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Abstract: The purpose of the laboratory test program described here will be to evaluate whether actual retrieved saltcake waste from tank 241-S-112 might provide opportunities for separations into streams suitable as feed to various supplemental treatment technologies. The separation process to be evaluated is fractional crystallization using a combination of heaing, evaporation, and cooling.

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Test Plan for Tank 241-S-112 Fractional Crystallization Study

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ACRONYMS AND ABBREVIATIONS

ESP	Environmental Simulation Program
GEA	gamma energy analysis
IC	ion chromatography
ICP	inductively coupled plasma spectroscopy
PLM	polarized light microscopy
SEM	scanning electron microscopy
SpG	specific gravity (or density)
TIC	total inorganic carbon
TOC	total organic carbon
wt%	weight percent
WTP	Waste Treatment Plant
XRD	x-ray diffraction

1.0 INTRODUCTION

Fractional crystallization is one of the oldest separation methods in the chemical industry, and is still used in a wide variety of industrial applications. It is a method of separating a mixture into its individual components. The objective of the laboratory program described in this Test Plan is to evaluate whether fractional crystallization could be used to support supplemental treatment of retrieved single shell tank saltcake waste at the Hanford site.

Based on current designs, the Waste Treatment Plant (WTP) does not have the capacity to treat all of Hanford tank waste by the Department of Energy's accelerated goal of 2028. Plans are to use one or more supplemental treatment technologies (bulk vitrification, steam reforming, or cast stone) to treat selected portions of the waste by alternative methods. Fractional crystallization may be used to separate the retrieved saltcake waste into streams that will provide appropriate feed to the WTP and the supplemental technologies.

For example, consider a simple hypothetical retrieved saltcake waste solution containing just cesium nitrate, sodium nitrate, and sodium sulfate, with the two sodium salts at saturation. The solution could be heated to precipitate anhydrous sodium sulfate, which has retrograde solubility (i.e., it becomes less soluble as the temperature increases). The sulfate salt could be removed from the slurry (by filtration, centrifuging, or settle/decant) to provide the feed to, perhaps, the cast stone supplemental treatment. (The sulfate salt may need to be washed or metathesized to provide sufficient decontamination before it is sent to supplemental treatment.) The remaining liquid, containing the sodium nitrate and cesium nitrate, could be cooled to precipitate some (but not all) of the sodium nitrate, leaving the cesium and remaining sodium nitrate in solution. The separated and decontaminated sodium nitrate could be sent to, perhaps, bulk vitrification. The remaining liquid stream containing all of the cesium, some of the nitrate, and very little sulfate would be the appropriate fraction to send to the WTP.

An important aspect of fractional crystallization development is that the "process" must be inexpensive to deploy. That will mean there can't be any "large" facility requirements and few new processing steps. The purpose of the laboratory test program described here will be to evaluate whether actual retrieved saltcake waste from tank 241-S-112 might provide opportunities for separations analogous to those described for this hypothetical example, within these narrow constraints. If the process shows promise, laboratory testing will be extended to other saltcake tanks. The current test plan, however, applies only to tank 241-S-112.

2.0 DESCRIPTION OF TEST

Samples of liquid waste retrieved by dissolving saltcake from tank 241-S-112 will be used to evaluate the feasibility of using fractional crystallization as a waste pretreatment method. Simulated waste solutions will be used to develop the specific sample handling methods, but the process evaluation will be made using actual tank waste samples.

Methods that may be used to initiate crystallization include any combination of the following:

- Evaporation (under atmospheric and/or vacuum conditions)
- Heating (from tank temperature up to as high as atmospheric boiling, ~130 °C)
- Cooling (from 130 °C to as low as 10 °C)

Identification of solid phases will be essential to the success of the program. In addition to traditional wet chemistry methods of analysis, three methods will be used to examine the solid phases directly: polarized light microscopy (PLM), scanning electron microscopy (SEM), and x-ray diffraction (XRD). Methods using these techniques are described in detail in "Identification of Solid Phases in Saltcake from Hanford Site Waste Tanks" (Herting et al., 2002).

Computer modeling using OLI's Environmental Simulation Program (ESP) will also be an important part of the test program. The ESP modeling will be performed by personnel from Pacific Northwest National Laboratory. The function of the modeling will be two-fold. First, ESP will be used to predict what combinations of evaporation, heating, and cooling are likely to provide the desired separation (based on the analysis of the feed solution). Second, ESP will be used to develop a proposed process flowsheet based on the separations actually achieved in the laboratory tests.

A literature survey will be conducted to find relevant examples of the use of fractional crystallization, and to provide some theory to support the process flowsheets that will be developed. One example is given here in Section 2.5.

2.0 Tank Samples

Several sampling events are planned at tank 241-S-112 during the course of saltcake retrieval (Banning 2003, Appel 2003). The first sampling event is projected to take place after approximately 300 kgal of liquid (dilute dissolved waste) has been pumped from the tank. Subsequent sampling events are planned after each additional 800 kgal of liquid has been pumped. Two 500-mL samples will be taken specifically for the fractional crystallization project during the second sampling event and each subsequent sampling event. A minimum of four sampling events

are planned (corresponding to a minimum of three fractional crystallization samples). The fractional crystallization samples will be taken from the liquid in the saltwell at an elevation of twelve inches above the level of solids in the saltwell.

For each sampling event, a composite sample will be created by combining the liquid phase from each of the two 500-mL samples. The first step will be to record visual observations of the individual samples (color, clarity, volume percent settled solids). The liquid phase from each sample will be collected by a combination of settle/decant and centrifugation. The overall weight percent centrifuged solids will be recorded. If the amount of centrifuged solids is significant (over 5% by weight), then the solids will be characterized by PLM/SEM/XRD to identify the major solid phases. However, the solids will not be used for the fractional crystallization test program.

The liquid composite sample from each sampling event will be analyzed to establish a baseline composition. The analyses to be performed on the liquid composite are shown in Table 2-1. This suite of analyses is sufficiently complete to allow the calculation of the important quality assurance parameters, mass balance and charge balance. The mass balance (sum of all the component analytes) should equal 100% by weight, and the charge balance (cation/anion equivalent ratio) should equal 1.00, if the analytical results are accurate.

Table 2-1. Analysis Menu for Liquid Samples

Procedure	Method	Analytes
LA-564-101	Gravimetric	Wt% H_2O
LA-510-112	Gravimetric	Specific Gravity (SpG)
LA-342-100	Acidification & Persulfate Ox.	TIC/TOC
LA-211-102	Potentiometric Titration	OH^- (free hydroxide)
LA-533-107	Ion Chromatography	Br^-, Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, $C_2O_4^{2-}$
LA-505-161	ICP/AES	Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Eu, Fe, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, S, Sb, Se, Si, Sm, Sr, Th, Ti, U, V, Y, Zn, Zr
LA-548-121	GEA	γ-emitting radionuclides, including ^{137}Cs
LA-438-101	Solvent Extraction/Liq. Scint.	^{99}Tc
LA-378-103	Extraction/gamma counting	^{129}I

2.2 Tests with Simulated Waste

Before beginning any testing with actual tank waste samples, the proposed methods will be tested using a simulated waste solution. The simulant will be made from sodium salts dissolved in water to achieve concentrations representative of anticipated actual waste samples. The concentrations proposed for the simulant are shown in Table 2-2. Whether the simulant is a perfect representation of any one of the actual waste composite samples is not important, because the only purpose of the simulant will be to develop methods and techniques.

Table 2-2. Composition of Simulated Waste Solution[1]

Salt	Molarity
$NaAl(OH)_4$	0.05
NaOH	0.25
$NaNO_3$	2.00
$NaNO_2$	0.10
Na_3PO_4	0.05
Na_2SO_4	0.60
Na_2CO_3	1.00

[1]density = 1.35 g/mL

2.3 Preliminary Evaporation of Composite Sample

With each composite 241-S-112 liquid sample, the first step will be to subject an aliquot of the sample to a preliminary evaporation test. The purpose of the test will be to identify some general characteristics of the waste and its behavior (to avoid surprises during subsequent tests), and to compare the observed solid phases with computer modeling (ESP) predictions.

The test will be done in a laboratory fume hood. A 100 mL aliquot of the composite sample will be placed in an open 150 mL beaker with a magnetic stirbar. The solution will be evaporated until the slurry contains approximately 20% settled solids by volume at ambient temperature. (Heat may be used during the early stages to speed evaporation.) When the slurry has reached the 20% settled solids endpoint, the solids will be identified using PLM/SEM/XRD. The solids will be separated by vacuum filtration, and the liquid phase will be returned to the beaker to resume evaporation. This process of *evaporate – crystallize – identify solids – separate phases* will continue until further solid/liquid separations become impractical.

2.4 Flowsheet Process Test Using Composite Sample

One or more potential process flowsheets will be developed to effect the desired separation of the waste into appropriate supplemental treatment feed streams. Flowsheet planning will be based on the results of the composite sample analysis, the results of the preliminary evaporation test, ESP modeling, and general chemical knowledge.

The individual processes within the proposed flowsheet will include some combination of evaporation, heating, cooling, and filtration. Frequent measurements of sample volumes and weights will be made, and sufficient samples will be analyzed, so that detailed mass balance calculations can be made.

The example cited in the Introduction can be used to describe the measurements to be taken during the flowsheet process test. To reiterate the example: consider a simple hypothetical retrieved saltcake waste solution containing just cesium nitrate, sodium nitrate, and sodium sulfate, the two latter salts at saturation. The solution could be heated to precipitate anhydrous sodium sulfate, which has retrograde solubility. The sulfate salt could be removed from the slurry (by filtration, centrifuging, or settle/decant) to provide the feed to, perhaps, the Cast Stone supplemental treatment. The remaining liquid, containing the sodium nitrate and cesium nitrate, could be cooled to precipitate some (but not all) of the sodium nitrate, leaving the cesium and remaining sodium nitrate in solution. The separated and decontaminated sodium nitrate could be sent to, perhaps, bulk vitrification. The remaining liquid stream containing all of the cesium, some of the nitrate, and very little sulfate would be the appropriate fraction to send to the WTP.

To carry out the process test for this hypothetical example, a 200-mL aliquot of the feed solution, pre-analyzed according to the menu in Table 2-1, is placed in a "boildown apparatus" of the type used to perform boildown tests for feed to the 242-A Evaporator (Bechtold 2002). The boildown pot is weighed to determine the exact weight of feed solution. The solution is heated to precipitate anhydrous sodium sulfate. The solution may also be reduced in volume from 200 mL to 150 mL to improve sulfate removal without risking precipitation of nitrate. The distillate (water) is collected in a graduated cylinder to constantly monitor the volume reduction. When the distillate volume reaches 50 mL, the slurry is vacuum filtered. The filtrate is returned to the boildown pot, which is then re-weighed. The wet crystals are weighed, then dissolved in water and analyzed for sulfate, nitrate, and cesium to determine the amount and purity of the sodium sulfate product. At this point, the dissolved salt could be recrystallized to improve purity. Alternatively, it could be metathesized by reacting the dissolved sodium sulfate with lime (CaO) or slaked lime [$Ca(OH)_2$] to convert the salt to $CaSO_4$ and NaOH.

The solution in the boildown pot is further reduced in volume by boiling under vacuum to keep the temperature low. The volume reduction is continued until solids form ($NaNO_3$ crystals). Additional product crystals may be obtained by cooling the solution further. The cooled solution is filtered. The filtrate is collected, weighed, and analyzed to determine the amount of each component remaining in the liquid phase (the WTP feed stream in this hypothetical case). The filtered solids are collected, weighed, dissolved in water, and analyzed to determine the amount and purity of the $NaNO_3$ recovered.

In this hypothetical case, the feed was divided into three product streams – a sulfate-rich stream, a nitrate-rich stream, and a cesium-rich WTP feed stream. From the test results, it would be possible to construct a complete mass balance for the flowsheet, showing the distribution of each feed component into the three streams. The "real world" samples from tank 241-S-112 will be far more complex, but the principles will be the same. Flowsheets involving more than three product streams are not envisioned, and some might involve as few as two streams, one for sulfate and one for WTP feed.

The flowsheet process test will be performed a minimum of once for each 241-S-112 sampling event. If ESP modeling and/or chemical knowledge suggests more than one potential flowsheet for any given sampling event, then the flowsheet process test will be performed for each flowsheet.

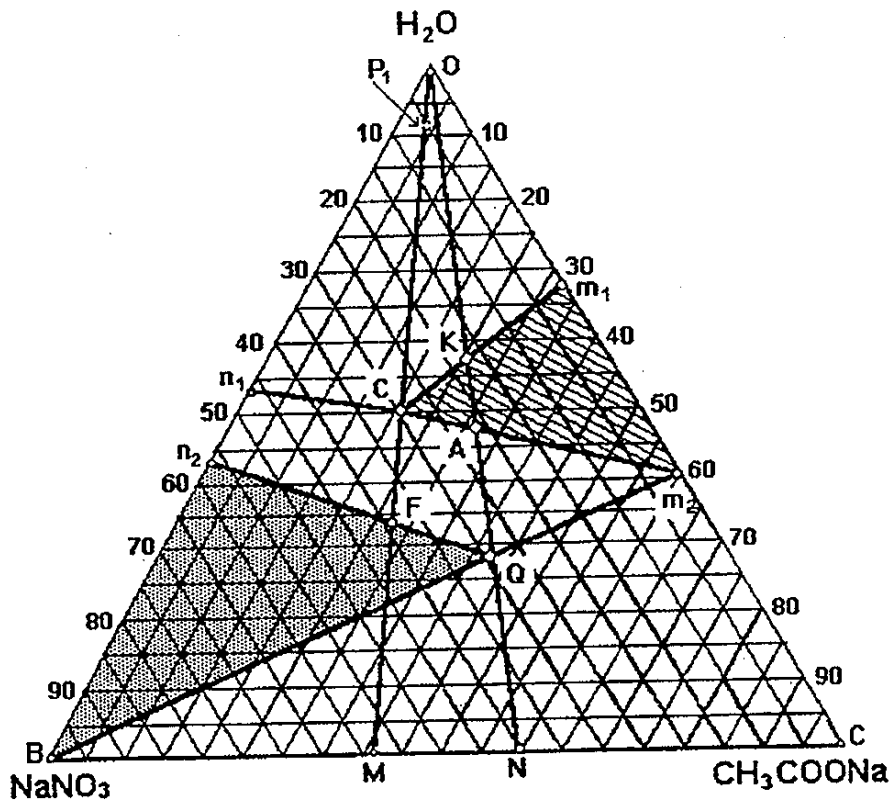
2.5 Example from Literature

Scientists at the Institute of Physical Chemistry of the Russian Academy of Sciences have done extensive work on fractional crystallization of radioactive tank waste (Krapukhin 1997). Their separation of sodium nitrate and sodium acetate is an elegant example of the importance of understanding phase diagram relationships in designing a successful flowsheet.

The solubilities of $NaNO_3$ and $NaC_2H_3O_2 \cdot 3H_2O$ are not very different, so effective separation by straightforward crystallization is difficult. Very nice separations were achieved, however, using the process shown schematically in Figure 2-1. (The figure is taken directly from the referenced document, without alteration.) The influence of temperature is included but not shown explicitly in the figure. The shaded areas of the figure represent regions in which crystallization of one salt is possible ($NaNO_3$ in the lower left region at 70 °C, $NaC_2H_3O_2 \cdot 3H_2O$ in the upper right region at 20 °C).

Consider a dilute feed solution at point P_1, containing 91% water, 5% $NaNO_3$, and 4% $NaC_2H_3O_2$ by weight. As the solution is evaporated at 70 °C, its composition moves along the line O–M until it reaches point F, where $NaNO_3$ begins to precipitate. Further evaporation causes more $NaNO_3$ to precipitate, and the composition of the solution moves along line n_2–Q until it reaches point Q. At that point, the crystals are harvested. Water is added to the solution to move the solution composition along line N–O from point Q to point A, and the solution is cooled to 20 °C to induce precipitation of $NaC_2H_3O_2 \cdot 3H_2O$. As the acetate salt precipitates, the solution composition moves from point A to point C, at which point the crystals are harvested. From point C, the process is repeated – heating and evaporating to point F, harvesting $NaNO_3$ at point Q, diluting and cooling to point A, harvesting $NaC_2H_3O_2 \cdot 3H_2O$ at point C, and so on until the salts have been separated. The activity of the separated crystals, coming from ^{106}Ru and ^{137}Cs, was 2-3% of the initial activity of the radioactive waste.

Figure 2-1. Sodium Nitrate / Sodium Acetate Phase Diagram (in weight percent).



3.0 QUALITY ASSURANCE

This document serves as a 'test plan' as described in *Laboratory Test Planning* (ASP-310, Section 1.9, Rev. 4). Review and approval of this document by a client representative will provide authorization to perform the described work. The associated laboratory 'test procedures' will be issued separately. Review and approval of the test procedures by 222-S laboratory management will constitute approval to initiate the work. Test instructions will be recorded in a controlled laboratory notebook before work begins; observations and data will be recorded as the work is done.

Minor changes to the test plan and/or test procedures that will neither adversely impact the quality or inclusiveness of the work scope nor result in significant cost or schedule overruns may be implemented at the discretion of the cognizant scientist without explicit client approval. These types of changes will be noted in the report presenting the results of the study. Other, more material changes will not be implemented before receiving explicit concurrence from client contacts.

4.0 SAFETY

The activities required to successfully complete this test plan are not associated with any hazards which are not commonly involved with the handling and analysis of hazardous, radiological tank waste samples within the 222-S laboratory complex. All test plan activities will be conducted in such a manner as to comply with the requirements of the *222-S Laboratory Complex Chemical Hygiene Plan* (ASP-310, Sec. 4.5, Rev. 3). Radiological hazards will be mitigated by working within the guidance provided in the *Radiation Protection Program* (HNF-MP-5184) and in compliance with the specific instructions and limiting conditions found in the authorizing Radiological Work Permit(s).

5.0 WASTE HANDLING

Three waste streams will be generated from this test program.

Stream #1 is the waste resulting from analysis of samples. Each waste generated from these routine analyses will be handled in accordance with the instructions in the procedures for the respective analyses.

Stream #2 is the used and left-over tank waste material. This material, expected to be less than 1 kg, will be discarded to the 219-S Building tanks via a hotcell drain, per procedure "*Cubicle Housekeeping, Waste Disposal, and Management,*" LO-100-107, Rev. H-1 (March 10, 2003).

Stream #3 is the solid hotcell waste and hood waste consisting of used centrifuge cones, sample vials, plastic syringes, filters, etc. This waste will be rinsed with water, loaded into waste cans, removed from the hotcell, and disposed of per procedure "*Segregate and Manage Solid Laboratory Wastes*," LO-100-151, Rev. H-3 (August 28, 2003).

Other than the waste streams just described, there will be no accumulating of hazardous waste. Therefore, no Waste Stream Fact Sheet or Waste Compatibility Assessment documentation will be required.

6.0 SCHEDULE AND DELIVERABLES

This test plan is scheduled to be issued by October 31, 2003. An interim report with the results of the literature survey will be issued by January 15, 2004. A complete report of the test results will be issued in the form of a draft supporting document by April 1, 2004. Informal interim status reports will be issued to the customer as needed.

7.0 REFERENCES

Appel, J. N. (2003), *Tank 241-S-112 Grab Sampling and Analysis Plan During Retrieval Operations*, RPP-17921, Rev. 0, CH2M HILL, September 19.

Banning, D. L. (2003), *Data Quality Objectives for Supplemental Treatment Evaluation of Saltcake Waste in Tank 241-S-112*, RPP-17624, Rev. 0, CH2M HILL, September 15.

Bechtold, D. B. (2002), *Determination of Boiling Pressures and Temperatures as a Function of %WVR (Boildown)*, Laboratory Technology Procedure LT-519-183, Rev B-0, April 8.

Herting, D. L. (2002), G. A. Cooke, and R. W. Warrant, *Identification of Solid Phases in Saltcake from Hanford Site Waste Tanks*, HNF-11585, Rev. 0, Fluor Hanford, September 26.

Krapukhin, V. B. (1997), E. P. Krasavina, and A. K. Pikaev, *Crystallization of Sodium Nitrate from Radioactive Waste*, PNNL-11616, Pacific Northwest National Laboratory, Richland, Washington.