams (gm) of the sample should be used in the table, rather than presenting the strength of an acid and dose (weight acid/weight sample) for experimental runs.

    EDTA is a good chelating agent which will form complexes with certain heavy metals. Precipitation of metal complexes is difficult and may require additional treatment steps to remove the metal complexes from the leachate. A separate flow sheet should be included for EDTA extraction. The formation of metal complexes with EDTA should be taken into consideration.

34. Subsection 4.4.2, page 17, lines 1-9: The text in this section is confusing. Except for sodium hydroxide (NaOH), the purpose of adding precipitation reagents and the types of precipitation reagents are not provided. This section should clearly explain step-by-step procedures for the vitrification process, the type of reagent, the amount of reagent in volume (ml) or in weight (gm), the final product, the side-stream waste products, and their treatment.

35. Figure 4-4, page 18: The steps shown in this figure should be explained in Subsection 4.4.2. The text should also include whether the vitrification reagents will be added in dry or wet form. The text in the box "Mix Reagent with Leachate" should be changed to "Mix Reagents with Concentrated Leachate." The side-stream condensate from the evaporation step should be shown on the flow sheet with treatment and disposal options after analysis of condensate.

36. Subsection 4.4.3.2, page 17, line 21: The text should define the term "promising."

37. Subsection 4.4.4, page 17, lines 27 and 28: The application of stabilization formulations from the stabilization testing is not justified. The precipitated metal solids will likely have very different physical and chemical properties than that of the sample matrix from silo; therefore, a separate study should be conducted to develop stabilization formulations for the precipitated materials.

38. Subsection 4.4.5.1, page 22, lines 5 and 14: The text should define how it will be determined if the polymer settling and filter aid tests are necessary.

39. Subsection 4.4.6, page 22, lines 20-26: A factorial experimental design should be used to obtain the optimal conditions for leaching time and temperature. The Cochran and Cox (1957) plan should be used to determine the number of experimental runs.

40. Section 6.0, general: Sampling and analysis methods for all proposed testing should be specifically provided in Section 6.0. This section should address all sampling and analytical methods for raw waste characterization, treated sample analysis, and additive characterization.

41. Section 8.0, general: The exact quantities of raw waste, liquid, and dry additives should be recorded. Interpretation of leachability test results should evaluate the sample leachability before and after treatment. Interpretation of the test results should also evaluate the treated sample results corrected for dilution, in order to separate the dilution effects of stabilization treatment from chemical fixation.

42. Section 13, general: Briefly describe the management and staffing responsibilities of individuals involved in the treatability testing project.

[redacted]

REFERENCES

Box, G.E.P. and R.B. Wilson, "On the Experimental Attainment of Optimum Conditions," Journal Roy. Stat. Soc. Ser. B, 13: 1-45 (1951).

Cochran, W.G. and Cox, G. N., 1957. Experimental Design, John Wiles & Sons, Inc. New York.

EPA, 1989. "Guide for Conducting Treatability Studies under CERCLA." Interim Final. EPA/540/2-89-058. December, 1989.

General Comments:

The scope of the treatment study is only with hazardous materials. However, the major contaminants are uranium, thorium, and decay products. The study omits consideration for stabilization of radiological components, particularly radon. The study should add investigation of radionuclides/radon or else justify omitting it. The study could also be suitably modified to include leachability and stability investigations of radionuclides including radon. Long term stabilization of radioactive contaminants, particularly radon will be essential to validation of a particular treatment technology. Therefore, the study in its current form cannot be used to make a definitive selection of treatment technology which would be best for comprehensive treatment of the residues preparatory to disposal.

Specific Comments:

1. Section 1.0, Table 1-1, page 4

a. The FMPC Action Level for multiple radionuclides shown in Table 1.1 must follow a sum rule, i.e. the sum of the ratios of concentrations to maximum contamination levels must be less than unity.

b. In the footnote denoted as "c" The proposed limits are 20 μg/L for total uranium, instead of the 20 g/L for total uranium, listed in the footnote.

2. Section 1.3, paragraph 1.3.1., page 6

The treatment to render the material nonleachable and not hazardous must also take in to account the emission of radon. The treatment method must not allow significant emission of radon in order to be considered a viable method for the final treatment of the residues.

3. Section 3.1, page 1

The performance objectives in this section need to address the stabilization of all radioactive constituents, especially radon.

[redacted]

4. Section 3.3, page 7

Current interpretation of 40 CFR 192 by the Office of Radiation Programs is that for situations where both Ra-226 and Ra-228 are present, the combined concentration should be less than 5 pCi/g. This will also impact situations where both thoriums are present.

5. Section 3.4, page 8

a. Paragraph 4 should consider alpha heating from precipitate concentration.
b. Table 3-3 - Modified TCLP and PCT entries reference relative leachabilities of radionuclides. Specific isotopes should be referenced. Radon-220 and Radon-222 should be specifically addressed.

6. Section 4.0, Table 4-3, page 6

In the Stabilization Matrices, the Potential Range of water needed in grams for run number 1 needs to be clarified. Should the range be 6.5 - 9, .9 - 6.5, or is 9 - 6.5 correct? The matrix should be consistent throughout in the manner that the values are presented.

7. Section 4.0, Table 4-6, page 19

In the footnote "a", the word "mixtrue" needs to be replaced with the word "mixture".

8. Section 4.1.2.1., page 2

A more accurate analysis for uranium would be through alpha spectroscopy. The method described may not be accurate enough to characterize the leachability of uranium.

9. Section 4.1.2.2, page 2

a. Need to specify how the Feigl Test is modified and to specify the effect of this modification on accuracy.
b. The reference to Appendix E is incorrect.

10. Section 4.3.1., page 3

Sulfur cement has been recommended by the staff at the Nevada Operations Office as a good cement for radon retention. It does not appear to be considered here.

11. Section 4.3.2., second paragraph, page 10

Need to justify the 20/80 and 10/90 weight percentages since only one foot of bentonite is to be added to approximately 20 feet of residue.

12. Section 4.4.8, page 24

In the fourth bullet under data to be recorded during the leachant screening, the word "lend" needs to be replaced with "lead". In the third bullet under

[redacted]

data to be recorded during the precipitation screening the word "is" needs to be replaced with the word "in".

13. Section 8.4, page 4

In the example of calculations of precision, the variable values do not correspond. In the equation the variable used is RFP, while in the key for the formula the variable used is RPD. This needs to be clarified.

14. Section 12.0, page 2

In the first sentence the word "communicated" is inappropriate in form and needs to be replaced with "communicate".

15. Section 1.0, page A-1-2

Part VIIa. needs to be clarified as to the number of samples to be used. It needs to be more specifically stated whether there will be 3 samples, 1 each at a pH of 9, 10, and 11, or if one sample is progressively changed in pH from 9 to 10 to 11 in the process.

16. Section 6.2, page A-6-1, second paragraph

a. Urine bioassay for thorium is not appropriate due to insolubility of thorium compounds. Uranium needs to be included due to chemical toxicity.

b. 3rd paragraph, "gross alpha activity" is inappropriately used for specifying an activity concentration.

17. Section 10.0, page A-10-1

In the last two paragraphs the term "client" needs to be clarified as to whom is being referenced.

18. Appendix B, Section 5.8.1 and 5.8.2, page 4

The values for "B" and "C" are unclear as stated. The value for "B" is the volume of water added to the sludge. The value "C" is the volume of water added to the treated sludge.