

COMPLETE

ENGINEERING CHANGE NOTICE

Page 1 of 2

1. ECN 614153

Proj.
ECN

2. ECN Category (mark one)		3. Originator's Name, Organization, MSIN, and Telephone No.		4. Date	
Supplemental ☐ Direct Revision ☒ Change ECN ☐ Temporary ☐ Standby ☐ Supersedure ☐ Cancel/Void ☐		J. P. Sederburg, Waste Tanks Process Control, 373-3327		8/3/94	
		5. Project Title/No./Work Order No.	6. Bldg./Sys./Fac. No.	7. Approval Designator	
		Tank 241-C-106 Sluicing	N/A	S	
		8. Document Numbers Changed by this ECN (includes sheet no. and rev.)	9. Related ECN No(s).	10. Related PO No.	
		WHC-SD-WM-ES-290, Rev. 1	N/A	N/A	
11a. Modification Work		11b. Work Package No.	11c. Modification Work Complete		11d. Restored to Original Condition (Temp. or Standby ECN only)
☐ Yes (fill out Blk. 11b) ☒ No (NA Blks. 11b, 11c, 11d)		N/A	N/A		N/A
		Cog. Engineer Signature & Date		Cog. Engineer Signature & Date	
12. Description of Change					
Revised WHC-SD-ES-290 to incorporate internal letter # 7E310-94-035.					
13a. Justification (mark one)					
Criteria Change ☒		Design Improvement ☐		Environmental ☐	
As-Found ☐		Facilitate Const. ☐		Const. Error/Omission ☐	
13b. Justification Details					
N/A					
14. Distribution (include name, MSIN, and no. of copies)				RELEASE STAMP	
See distribution page.				OFFICIAL RELEASE 13 BY WHC DATE AUG 24 1994 STA 4	

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ENGINEERING CHANGE NOTICE

Page 2 of 2

1. ECN (use no. from pg. 1)

614153

15. Design Verification Required

☐ Yes
☒ No

16. Cost Impact

ENGINEERING

Additional ☐ \$
Savings ☐ \$

CONSTRUCTION

Additional ☐ \$
Savings ☐ \$

17. Schedule Impact (days)

Improvement ☐
Delay ☐

18. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 12. Enter the affected document number in Block 19.

SDD/DD	☐	Seismic/Stress Analysis	☐	Tank Calibration Manual	☐
Functional Design Criteria	☐	Stress/Design Report	☐	Health Physics Procedure	☐
Operating Specification	☐	Interface Control Drawing	☐	Spares Multiple Unit Listing	☐
Criticality Specification	☐	Calibration Procedure	☐	Test Procedures/Specification	☐
Conceptual Design Report	☐	Installation Procedure	☐	Component Index	☐
Equipment Spec.	☐	Maintenance Procedure	☐	ASME Coded Item	☐
Const. Spec.	☐	Engineering Procedure	☐	Human Factor Consideration	☐
Procurement Spec.	☐	Operating Instruction	☐	Computer Software	☐
Vendor Information	☐	Operating Procedure	☐	Electric Circuit Schedule	☐
OM Manual	☐	Operational Safety Requirement	☐	ICRS Procedure	☐
FSAR/SAR	☐	IEFD Drawing	☐	Process Control Manual/Plan	☐
Safety Equipment List	☐	Cell Arrangement Drawing	☐	Process Flow Chart	☐
Radiation Work Permit	☐	Essential Material Specification	☐	Purchase Requisition	☐
Environmental Impact Statement	☐	Fac. Proc. Samp. Schedule	☐	Tickler File	☐
Environmental Report	☐	Inspection Plan	☐		☐
Environmental Permit	☐	Inventory Adjustment Request	☐		☐

19. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing organization has been notified of other affected documents listed below.

Document Number/Revision

Document Number/Revision

Document Number Revision

20. Approvals

Signature

Date

Signature

Date

OPERATIONS AND ENGINEERING

Cog. Eng. J. P. Sederburg

Cog. Mgr. N. W. Kirch

QA

Safety L. E. Thomas

Environ.

Other

D. A. Reynolds

H. Babad

ARCHITECT-ENGINEER

PE

QA

Safety

Design

Environ.

Other

J. P. Harris

DEPARTMENT OF ENERGY

Signature or a Control Number that tracks the Approval Signature

ADDITIONAL

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

RELEASE AUTHORIZATION

Document Number: WHC-SD-WM-ES-290 REVISION 2

Document Title: CHEMICAL COMPATIBILITY OF TANK WASTES IN 241-C-106,
241-AY-101, AND 241-AY-102

Release Date: 08-24-94

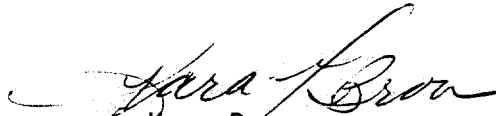
* * * * *

This document was reviewed following the
procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

* * * * *

WHC Information Release Administration Specialist:



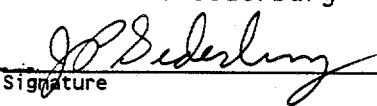
Kara Broz

(Signature)

08-24-94

(Date)

KE 8/24/94

SUPPORTING DOCUMENT		1. Total Pages
2. Title Chemical Compatibility Of Tank Wastes In 241-C-106, 241-AY-101, And 241-AY-102		3. Number WHC-SD-WM-ES-290
		4. Rev No. 2
5. Key Words Tank 241-C-106, Tank 241-AY-101, Tank 241-AY-102, Chemical Compatibility, Waste Compatibility, Sluicing, Waste Recovery Sluicing System, Single- Shell Tank, Retrieval, 241-C Tank Farm, 241-AY Tank Farm, Project W-320		6. Author Name: J. P. Sederburg  Signature Organization/Charge Code 7E310/D2M53
7. Abstract APPROVED FOR PUBLIC RELEASE This report documents the chemical compatibility of waste types within tanks 241-C-106, 241-AY-101, and 241-AY-102. This information was compiled to facilitate the transfer of tank C-106 waste to tank AY-102 utilizing supernatant from AY-101 as the sluicing medium. This document justifies that no chemical compatibility safety issues currently understood, or theorized from thermodynamic modeling, will result from the intended sluice transfer operation.		
8. ~~PURPOSE AND USE OF DOCUMENT - This document was prepared for use within the U.S. Department of Energy and its contractors. It is to be used only to perform, direct, or integrate work under U.S. Department of Energy contracts. This document is not approved for public release until reviewed.~~ ~~PATENT STATUS - This document copy, since it is transmitted in advance of patent clearance, is made available in confidence solely for use in performance of work under contracts with the U.S. Department of Energy. This document is not to be published nor its contents otherwise disseminated or used for purposes other than specified above before patent approval for such release or use has been secured, upon request, from the Patent Counsel, U.S. Department of Energy Field Office, Richland, WA.~~ ✓ DISCLAIMER - This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.		10. RELEASE STAMP OFFICIAL RELEASE BY WHC DATE AUG 24 1994  31A 4
9. Impact Level S		

MASTER

870

[illegible]

EXECUTIVE SUMMARY

This document evaluates the chemical compatibility of wastes currently stored in tanks 241-C-106, 241-AY-101, and 241-AY-102. Specifically, this document describes the acceptability to transfer these wastes in the following sequence:

1. Tank 241-AY-102 supernatant to any other tank
2. Tank 241-AY-101 supernatant to tank 241-AY-102
3. Sluice tank 241-C-106 to tank 241-AY-102 using the supernatant of tank 241-AY-102 as the sluicing medium.

Four safety-related decision elements applicable to the Waste Compatibility Program were reviewed, as follows:

1. Criticality
2. Energetics
3. Corrosivity
4. Flammable gas accumulation.

Three transfer steps were reviewed against these elements, as follows:

1. Transfer of 2,044,116 L (540,000 gal) of supernatant from tank 241-AY-101 to tank 241-AY-102
2. Transfer of supernatant (sluicing medium) from tank 241-AY-102 to tank 241-C-106
3. Transfer of tank 241-C-106 contents to tank 241-AY-102 to mitigate the current high-heat safety concern in tank 241-C-106.

Of the 12 decision elements identified as needing analysis, only 1 was not within acceptable limits. However, this element will not hinder the sluicing of tank 241-C-106 provided that appropriate chemical adjustments are made before, or during, the specific transfer of tank 241-C-106 contents to tank 241-AY-102.

Following the completion of Revision 1 of this document, an issue was raised regarding aluminum-containing compounds (hereinafter aluminum is used in place of aluminum-containing compounds) in tank 241-C-106 solids and whether the solids could form gels that trap flammable gases. The base case sluicing sequence was evaluated against three alternatives (refer to Appendix G of this document, internal letter 7E310-94-035 [Reynolds 1994]*). Although all evaluated sluicing alternatives are not expected to result in gas retention behavior, the alternative of sluicing with tank 241-AY-101 supernate adjusted to 2.5 molar hydroxide is recommended as the project baseline.

*Reynolds, D. A., 1994, *Evaluation of 241-C-106 Sluicing Fluid Options for Preventing Flammable Gas Retention* (internal letter 7E310-94-035 to J. P. Harris, July 25), Westinghouse Hanford Company, Richland, Washington.

This allows flexibility to introduce sodium hydroxide for aluminum dissolution while analysis and mixing studies are completed, thereby reducing technical risk to the sluicing project.

CONTENTS

1.0	INTRODUCTION	1
2.0	SCOPE	1
3.0	DISCUSSION	1
3.1	WASTE DESCRIPTIONS	7
3.2	WASTE TRANSFERS	8
3.2.1	AY-102 Supernatant to Any Other Tank	8
3.2.2	AY-101 Supernatant to AY-102	9
3.2.3	C-106 to AY-102	10
3.3	WASTE COMPATIBILITY	10
3.3.1	Commingling of AY-102 Waste with Any Other Tank Waste	12
3.3.2	Commingling of AY-101 Waste with AY-102 Waste	12
3.3.3	Commingling of C-106 Waste with AY-102 Waste	16
3.3.4	Flammable Gas Watch List Issue	21
4.0	CONCLUSION	22
5.0	REFERENCES	23
6.0	BIBLIOGRAPHY	24
7.0	GLOSSARY	24
APPENDIXES		
A	CHARACTERIZATION DATA FOR TANKS	A-1
B	CHEMICAL COMPATIBILITY EVALUATION CRITERIA	B-1
C	TANK WASTE MASS RATIOS NORMALIZED TO PLUTONIUM	C-1
D	TANK 241-C-106 WASTE HEAT GENERATION PROFILES	D-1
E	SELECTION OF PROJECT W-320 RECEIVER TANK AND WASTE TYPE	E-1
F	CHEMISTRY OF MIXING TANKS 241-AY-101 AND 241-AY-102	F-1
G	EVALUATION OF 241-C-106 SLUICING FLUID OPTIONS FOR PREVENTING FLAMMABLE GAS RETENTION	G-1

LIST OF FIGURES

1	Schematic of Tank 241-C-106 to Tank 241-AY-102 Slurry	3
---	---	---

LIST OF TABLES

1	Initial Tank Inventories	7
2	Tank Inventories after Transfer of Tank 241-AY-102 Supernatant	9
3	Tank Inventories after Transfer of Tank 241-AY-101 Supernatant	10
4	Tank Inventories at Completion of Project W-320	11
5	Waste Compatibility Summary	13

CHEMICAL COMPATIBILITY OF TANK WASTES IN
TANKS 241-C-106, 241-AY-101,
AND 241-AY-102

1.0 INTRODUCTION

Tank 241-C-106 (C-106) is a high-heat single-shell tank. By definition this means that the contents of this tank generate heat at a rate greater than 1.2×10^4 W (4×10^4 Btu/h). Radionuclides such as strontium-90 (^{90}Sr) are believed to be responsible for this excessive heat flux. Furthermore, it is believed that these heat-generating elements are predominantly in the sludge that has settled to the bottom of C-106.

The chemical compatibility of the wastes currently stored in C-106, 241-AY-101 (AY-101), and 241-AY-102 (AY-102) is the focus of this document. At issue is whether the transfer of materials planned in the Project W-320, Tank 241-C-106 Waste Retrieval Sluicing System, work scope would cause adverse chemical reactions in the tank farms.

This study examines the retrieval action associated with sluicing C-106 waste into double-shell tank AY-102. The sluicing medium planned in this effort is supernatant from AY-101. To accomplish this sluicing, AY-102 needs to be emptied as much as practical. The necessary quantity of AY-101 waste would subsequently be transferred into AY-102, and this liquid would serve as the sluicing medium for this project.

2.0 SCOPE

Available specific characterization data for C-106, AY-101, and AY-102 are presented in Appendix A of this document. The interactions of these wastes are discussed by defining specific portions of the C-106 sluicing sequence (steps). Analyses are performed on these steps for potential safety problems that could result from commingling of the different wastes.

Evaluation criteria applicable to the chemical compatibility of the intended transfers are presented in Appendix B.

3.0 DISCUSSION

Decisions about allowing, or prohibiting, the completion of transfers within the double-shell tank farm system are based on waste compatibility (Carothers 1994). The primary objective of the Waste Compatibility Program is to prevent formation of an unreviewed safety question (USQ). Unreviewed safety questions have resulted from past operations of the double-shell tank

system limiting the ability to receive, process, and store waste. Therefore, preventing a USQ in the double-shell tank system as the result of sluicing C-106 is desired.

The goal of Project W-320 is to retrieve high-heat-generating sludge from C-106. This is intended to be performed by slurrying the solids (sluicing) using supernatant from AY-101. It is preferred that the sluicing of C-106 be performed in a continuous fashion. Therefore, the supernatant from AY-101 is first planned to be transferred to AY-102.

Tank AY-102 is ventilated by the tank 241-A-702 (702-A) vessel ventilation system. *Operating Specifications for Aging-Waste Operations in 241-AY and 241-AZ*, OSD-T-151-00017 (Bergmann 1989a) specifies a maximum heat generation of 1.2×10^6 W (4×10^6 Btu/h) for waste vented by the 702-A system. Other double-shell tanks specified in OSD-T-151-00007, *Operating Specifications for the 241-AN, AP, AW, AY, AZ, and SY Tank Farms* (Harris 1992) are limited to 20,000 W (70,000 Btu/h) or less. The high-heat removal capability of AY-102 makes it an optimum receiver tank for the waste from C-106.

From AY-102, supernatant will be transferred to C-106. In turn, the resultant slurry formed in C-106 will be transferred to AY-102. Clarification of this fluid by settling is planned such that it can be used in retrieving additional sludge.

The current AY-102 supernatant will be transferred to a tank other than AY-102, AY-101, or C-106. This will accommodate the transfer of waste from AY-101 and C-106 into AY-102. These transfers (AY-102 to another tank, and AY-101 to AY-102) will be completed before waste is transferred out of C-106.

The resulting sluicing configuration will be a closed system composed of: C-106, AY-102, and the associated waste transfer and receiving systems. Graphically, this final step is illustrated in Figure 1.

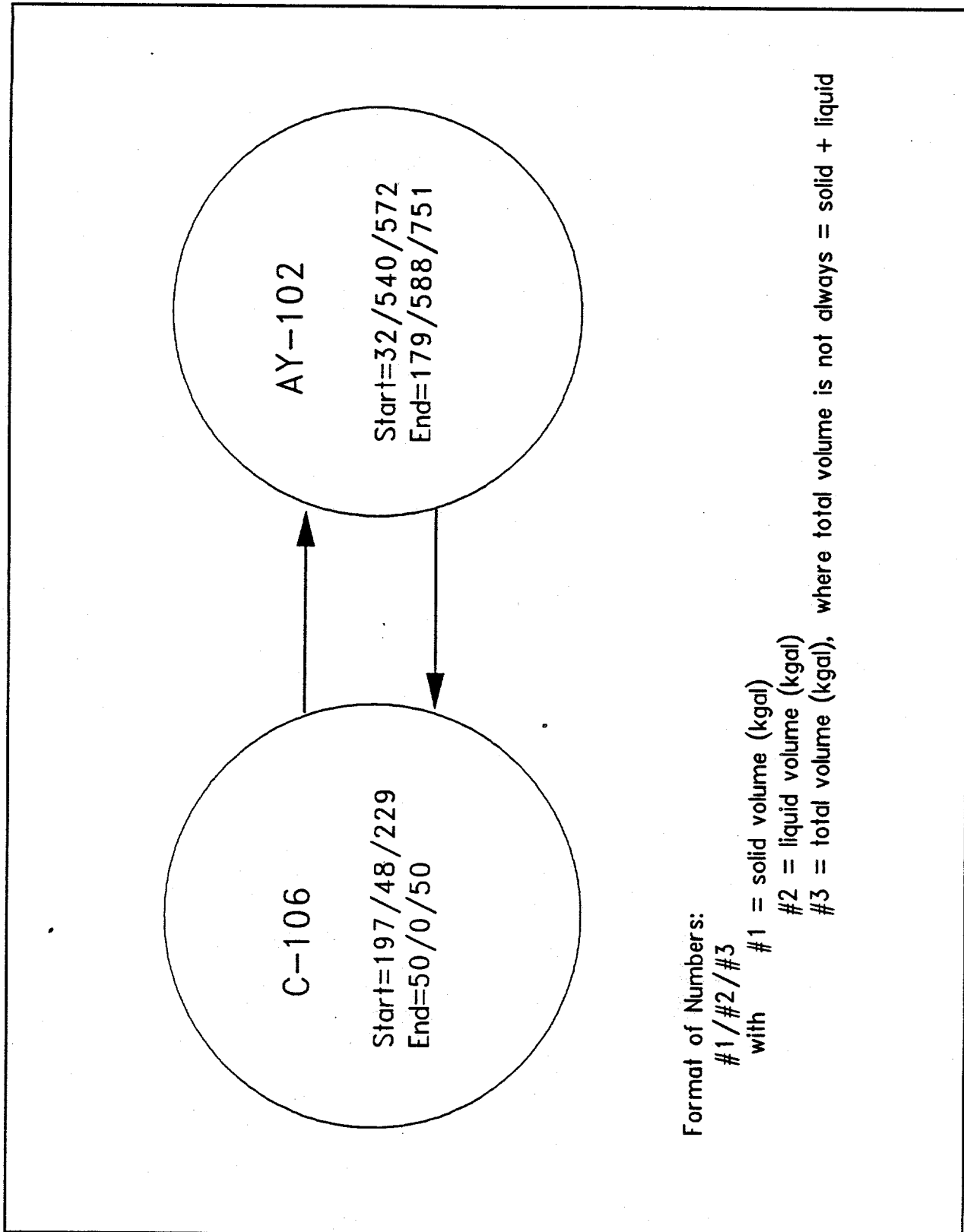
This document analyzes the transfers specified above against the four safety criteria of WHC-SD-WM-DQO-001, *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994):

1. Criticality
2. Reactivity
3. Corrosivity
4. Prevention of Flammable Watch List tank.

These safety criteria are based on empirical study of previous waste transfers within the tank farm system as well as the resulting behavior of the waste tanks after transfer.

The bases for criticality safety in the waste tanks are provided by WHC-SD-SQA-CSA-20363, *CSER 94-001: Criticality Safety of Single-Shell Waste Storage Tanks* (Rogers 1994). This Safety Assessment has been further clarified by WHC-SD-SQA-CSA-20363. The basic principles by which Project W-320 shows criticality safety are derived from the double-contingency principle using fuel concentration and poison content. This implies that the waste tanks are subcritical if plutonium concentration is limited independent

Figure 1. Schematic of Tank 241-C-106 to Tank 241-AY-102 Sluicing.



of the poisons in the tanks; and the tanks are subcritical if the poison to plutonium ratios are sufficient independent of the fuel concentration.

None of the sluicing operations will increase the plutonium concentration past 1.0 g/L. Additionally, the sluicing operation will not change the form of the dominant plutonium species. The highly basic waste tank environment designed to limit corrosion of tank structural materials yields a pH in excess of 8.0, the limit above which insoluble plutonium predominates. The waste tank chemistry specifications ensure that the dominant plutonium species in the tanks will be an insoluble hydroxide.

Additional safety margins can be demonstrated because waste tank criticality does not depend on geometry, mass, or plutonium distribution. The tanks are much larger than the geometry required for criticality. The tank contents are known to be heterogeneous, and proving that the plutonium is nearly uniformly distributed in the tanks is difficult.

The tanks are safe by the plutonium concentration as the tanks currently exist. The maximum plutonium concentration in C-106, AY-101, and AY-102 is less than 0.2 g/L. The minimum critical concentration for plutonium in waste is 2.6 g/L (Rogers 1993).

The tanks are safe by poisons with the plutonium. If the necessary absorber to plutonium ratios can be demonstrated, subcriticality can be shown based solely on that fact (Rogers 1993). The safe poison mass ratios for selected materials are as follows: 770 for natural or depleted uranium, 160 for iron, 32 for manganese, 135 for chromium, and 105 for nickel. These materials were formed as insoluble hydroxide complexes with the plutonium during waste processing. The safe poison mass ratios for selected soluble materials are as follows: 910 for aluminum, 360 for sodium, and 270 for nitrates. The safe poison mass ratio is defined such that k-effective will be less than 0.95 for any combination of water and plutonium. The solid and liquid portions of C-106, AY-101, and AY-102 meet at least one of these poison ratios. Appendix C reproduces the analysis of Project W-320 contained in CSER 94-001 (Rogers 1994). Additionally, it carries the argument further by analyzing the wastes assuming they have been transferred to the receiver tank (AY-102). This is done by looking at the mass ratios existing in the waste at the completion of sluicing operations.

The basis for reactivity safety is provided by actual measure of the energetic potential of the wastes. Energetics safety is demonstrated by the absence of net exotherms in the waste conducted by laboratory thermal analyses up to 500 °C. However, historical characterization data that support these analyses for Project W-320 do not exist. Therefore, an engineering analysis is made based on additional criteria that are judged to evaluate the same potential for adverse waste behavior.

These additional criteria have been developed by the Waste Tank Safety Program (Turner 1993). The criteria are based on conservative bounding assumptions about the nature of the energetic chemical reactants present in the waste as well as additional factors that could affect an energy release:

- The waste organic concentration
- The waste moisture content

- The waste temperature.

The Waste Tank Safety Program justifies that sodium acetate is energetically representative of the water soluble organic complexants used in various Hanford Site chemical processing operations, and likely to bound the organic contents of the waste tanks to be used by Project W-320. This justification is qualified in several ways. First, it does not account for the presence of process solvents (e.g., normal paraffin hydrocarbon [NPH] and tributyl phosphate [TBP]) that were inadvertently sent to single-shell tanks in unknown, but possibly significant, quantities. Second, it is believed that the organic complexants have undergone significant degradation by oxidation over the years, lowering the potential energy content of the organics. Finally, any carboxylic acids generated from contact of NPH/TBP mixtures with nitric acid, which exhibit significant reactivity with nitrate-nitrite oxidizer systems, are assumed to not be present in the waste tanks in sufficient concentrations to enhance the fuel value of the waste tank organics.

With these qualifications, testing of surrogate sodium acetate waste mixtures led to the development of criteria that specify the degree to which the energetic content of the waste poses a safety problem. Because Hanford Site waste tank organic analyses have almost exclusively been historically reported in terms of total organic carbon (TOC), TOC is equated to an energetically equivalent mass of sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) by the mass ratio of the sodium acetate molecule to the mass of carbon contained within it (mass of $\text{NaC}_2\text{H}_3\text{O}_2$ equals $3.4 \times$ mass of TOC). The degree of hazard caused by chemical energetics falls into three categories: safe, conditionally safe, and unsafe. These categories, specified with the organic concentration in terms of TOC mass in dry waste, are as follows:

- Safe: ≤ 5 wt% TOC and waste temperature < 149 °C
- Conditionally safe: > 5 wt% TOC, water content ≥ 17 wt%, and waste temperature ≤ 90 °C
- Unsafe: Failure to meet either of the above criteria.

The controlling document (Turner 1993) develops the analytical model used in evaluating the above energetic safety conditions. This compatibility study uses the model to evaluate the chemical energetic conditions that are posed by the sequence of Project W-320 waste processing operations. Any condition evaluated as "safe" or "conditionally safe" is equated to satisfying the energetics requirements of the Waste Compatibility Program (Carothers 1994).

Energy release from Hanford Site waste has been evaluated, and it has been established that use of sodium acetate (NaAc) as the surrogate form the reported TOC takes provides a conservative boundary for the maximum energy release (Turner 1993).

An analysis of the radioactive decay heat loading in C-106 wastes and potential relationships with chemical reactivity are presented in Appendix D.

The waste compatibility requirements for corrosion are provided by the *Operating Specifications for the 241-AN, AP, AW, AY, AZ, and SY Tank Farms*,

OSD-T-151-00007 (Harris 1992). The intent is to limit the corrosion rate of tank structural materials to minimize structural damage and possible leak formation. The waste chemistry is controlled with the intent of restricting general corrosion rates to less than 1 mil/year and to inhibit stress corrosion cracking. These criteria are based on waste temperature and the concentrations of hydroxide, nitrate, and nitrite.

In regards to the prevention of waste formation that has the potential to trap and contain flammable gases, it is stated in WHC-SD-WM-DQO-001, *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994) that:

"The premise of the current approach is that we can use SpG of the source and receiving waste to identify transfers that may lead to flammable gas accumulation. A key consideration in future revisions to this Waste Compatibility DQO is the validation of this approach through evaluation of historical data and development of other potential indicators of potential indicators."

All tanks at the Hanford Site generate hydrogen, which could originate from corrosion, radiolysis of water, or an organic chemical reaction. The rate of hydrogen generation in any tank is low. If the hydrogen is vented at the same rate it is being made, then there is no problem with hydrogen flammability. The main issue for gas flammability is the trapping of potentially flammable gases in the wastes of a tank.

The question that is posed, then, is what parameters in tanks can be used to prevent the waste from trapping gas. It is believed that solids must be present in the tanks to trap gas; those tanks which contain only, or predominately, clear liquid do not present any problem with gas retention. The parameter used to identify which tanks may retain gas was chosen to be specific gravity (SpG). Specific gravity is a measure of waste concentration. Below about 1.35 SpG, the waste is liquid with only small amounts of solids. Once the wastes are concentrated above 1.35 SpG, chemicals start to precipitate from the waste. It was noted that all the double-shell tanks on the Flammable Gas Watch List had an average specific gravity of greater than 1.4. None of the double-shell tanks not on the Flammable Gas Watch List had an average specific gravity of greater than 1.4. This seemed to be a prudent limit to set until further study could define better limits. Those studies are ongoing and not complete at this time. As of this writing, a specific gravity of greater than 1.4 has been the only waste property identified that is exclusive to tanks on the Flammable Gas Watch List, and the 1.4 SpG limit remains the most defensible discriminator yet identified.

It should be pointed out that the average specific gravity of the tanks to be used in the retrieval operations are all below 1.4. Mixing them will not raise the specific gravity beyond the 1.4 limit.

The implemented method of mitigating tank 241-SY-101 (SY-101) is by mixing the waste contents. The mixing disturbs the solids and allows any trapped gases to escape. The tanks used in Project W-320 will be mixed during sluicing operations. The sluicing activity will consequently perform the same function for the wastes in C-106 and AY-102.

The ventilation system will be operating in both tanks and will sweep away any hydrogen that is released. The balance of tank farm experience and modeling of hydrogen radiolysis indicates that the generation of steady state hydrogen is not a problem--either the hydrogen generation is low enough, natural ventilation of the tank is high enough, or a combination of both indicate this is so. The highest flammable gas concentration ever measured in naturally aspirated Hanford Site waste tanks has only been a few percent of the lower explosive limit.

The safety documentation for this project will look specifically at hydrogen and will address hydrogen burns and applicable administrative controls on ignition sources.

Appendix E documents the outcome of previous waste compatibility work performed in support of Project W-320. These studies yielded the basis for selection of the receiver tank and sluicing material.

3.1 WASTE DESCRIPTIONS

Tank inventories for C-106, AY-101, and AY-102 are reported in Table 1.

Table 1. Initial Tank Inventories.

Waste type	Volume L (gal)		
	Tank 241-C-106	Tank 241-AY-101	Tank 241-AY-102
Solid	746,000 (197,000)	314,000 (83,000)	121,000 (32,000)
Liquid	182,000 (48,000)	3,100,000 (820,000)	3,433,831 (907,125) ^(a)
Total ^(b)	867,000 (229,000)	3,410,000 (901,000)	3,554,964 (939,125)

^(a)All data presented are from *Tank Farm Surveillance and Waste Status Summary Report for September 1993*, WHC-EP-0182-66, Westinghouse Hanford Company, Richland, Washington, B. M. Hanlon, 1994, except tank 241-AY-102 liquid volume, which was obtained from the Computer Automated Surveillance System (CASS) (2/24/94).

^(b)As a result of the presence of interstitial liquid, waste volume totals $\neq$ solid volumes + liquid volumes.

Of the data reported:

- For C-106 liquid
 - 61,000 L (16,000 gal) are interstitial
 - 121,000 L (32,000 gal) are supernatant
- For AY-101 liquid
 - 7,600 L (2,000 gal) are interstitial
 - 3,096,000 L (818,000 gal) are supernatant
- For AY-102 liquid
 - All is supernatant.

Specific chemical characteristics of these wastes are reported in Appendix A.

3.2 WASTE TRANSFERS

The transfers needed to sluice C-106 can be separated into three sequential steps:

- Step 1: AY-102 supernatant to any other tank
- Step 2: AY-101 supernatant to AY-102
- Step 3: C-106 to AY-102 (see Figure 1).

To effectively apply the guidelines of WHC-SD-WM-DQO-001, *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994), a waste compatibility determination is required before the start of a transfer. However, Step 1 is outside the scope of this report. Step 3 involves "recycle" and effectively is two transfers in one. Three separate analyses of waste compatibility are thus necessary to allow the sluicing of C-106.

If an acceptable waste compatibility conclusion is to be reached, the variables delineated in WHC-SD-WM-DQO-001 (Carothers 1994) must be known before the transfer. One of two events must therefore take place if an appropriate chemical compatibility evaluation is to be made. These two event choices are:

- Sample the sending and receiving tank(s) before each transfer step
- Build a model that predicts intermediary waste stream compositions.

It is preferred that waste compatibility questions for all transfers applicable to Project W-320 be answered in advance. Therefore, a chemical model has been chosen for this analysis. To this end, a material balance around the three transfers of importance is presented.

3.2.1 AY-102 Supernatant to Any Other Tank

The intent of Step 1 is to remove the contents of AY-102 to the maximum extent practicable.

Step 1

There are three primary factors important to successful completion of this transfer as follows:

- The hydrostatic head specifications for the tank bottom (Bergmann 1989a)
- The effect of operating the annulus ventilation (Bergmann 1989b)
- The volume of solids presently in the tank (Hanlon 1994).

These factors influence the minimum volume of waste allowed in AY-102 and therefore have an indirect impact on the chemical behavior of the waste in this tank. For the purposes of this document, it is assumed that a minimum AY-102 volume of 121,000 L (32,000 gal) can be achieved.

Tanks C-106 and AY-101 are not involved in this transfer action and therefore will not be affected.

Upon completion of this step, the inventories of the tanks will become those values reported in Table 2.

3.2.2 AY-101 Supernatant to AY-102

The second step in influencing the overall C-106 sluicing effort is the transfer of supernatant from AY-101 to AY-102. This supernatant is intended to serve two purposes:

- Function as the source of fluid to be used when performing the sluicing of C-106
- Allow ample time for settling of solids in the receiving tank (AY-102).

Step 2

The slurry that is transferred out of C-106 will need to settle within AY-102. The nominal supernatant volume identified for this is 2,040,000 L (540,000 gal) (Estey 1993).

Before this step, there will be 3,100,000 L (818,000 gal) of supernatant available in AY-101. Furthermore, ample receiving space will have been created in AY-102 at the completion of Step 1. Hence, no volumetric limitations are expected that might hinder occurrence of this transfer.

Upon completion of this step, the inventories of the tanks will become those values reported in Table 3.

Table 2. Tank Inventories after Transfer of Tank 241-AY-102 Supernatant.

Waste type	Volume L (gal)		
	Tank 241-C-106	Tank 241-AY-101	Tank 241-AY-102
Solid	746,000 (197,000)	314,000 (83,000)	121,000 (32,000)
Liquid	182,000 (48,000)	3,100,000 (820,000)	0
Total	867,000 (229,000)	3,410,000 (901,000)	121,000 (32,000)

Table 3. Tank Inventories after Transfer of Tank 241-AY-101 Supernatant.

Waste type	Volume L (gal)		
	Tank 241-C-106	Tank 241-AY-101	Tank 241-AY-102
Solid	746,000 (197,000)	314,000 (83,000)	121,000 (32,000)
Liquid	182,000 (48,000)	1,060,000 (280,000)	2,040,000 (540,000)
Total	867,000 (229,000)	1,370,000 (361,000)	2,170,000 (572,000)

3.2.3 C-106 to AY-102

The final step in the overall sluicing process is the actual "sluicing" of C-106. This step was defined earlier as Step 3 and involves the complication of "recycle" as shown in Figure 1. To aid in further discussion of this step, two sub-steps are offered:

- Step 3a: Transfer from AY-102 to C-106
- Step 3b: Transfer from C-106 to AY-102.

Step 3

During this step, a closed-loop continuous transfer system will exist between C-106 and AY-102. A graphical description of this process is shown in Figure 1. Because of the low waste-volume inventories relative to the tanks' capacities, no volumetric limitations are expected to hinder occurrence of this step.

At the completion of Project W-320, the inventories of the three affected tanks will become those values reported in Table 4.

From this representation, a final C-106 volume of less than or equal to 189,000 L (50,000 gal) is expected. It is also expected that this reduction in inventory will be sufficient to mitigate the current high-heat safety issue. Any additional sludge removal from C-106 will exceed the minimum success criteria.

3.3 WASTE COMPATIBILITY

The basis for assessing chemical compatibility of wastes within the tank farms is formed by WHC-SD-WM-DQO-001, *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994). Five generic steps from that document constitute a recipe for performing the following analyses:

1. Characterize the sending and receiving tanks' wastes. Generally this is accomplished by in-tank sampling and analysis.
2. Compare these data with the guidelines in WHC-SD-WM-DQO-001 (Carothers 1994).

Table 4. Tank Inventories at Completion of Project W-320.

Waste type	Volume L (gal)		
	Tank 241-C-106	Tank 241-AY-101	Tank 241-AY-102
Solid	189,000 (50,000)	314,000 (83,000)	678,000 (179,000)
Liquid	0	1,060,000 (280,000)	2,230,000 (588,000)
Total	189,000 (50,000)	1,370,000 (361,000)	2,840,000 (751,000)

NOTE: The maximum operating limit for the 241-AY tanks (*Operating Specifications for the 241-AN, AP, AW, AY, AZ, and SY Tank Farms*, OSD-T-151-00007, Rev./Mod. H-5, Westinghouse Hanford Company, Richland, Washington, J. P. Harris, 1992; and *Operating Specifications for Aging-Waste Operations in 241-AY and 241-AZ*, OSD-T-151-00017, Rev./Mod. D-0, Westinghouse Hanford Company, Richland, Washington, L. M. Bergmann, 1989) is reported as 3,710,000 L (980,000 gal). Therefore, a substantial contingency volume will result for both tanks 241-AY-101 and 241-AY-102.

3. If there are no discrepancies between "as found" conditions and the criteria, then the transfer is allowed. If there are discrepancies in this step, then a more detailed analysis is required.
4. This "more detailed analysis" requires a determination of the resultant waste properties produced.
5. If the resulting waste properties obtained from this "more detailed analysis" are found to satisfy the criteria of WHC-SD-WM-DQO-001 (Carothers 1994), then the waste transfer is allowed.

Analysis of C-106 sluicing requires multiple applications of the recipe specified above.

To effectively manage these analyses, the model outlined in Section 3.2 of this document is employed below. Analysis of three specific events ensures complete chemical compatibility of the waste in AY-101, AY-102, and C-106. The relationships between the transfer steps identified in Section 3.2 and the needed analyses are as follows:

<u>Transfer step</u>	<u>Event needing analysis</u>
2	Transfer of the 2,040,000 L (540,000 gal) of supernatant from AY-101 to AY-102
3a	Startup of the initial sluicing; transfer of AY-102 supernatant to C-106
3b	Completion of the sluicing; transfer of C-106 slurry to AY-102.

These 3 events, when combined with the 4 safety criteria (Carothers 1994), result in 12 total elements requiring analysis. These 12 safety elements are presented in Sections 3.3.1 through 3.3.3. A summary of findings from analysis of these elements is provided in Table 5.

3.3.1 Commingling of AY-102 Waste with Any Other Tank Waste

This activity corresponds to Step 1 of Section 3.2.1.

It is implied that there would be no adverse chemical or physical behavior at the "source" tank as a result of transferring waste (Carothers 1994). Consequently, the act of removing liquid from AY-102 in Step 1 will result in favorable chemical compatibility for this step.

Step 1 will not increase the concentration of the plutonium in 241-AY-102 past 1.0 g/L. Step 1 will not remove enough poison from the plutonium to decrease all the poisons below the safe poison mass ratio. Also, Step 1 will not reduce the hydroxide concentration or pH below acceptable values. The two controls on criticality will be maintained during this step.

3.3.2 Commingling of AY-101 Waste with AY-102 Waste

This activity corresponds to Step 2 of Section 3.2.2.

A model depicting the intermixing of AY-101 supernatant and AY-102 contents is offered in Appendix F. The AY-102 contents presented as feed material to this model are the solids that result from the transfer described in Step 1 above.

Step 2 Safety Decision Elements

1. Criticality

"The plutonium concentration is reported as 0.072 g/L for the solids, a value less than 3% of the minimum value which can be made critical under conditions of optimal moderation. The plutonium concentration in the liquid is reported as 0.000004 g/L. The total plutonium content for AY-102 is estimated to be 8.7 kg.

For AY-102 the measured Fe/Pu mass ratio of 1,579 is 9.8 times as large as the subcritical limit. The measured Mn/Pu mass ratio of 166 is 5.1 times as large as the subcritical limit. The concentrations of both cadmium and boron are far larger than required to ensure subcriticality for the plutonium present" (Rogers 1994).

Step 2 will not increase the concentration of the plutonium in AY-102 or AY-101 past 1.0 g/L. Also, Step 2 will not remove enough poison from the plutonium to decrease all the poisons below the safe poison mass ratio, and will not reduce the hydroxide concentration or pH below unacceptable values. The two controls on criticality will be maintained in Step 2.

Table 5. Waste Compatibility Summary.

Safety criteria	Safety limit	Step		
		2	3a	3b
Criticality	Source waste plutonium equivalent concentration ≤ 0.05 g/gal	a	a	a
Reactivity	No separable organic in source waste; and source and receiving wastes individually have an [exotherm/endothrm] < 1.0 from DSC and TGA conducted up to 500 °C	b	b	b
Corrosion	Source waste: [NO ₃ ⁻] ≤ 1 M 0.01 M $\leq$ [OH ⁻] ≤ 8 M, and 0.011 M $\leq$ [NO ₂ ⁻] ≤ 5.5 M with receiving tank < 75 °C (167 °F)	NO ₃ ⁻	0.82	c
		OH ⁻	0.45	c
		NO ₂ ⁻	0.25	c
		°C (°F)	18 °C (64 °F)	23 °C (74 °F)
Prevention of Flammable Watch List tank	Specific gravity of source waste < 1.3	1.1	1.1	c

^aCSER 94-001: *Criticality Safety of Single-Shell Waste Storage Tanks*, WHC-SD-SQA-CSA-20363, Rev. 0, Westinghouse Hanford Company, Richland, Washington, C. A. Rogers, 1994.

^bConfirmed by engineering analysis in lieu of analytical data.

^cWill be within limits because of nature of transfer.

DSC = Differential scanning calorimetry

TGA = Thermal gravimetric analysis

Therefore, the transfer is permitted.

2. Reactivity

No separable organic layer is reported for the waste in AY-101 and AY-102. Furthermore, TOC data for the two tanks are reported as:

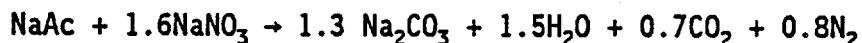
<u>Tank</u>	<u>TOC</u>
AY-101 (liquid)	<6,780 mg/L
AY-102 (liquid)	<2,724 mg/L
AY-102 (solids)	<3.82 mol/kg.

Energy release from Hanford Site waste has been evaluated, and it has been established that use of NaAc as the surrogate form the reported TOC takes provides a conservative boundary for the maximum energy release (Turner 1993).

Therefore, if all this carbon is assumed to be in the form of NaAc, then the "NaAc equivalent concentrations" of these tanks would be:

<u>Tank</u>	<u>NaAc equivalent concentration</u>
AY-101 (liquid)	23.165 g NaAc/L solution
AY-102 (liquid)	9.307 g NaAc/L solution
AY-102 (solids)	211.437 g NaAc/L solids.

Sodium acetate reacts according to the following equation (Turner 1993):



where:

$$\Delta H_{\text{rxn}} < 7.85 \text{ MJ/Kg NaAc (theoretical).}$$

The maximum expected energy from AY-101 and AY-102 is:

<u>Tank</u>	<u>Maximum energy potential of TOC</u>
AY-101 (liquid)	0.18 MJ/L solution
AY-102 (liquid)	0.07 MJ/L solution
AY-102 (solids)	1.66 MJ/L solids.

It is possible to calculate the weight fraction of water needed to suppress a propagating exothermic reaction = $x_{\text{H}_2\text{O}}$, by the following equation (Turner 1993):

$$x_{\text{H}_2\text{O}} > N/(1+N)$$

where:

$$N = \frac{[(x - x_n)\Delta H_R - C_M(T_o - T_i)]}{[\lambda + C_{\text{H}_2\text{O}}(T_B - T_i)]}$$

- x = Weight fraction of sodium acetate in a dry mixture for which x_{H_2O} is to be calculated (bounding value = 0.38, i.e., 11 wt% TOC equivalent)
- x_n = Estimated weight fraction of fuel (sodium acetate) in a dry sample to produce a propagating reaction ($x_n = 0.172$)*
- ΔH_R (J/kg) = Estimated heat of reaction per kilogram of sodium acetate (-7.85 MJ)
- C_H (J kg⁻¹K⁻¹) = Specific heat of dry sample (~1,000 J kg⁻¹K⁻¹)
- T_o (K) = Onset temperature for propagating reaction (~573 °K)
- T_i (K) = Waste tank operating temperature
- λ (J/kg) = Latent heat of vaporization of water (~2.25 MJ/kg)
- C_{H_2O} (J kg⁻¹ K⁻¹) = Specific heat of water (-4,300 J kg⁻¹ K⁻¹)
- T_B (K) = Boiling temperature of waste (-393 °K).

The approximate tank operating temperatures are currently:

<u>Tank</u>	<u>Temperature (°K)</u>
AY-101 (liquid)	296
AY-102 (liquid)	291
AY-102 (solids)	291

This results in the following N and x_{H_2O} values for the tanks:

<u>Tank</u>	<u>N</u>	<u>x_{H_2O}</u>
AY-101 (liquid)	0.5	0.337
AY-102 (liquid)	0.5	0.334
AY-102 (solids)	0.5	0.334.

*17.2 wt% sodium acetate, corresponding to 5 wt% total organic carbon (TOC) (dry basis), from Table 5-2 (see *Interim Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-EP-0681, Westinghouse Hanford Company, Richland, Washington, D. A. Turner, 1993). Although the 5 wt% TOC test mixture did not support a propagating reaction (refer to Section 5.2), this value is used in the calculations shown here to estimate a conservative value for minimum required waste moisture content.

The water content for each of these tanks is known to be:

<u>Tank</u>	<u>wt% water</u>	<u>X_{H₂O}</u>
AY-101 (liquid)	86	0.86
AY-102 (liquid)	95	0.95
AY-102 (solids)	60	0.60.

This evidence shows the presence of more than twice the quantity of water needed to suppress any possible exotherms. Consequently, a substantial safety margin exists for these wastes.

Therefore, the transfer is permitted.

3. Corrosion

Tank 241-AY-101 supernatant consists of the following:

$[\text{OH}] \approx 7.6 \text{ g/L} = 0.45 \text{ M}$ within limits of $0.01 \text{ M} \leq [\text{OH}] \leq 8 \text{ M}$
 $[\text{NO}_3] \approx 50.7 \text{ g/L} = 0.82 \text{ M}$ within the limit of $[\text{NO}_3] \leq 1 \text{ M}$
 $[\text{NO}_2] \approx 11.7 \text{ g/L} = 0.25 \text{ M}$ within limits of $0.011 \text{ M} \leq [\text{NO}_2] \leq 5.5 \text{ M}$.

The average temperature of AY-102 is approximately 64 °F, which is less than the limit of <167 °F.

A chemical model for mixing the supernatant in AY-101 with the solids in AY-102 is provided in Appendix F. Results of this mixture demonstrate that both solid and liquid phases remain virtually unchanged in their respective chemical compositions.

Therefore, the transfer is permitted.

4. Prevention of Flammable Watch List Tank

Tank 241-AY-101 liquid has an SpG $\approx 1.1 \text{ g/mL}$. This is less than the limit of SpG <1.3.

Therefore, the transfer is permitted.

5. Summary

The proposed transfer of 2,044,000 L (540,000 gal) of supernatant from AY-101 to AY-102 is acceptable from an engineering process control perspective. The large margins of safety identified in this analysis eliminate the need for further sampling of these tanks.

The analyses conducted above demonstrate that the transfer of supernatant from AY-101 to AY-102 is allowable.

3.3.3 Commingling of C-106 Waste with AY-102 Waste

This activity corresponds to Step 3 of Section 3.2.3.

The sub-steps describing this activity are as follows:

Step 3a: Intermixing of AY-102 supernatant (resulting from Step 3) with C-106

Step 3b: Intermixing of C-106 with AY-102.

Step 3a Safety-Decision Elements

1. Criticality

"A sizable margin of criticality safety will be maintained throughout the process of transferring waste from C-106 to AY-102. No mechanism capable of causing criticality as the result of mixing these wastes has been found" (Rogers 1994).

Although this analysis does not take waste from AY-101 into account, a substantial safety margin will still exist. This is evidenced by the following statement:

"A conservative estimate of the plutonium concentration in C-106 solids based upon 3 samples is 0.127 g/L. The minimum concentration of plutonium which can be made critical in conservatively defined waste was calculated to be 2.6 g/L. Therefore, the measured plutonium concentration is less than 5% of the minimum value which can be made critical under conditions of optimal moderation.

Although the actual water content of the waste has not been determined, it is very likely that the waste is overmoderated. As the level of moderation increases, so also increases the concentration of plutonium required to achieve criticality. In a solution of plutonium in full density water the minimum critical concentration is 7.2 g Pu/L. The presence of absorbers in the waste would increase the minimum concentration of plutonium required for criticality.

The use of water for sluicing actually increases the margin of safety. Allowing the waste to dry out, as it would eventually if no water were to be added, would actually increase the reactivity. However, the waste is so far subcritical that the increase would have no significance to safety. Even with complete drying, the waste would remain well subcritical" (Rogers 1994).

Step 3a will not increase the concentration of plutonium in AY-102 or C-106 past 1.0 g/L. Also, Step 3a will not remove enough poison from the plutonium to decrease all the poisons below the safe poison mass ratio, or reduce the hydroxide concentration or pH below unacceptable values. The two controls on criticality will be maintained in Step 3a.

Therefore, this transfer is permitted.

2. Reactivity

There has been no separable organic layer reported for C-106 or AY-102 waste. Furthermore, at this step, TOC data for these two tanks will be:

<u>Tank</u>	<u>TOC</u>
C-106 (liquid)	<20,000 mg/L
C-106 (solids)	<4,620 mg/kg
AY-102 (liquid)	<6,780 mg/L
AY-102 (solids)	<3.82 mol/kg.

Evaluating these data using the approach employed in Section 3.3.2:

<u>Tank</u>	<u>NaAc equivalent concentration</u>
C-106 (liquid)	68.3 g NaAc/L solution
C-106 (solids)	22.6 g NaAc/L solids
AY-102 (liquid)	23.165 g NaAc/L solution
AY-102 (solids)	211.437 g NaAc/L solids

<u>Tank</u>	<u>Maximum energy potential of TOC</u>
C-106 (liquid)	0.536 MJ/L solution
C-106 (solids)	0.177 MJ/L solids
AY-102 (liquid)	0.182 MJ/L solution
AY-102 (solids)	1.66 MJ/L solids

<u>Tank</u>	<u>Temperature (°K)</u>
C-106 (liquid)	328
C-106 (solids)	328
AY-102 (liquid)	296
AY-102 (solids)	296

<u>Tank</u>	<u>N</u>	<u>X_{H₂O}</u>
C-106 (liquid)	0.5	0.354
C-106 (solids)	0.5	0.354
AY-102 (liquid)	0.5	0.337
AY-102 (solids)	0.5	0.337

<u>Tank</u>	<u>wt% water</u>
C-106 (liquid)	77
C-106 (solids)	45
AY-102 (liquid)	88
AY-102 (solids)	60.

As in the analysis presented in Section 3.3.2, there is sufficient water in the waste of these two tanks to suppress any exotherms that might result from the presence of organic carbon. A substantial margin of safety is again maintained.

Therefore, the transfer is permitted.

3. Corrosion

At the beginning of this step, AY-102 supernatant will consist of the following:

$[\text{OH}] \approx 7.6 \text{ g/L} = 0.45 \text{ M}$ within the limits of $0.01 \text{ M} \leq [\text{OH}] \leq 8 \text{ M}$
 $[\text{NO}_3] \approx 50.7 \text{ g/L} = 0.82 \text{ M}$ within the limit of $[\text{NO}_3] \leq 1 \text{ M}$
 $[\text{NO}_2] \approx 11.7 \text{ g/L} = 0.25 \text{ M}$ within limits of $0.011 \text{ M} \leq [\text{NO}_2] \leq 5.5 \text{ M}$.

The average temperature of C-106 is approximately 132 °F, which is less than the limit of <167 °F.

Therefore, the transfer is permitted.

4. Prevention of Flammable Watch List Tank

Tank 241-AY-102 liquid will have an SpG $\approx 1.1 \text{ g/mL}$. This is less than the limit of SpG <1.3.

Therefore, the transfer is permitted.

5. Summary

The proposed transfer of supernatant from AY-102 to C-106 is acceptable from an engineering process control perspective. The large margins of safety identified in this analysis eliminate the need for further sampling of these tanks.

The analyses conducted above demonstrate that the transfer of supernatant from AY-102 to C-106 is allowable.

Step 3b Safety Decision Elements

1. Criticality

The criticality evaluation presented in Step 3a also applies in this step. Furthermore, confirmation of criticality safety is presented.

"The slurry distributor for AY-102 is designed to spread the incoming slurry over the surface of the waste. For criticality to occur the plutonium would have to be concentrated more than 20-fold without at the same time concentrating the iron, manganese, boron, and cadmium. In addition to this, the presence of water, or other hydrogenous compounds, would increase the required plutonium concentration by a factor of nearly 3. For these reasons subcriticality is not dependent upon the distribution of the waste. No criticality safety requirements need be placed on the slurry distributor" (Rogers 1994).

Step 3b will not increase the concentration of the plutonium in AY-102 or C-106 past 1.0 g/L. Also, Step 3b will not remove enough poison from the plutonium to decrease all the poisons below the safe

poison mass ratio, or not reduce the hydroxide concentration or pH below unacceptable values. The two controls on criticality will be maintained in Step 3b.

Therefore, the transfer is permitted.

2. Reactivity

The elements required for determining the safety of reactive components in this step are the same as those of Step 3a. The only difference is that the source and receiver tanks are reversed; however, the conclusion is identical regardless of the tank order.

Therefore, the transfer is permitted.

3. Corrosion

Tank 241-C-106 liquid consists of the following:

$[\text{OH}] \approx 0.176 \text{ mg/L} = 1 \times 10^{-5} \text{ M}$ and the limit is $0.01 \text{ M} \leq [\text{OH}] \leq 8 \text{ M}$
 $[\text{NO}_3] \approx 67,156 \text{ mg/L} = 1.08 \text{ M}$ and the limit is $[\text{NO}_3] \leq 1 \text{ M}$
 $[\text{NO}_2] \approx 9.75 \text{ g/L} = 0.212 \text{ M}$ within the limit of $0.011 \text{ M} \leq [\text{NO}_2] \leq 5.5 \text{ M}$.

Tank 241-C-106 solids consist of the following:

No reported $[\text{OH}]$ and the limit is $0.01 \text{ M} \leq [\text{OH}] \leq 8 \text{ M}$
 $[\text{NO}_3] \approx 1,129 \text{ mg/kg} = 0.0255 \text{ M}$ within the limit of $[\text{NO}_3] \leq 1 \text{ M}$
 No reported $[\text{NO}_2]$ and the limit is $0.011 \text{ M} \leq [\text{NO}_2] \leq 5.5 \text{ M}$.

Therefore, based on this data alone, C-106 as a source tank would be unacceptable for transfer into the double-shell tank system. However, Project W-320 will be capable of adding sodium hydroxide (NaOH) and/or sodium nitrite (NaNO_2) to adjust these concentrations before transferring this waste into AY-102. The range of NaOH that may be necessary is specified as 0 kg to 1,400 kg. Based on the expected intermixing of C-106 with AY-102, the resultant NaNO_2 concentration is expected to be within specifications (Estey 1993).

The average temperature of AY-102 at the beginning of this step will be approximately 23°C (74°F), which is less than the limit of 75°C ($<167^\circ\text{F}$).

Therefore, the transfer is permitted as long as any needed chemical adjustments are made.

4. Prevention of Flammable Watch List Tank

Tank 241-C-106 waste has a liquid SpG $\approx 1.18 \text{ g/mL}$ and a solids SpG $\approx 1.43 \text{ g/mL}$. This is greater than the limit of SpG <1.3 so an analyses of the weighted mean specific gravity of the commingled waste is necessary.

At the beginning of this step, AY-102 will have a liquid Spg $\approx$ 1.12 g/mL and a solids SpG $\approx$ 1.4 g/mL. As an extreme case, the respective volumes of waste applicable to this transfer will be:

Tank	Waste Volume L (gal)	
	Start	End
C-106 (liquid)	182,000 (48,000)	0
C-106 (solids)	746,000 (197,000)	0
AY-102 (liquid)	2,040,000 (540,000)	2,230,000 (588,000)
AY-102 (solids)	121,000 (32,000)	867,000 (229,000).

The weighted mean SpG of the commingled waste would therefore be calculated by the following equation:

$$\text{Weighted mean SpG} = \frac{(\text{Volume}_1 * \text{SpG}_1 + \text{Volume}_2 * \text{SpG}_2)}{(\text{Volume}_1 + \text{Volume}_2)}$$

Therefore, the weighted mean SpG that would result in AY-102 would be:

$$[(48)(1.18) + (197)(1.43) + (540)(1.12) + (32)(1.4)] / (48 + 197 + 540 + 32)$$

where:

$$\text{Weighted mean SpG} = 1.2.$$

This is less than the limit of weighted mean SpG ≤ 1.41 .

Therefore, the transfer is permitted.

5. Summary

The proposed sluicing of C-106 to AY-102 is acceptable from an engineering process control perspective. Large margins of safety have again been identified in the analysis eliminating the need for further sampling of these tanks.

The analyses conducted above demonstrate that the transfer of waste from C-102 to AY-102 is allowable. The only provision is that the corrosion specifications be met by chemical adjustment either before, or during, the transfer.

3.3.4 Flammable Gas Watch List Issue

The decision rules from WHC-SD-WM-DQO-001, *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994) provide guidance for evaluating commingled waste for flammable gas accumulation. Additional issues not addressed in WHC-SD-WM-DQO-001 have been raised regarding the planned sluicing approach and whether AY-102 will exhibit Flammable Gas Watch List tank behavior during or after completion of C-106 retrieval. It has been proposed that aluminum solids that exist in certain pH ranges (hydroxide concentrations) create gels that trap gases. An evaluation of four sluicing fluid alternatives against aluminum phase chemistry has been performed (see

Appendix G, internal letter 7E310-94-035 [Reynolds 1994])). These four alternatives are:

- Sluicing with AY-101 liquid
- Sluicing with AY-101 liquid adjusted to 2.5 molar hydroxide
- Sluicing with dilute waste
- Sluicing with inhibited raw water.

In all sluicing fluid alternatives, the resulting waste combinations are in the dilute aluminum region of the phase chemistry information. The Flammable Gas Watch List double-shell tanks are more concentrated in aluminum and/or hydroxide. In the alternatives of using AY-101 liquid, other dilute waste, or inhibited raw water, the final combined streams are in the insoluble aluminum region. It is expected that the aluminum in these solids would be in the same form as the aluminum currently in C-106, and therefore, not exhibit flammable gas retention behavior. There is a low likelihood that these solids would change aluminum form and retain gas. The combined stream resulting from sluicing with 2.5 molar hydroxide is in the dissolved aluminum region.

The alternative of sluicing with AY-101 liquid adjusted to 2.5 molar hydroxide requires the addition of more than 227,124 L (60,000 gal) of 50% sodium hydroxide solution. The added sodium will result in approximately 9,000 ft³ of low-level waste glass requiring disposal.

It is recommended that the alternative of sluicing with AY-101 liquid adjusted to 2.5 molar hydroxide be used as the project baseline to reduce the technical risk to the project. The uncertainty in aluminum phase chemistry can be reduced by mixing studies with actual C-106 waste material. These studies will be used to optimize the amount of sodium hydroxide adjustment. This alternative allows the C-106 sluicing to proceed with minimum technical risk.

4.0 CONCLUSION

This study reaffirms the findings "that the safety issues central to Waste Tank Safety Program are not adversely impacted by the Project W-320 effort" (Fulton 1993).

Furthermore, the chemical models presented in this document demonstrate that no chemical reactions identified in Appendix F will result in future waste incompatibility. Thus, no chemical safety issues will be exacerbated in any way by retrieving the contents from C-106 and transferring them to AY-102. In fact, a safer overall tank farm configuration is envisioned.

The use of AY-101 liquid adjusted to 2.5 molar hydroxide is recommended for the project baseline. This allows the technical risk caused by uncertainties in aluminum phase chemistry to be reduced while mixing studies to optimize the amount of hydroxide addition proceed.

5.0 REFERENCES

- Bergmann, L. M., 1989a, *Operating Specifications for Aging-Waste Operations in 241-AZ and 241-AY*, OSD-T-151-00017, Rev./Mod. D-0, Westinghouse Hanford Company, Richland, Washington.
- Bergmann, L. M., 1989b, *Operating Specifications for the 241-A-702 Vessel Ventilation System*, OSD-T-151-00016, Rev./Mod. C-0, Westinghouse Hanford Company, Richland, Washington.
- Carothers, K. G., 1994, *Data Quality Objectives for the Waste Compatibility Program*, WHC-SD-WM-DQO-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Estey, S. D., 1993, *241-C-106 to 241-AY Tank Farm Waste Transfer Compatibility Study (Preliminary)*, WHC-SD-WM-ES-244, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Fulton, J. C., 1993, *Tank 241-C-106 Waste Retrieval* (internal letter 7A700-93-002), Westinghouse Hanford Company, Richland, Washington.
- Hanlon, B. M., 1994, *Tank Farm Surveillance and Waste Status Summary Report for September 1993*, WHC-EP-0182-66, Westinghouse Hanford Company, Richland, Washington.
- Harris, J. P., 1992, *Operating Specifications for the 241-AN, AP, AW, AY, AZ, and SY Tank Farms*, OSD-T-151-00007, Rev./Mod. H-5, Westinghouse Hanford Company, Richland, Washington.
- Reynolds, D. A., 1994, *Evaluation of 241-C-106 Sluicing Fluid Options for Preventing Flammable Gas Retention* (internal letter 7E310-94-035 to J. P. Harris, July 25), Westinghouse Hanford Company, Richland, Washington.
- Rogers, C. A., 1993, *CSER 92-009: An Analytical Model for Evaluating Subcritical Limits for Waste in Hanford Site Storage Tanks*, WHC-SD-SQA-CSA-20356, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Rogers, C. A., 1994, *CSER 94-001: Criticality Safety of Single-Shell Waste Storage Tanks*, WHC-SD-SQA-CSA-20363, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Turner, D. A., 1993, *Interim Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-EP-0681, Westinghouse Hanford Company, Richland, Washington.

6.0 BIBLIOGRAPHY

Boyles, V. C., 1992, *Operating Specifications for Single-Shell Waste Storage Tanks*, OSD-T-151-00013, Rev./Mod. D-1, Westinghouse Hanford Company, Richland, Washington.

Leach, C. E., and S. M. Stahl, 1993, *Hanford Site Tank Farm Facilities Interim Safety Basis*, WHC-SD-WM-ISB-001, vols. 1 and 2, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Wilkins, D. G., 1984, *Specific Activity and Heat Generation for Selected Radionuclides*, SD-RE-TI-121, Rev. 0, Rockwell Hanford Operations, Richland, Washington.

7.0 GLOSSARY

ABBREVIATIONS AND ACRONYMS

CASS	computer automated surveillance system
DSC	differential scanning calorimetry
NPH	normal paraffin hydrocarbon
TBP	tributyl phosphate
TGA	thermal gravimetric analysis
TOC	total organic carbon
USQ	unreviewed safety question

APPENDIX A

CHARACTERIZATION DATA FOR TANKS

This page intentionally left blank.

APPENDIX A
CHARACTERIZATION DATA FOR TANKS

The tables in this appendix have been excerpted from 101-AY, 102-AY, & 106-C Data Compendium, WHC-SD-WM-TI-578, Rev. 0, Westinghouse Hanford Company, Richland, Washington, B. A. Castaing, 1993.

C-106 Solids				
Component	Range		Average	Units
	Low	High		
%Solids	-	-	55	-
%Water	-	-	45	-
Bulk Density	1.37	1.43	1.40	g/mL
F	86	720	403	mg/kg
NO3	928	1,330	1,129	mg/kg
PO4	-	-	93,700	mg/kg
SO4	936	4,850	2,893	mg/kg
Al	30,000	40,900	35,450	mg/kg
Ba	-	-	4,890	mg/kg
Ca	-	-	11,900	mg/kg
Cr	984	1,350	1,167	mg/kg
Fe	52,100	64,100	58,100	mg/kg
La	-	-	5,960	mg/kg
Pb	-	-	1,060	mg/kg
Hg	461	6,560	3,511	mg/kg
Mn	1,840	14,100	7,970	mg/kg
P	-	-	9,210	mg/kg
K	-	-	1,470	mg/kg
Si	20,600	71,000	45,800	mg/kg
Na	35,800	117,000	76,400	mg/kg
U	.00088	406	203	mg/kg
Zr	735	2,170	1,453	mg/kg
TOC	-	-	4,620	mg/kg
TRU	-	-	3,050	μCi/kg
Tgamma	-	-	363,000	μCi/kg
Pu-239/240	1,530	5,520	3,367	μCi/kg
Rare Earths	-	-	450,000	μCi/kg
Cs-137	213,000	330,000	271,500	μCi/kg
Sr-89/90	6	1,980,000	990,003	μCi/kg

WHC-SD-WM-ES-290
Revision 2

C-106 Liquid				
Component	Range		Average	Units
	Low	High		
%Solids	-	-	22.57	-
%Water	-	-	77.43	-
SpG	1.14	1.18	1.16	g/mL
Cl	147	802	554	mg/L
CO3	18,600	91,900	44,860	mg/L
F	15	530	164	mg/L
NO2	2,985	13,248	9,750	mg/L
NO3	1,400	112,220	67,156	mg/L
OH	.029	.324	.176	mg/L
PO4	846	11,100	4,039	mg/L
SO4	3,520	6,470	4,995	mg/L
Al	34	752.6	270.1	mg/L
Bi	111	2,000	1,056	mg/L
Si	105	2,580	1,343	mg/L
Na	73,830	127,420	91,094	mg/L
U	162	958	560	mg/L
TOC	2,520	20,000	11,260	mg/L
pH	9.81	10.7	10.3	-
TRU	-	-	991.9	μCi/L
Tgamma	-	-	27,800	μCi/L
Pu-239/240	13.9	978	216	μCi/L
Am-241	-	-	13.9	μCi/L
Cs-137	27,800	178,600	115,761	μCi/L
Sr-89/90	1,650	133,000	67,325	μCi/L

WHC-SD-WM-ES-290
Revision 2

AY-101 Liquid				
Component	Range		Average	Units
	Low	High		
%Solids	10.0	13.2	11.6	-
%Water	86.8	90.0	88.4	-
SpG	1.09	1.12	1.10	g/mL
Cl	430	518	462	mg/L
CO ₃	13,740	19,740	16,965	mg/L
F	380	760	559	mg/L
NO ₂	9154	13,570	11,696	mg/L
NO ₃	38,380	63,860	50,763	mg/L
OH	2,278	14,977	7,608	mg/L
PO ₄	770	1,425	974	mg/L
SO ₄	4,830	7,602	6,277	mg/L
Al	1,431	1,951	1,778	mg/L
Na	44,830	68,080	56,748	mg/L
U	16.1	23.3	19.7	mg/L
TOC	4,470	6,780	5,735	mg/L
EDTA	-	-	.00096	M
HEDTA	-	-	.00086	M
pH	12.1	12.8	12.45	-
TRU	26.51	42.4	31.3	μCi/L
Talpha	-	-	109,000	μCi/L
Pu-239/240	.004	12.1	6.34	μCi/L
Am-241	19.6	30.3	25.0	μCi/L
Cs-137	115,000	140,000	129,333	μCi/L
Sr-89/90	144,000	200,000	169,667	μCi/L
CO-60	-	-	95.2	μCi/L

WHC-SD-WM-ES-290
Revision 2

AY-102 Solids				
Component	Range		Average	Units
	Low	High		
%Solids	34	45.6	39.8	-
%Water	54.4	66	60.2	-
Density	1.3	1.4	1.35	g/mL
Cl	-	-	8,343	mg/kg
F	-	-	2,660	mg/kg
NO ₂	-	-	2,944	mg/kg
NO ₃	-	-	682	mg/kg
PO ₄	-	-	1,710	mg/kg
Al	-	-	37,800	mg/kg
Ba	-	-	2,055	mg/kg
B	-	-	2,808	mg/kg
Ca	-	-	14,000	mg/kg
Cr	-	-	3,744	mg/kg
Fe	-	-	83,700	mg/kg
La	-	-	4,031	mg/kg
Mg	-	-	6,804	mg/kg
Mn	-	-	8,784	mg/kg
Ni	-	-	3,052	mg/kg
P	-	-	6,200	mg/kg
K	-	-	1,443	mg/kg
Si	-	-	12,040	mg/kg
Ag	-	-	7,236	mg/kg
Na	-	-	41,400	mg/kg
U	-	-	14,756	mg/kg
TOC	-	-	3.82	mol/kg
TRU	21,200	30,610	25,905	μCi/kg
Pu-239/240	3,000	3,610	3,305	μCi/kg
Am-241	18,200	27,000	22,600	μCi/kg
Cs-137	-	-	265,000	μCi/kg
Sr-89/90	-	-	29,500,000	μCi/kg
Eu-154	-	-	51,400	μCi/kg

WHC-SD-WM-ES-290
Revision 2

AY-102 Liquid				
Component	Range		Average	Units
	Low	High		
%Solids	-	-	5.2	-
%Water	-	-	94.8	-
SpG	-	-	1.04	g/mL
Cl	-	-	355	mg/L
CO3	-	-	3,660	mg/L
F	-	-	171	mg/L
NO2	828	1,150	989	mg/L
NO3	248	23,126	11,687	mg/L
OH	-	-	5,032	mg/L
PO4	27	285	156	mg/L
SO4	106	1,344	725	mg/L
Al	1.5	135	68.2	mg/L
Na	-	-	2,162	mg/L
TOC	288	2,724	1506	mg/L
TIC	-	-	348	mg/L
pH	-	-	9.5	-
TRU	-	-	.236	μCi/L
Pu-239/240	-	-	.234	μCi/L
Am-241	-	-	.0015	μCi/L
Cs-137	4,320	296,000	150,160	μCi/L
Sr-89/90	6,580	23,180	14,880	μCi/L

This page intentionally left blank.

APPENDIX B

CHEMICAL COMPATIBILITY EVALUATION CRITERIA

This page intentionally left blank.

APPENDIX B

CHEMICAL COMPATIBILITY EVALUATION CRITERIA

Objectives of the Waste Compatibility Program applicable to the Hanford Site double-shell tank system are delineated in WHC-SD-WM-DQO-001, *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994). These objectives have been extracted from that document and are listed in this appendix. The objectives form a set of criteria by which the intended transfers are then evaluated against.

Two specific rules serve as guidelines for deciding whether individual transfers are to be permitted. Four sub-rules for each of these two rules exist.

However, it is noted at this point that the general waste compatibility decision element for criticality was originally developed in WHC-SD-SQA-CSA-20109, *CSAR 79-007, Addendum 1, Waste Storage Tanks and Associated Equipment* (Friar 1989). Thus, 0.01 g/L (0.05 g/gal) is an historical limit that arose from the simple calculation of the concentration of plutonium in a million-gallon tank with a 50 kg inventory. This limit has carried over in subsequent criticality safety evaluation reports (CSAR) and continues to be used in Tank Waste Remediation System criticality analyses.

Because the plutonium concentration in the sludge of tank 241-C-106 is approximately 0.05 g/kg, and the sludge density is about 1.4, the waste compatibility data quality objectives limit for criticality may place restraints on the maximum slurry concentration that can be formed during waste transfer operations. The key argument for criticality concerns for Project W-320 is that none of the sluicing operations will significantly increase plutonium concentrations or change the form of the dominant plutonium species, or will not significantly alter the preponderance of the poison to plutonium ratios.

The "key decision rules used for design purposes" are as follows.

Safety Rules

1. Criticality--If measurement of the waste to be transferred indicates that the plutonium equivalent concentration ≤ 0.01 g/L (0.05 g/gal), then allow transfer; otherwise, the transfer may occur if after resampling, the mean of the new data is ≤ 0.01 g/L (0.05 g/gal). If the mean of the resampling data is > 0.01 g/L (0.05 g/gal), then the transfer will not be allowed.
2. Energetics--If the source waste has no separable organic, and the source and receiving wastes (individually) have an absolute value of the exotherm/endortherm ratio < 1.0 (i.e., no net exotherms) evaluated from laboratory thermal analysis (differential scanning calorimetry [DSC] and thermal gravimetric analysis [TGA]) conducted up to 500 °C (932 °F), then allow the transfer. Otherwise, delay the transfer and perform a detailed technical evaluation of the reactivity of the

waste exhibiting the potential reactive behavior to determine the conditions needed for safely receiving and/or storing the waste.

3. Corrosion--If measurement of the waste to be transferred is $[\text{NO}_3^-] \leq 1 \text{ M}$, $0.01 \text{ M} \leq [\text{OH}^-] \leq 8 \text{ M}$, and $0.011 \text{ M} \leq [\text{NO}_2^-] \leq 5.5 \text{ M}$, then allow transfer (assuming receiver tank is operating at $<75^\circ\text{C}$ (167°F)). Otherwise, the transfer will occur after additions to the source have mitigated the problem.
4. Flammable Gas Accumulation
 - a. If the specific gravity (SpG) of the source is <1.3 , then allow the transfer or determine the weighted mean specific gravity of the commingled waste.
 - b. If the weighted mean SpG ≤ 1.41 , then allow the transfer. If the weighted mean SpG >1.41 , then perform a detailed technical evaluation of the potential for flammable gas accumulation in the commingled waste.

Operations Rules

1. If the waste source (transuranic [TRU]) is $\geq 100 \text{ nCi/g}$, then transfer waste to a TRU storage tank, transfer to non-TRU tanks, or perform a technical evaluation demonstrating that TRU segregation in a TRU storage tank will not be jeopardized.
2. If the receiving tank plus waste transfer heat generation rate (estimated from the mean strontium-90 and cesium-137 concentrations) is less than or equal to the operating specifications documents (Bergmann 1989; Boyles 1992; Harris 1992) limit for the receiving tank, then allow transfer or select a different tank.
3. If the mean (total organic carbon [TOC]) is $>10 \text{ g/L}$ at double-shell slurry feed composition, then transfer to a complexant waste receiver tank.
4. If the $N_{\text{Re}} = \rho Dv/\mu$ [calculated using density (ρ), viscosity (μ), pipe diameter (D), and velocity (v)] at the conditions of the transfer is $\geq 20,000$, and the volume percent solids is ≤ 30 , then allow the transfer or perform a technical evaluation to justify transfer without plugging.

Specific data needed as input to this decision process are as follows:

^{238}Pu	$[\text{NO}_2^-]$
^{239}Pu	Temperature
^{240}Pu	$[\text{Cl}^-]$
^{241}Pu	$[\text{CO}_3^{-2}]$
^{233}U	$[\text{SO}_4^{-2}]$
^{235}U	$[\text{PO}_4^{-3}]$
^{237}Np	$[\text{Na}^+]$
^{241}Am	$[\text{F}^-]$
SpG	wt% water
$[\text{Al}^{+3}]$	^{90}Sr
TOC	^{137}Cs
TIC	Viscosity
DSC	% Solids
TGA	Cooling curve
RSST	Pipe diameter
$[\text{OH}^-]$	Pump velocity
$[\text{NO}_3^-]$	Homogeneity
	Heterogeneity.

However, the purpose of this study is to confirm safety of the subject waste from a chemical compatibility perspective. Therefore, of greatest importance are the safety-decision rules. The safety criteria and data needed in this study are as follows.

Safety criteria	Data needed
Criticality	Source waste plutonium-equivalent concentration
Reactivity	Quantity of separable organic in source waste, and source and receiving wastes individual [exotherm/endotherm] from DSC and TGA conducted up to 500 °C (932 °F)
Corrosion	Source waste $[\text{NO}_3^-]$, $[\text{OH}^-]$, and $[\text{NO}_2^-]$, and receiving tank temperature
Prevention of Flammable Watch List tank	Specific gravity of source waste

DSC = Differential scanning calorimetry
TGA = Thermal gravimetric analysis

REFERENCES

- Bergmann, L. M., 1989, *Operating Specifications for Aging-Waste Operations in 241-AY and 241-AZ*, OSD-T-151-00017, Rev./Mod. D-0, Westinghouse Hanford Company, Richland, Washington.
- Boyles, V. C., 1992, *Operating Specifications for Single-Shell Waste Storage Tanks*, OSD-T-151-00013, Rev./Mod. D-1, Westinghouse Hanford Company, Richland, Washington.
- Carothers, K. G., 1994, *Data Quality Objectives for the Waste Compatibility Program*, WHC-SD-WM-DQO-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Friar, D. E., 1989, *CSAR 79-007, Addendum 1, Waste Storage Tanks and Associated Equipment*, WHC-SD-SQA-CSA-20109, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Harris, J. P., 1992, *Operating Specifications for the 241-AN, AP, AW, AY, AZ, and SY Tank Farms*, OSD-T-151-00007, Rev./Mod. H-5, Westinghouse Hanford Company, Richland, Washington.

APPENDIX C

TANK WASTE MASS RATIOS NORMALIZED TO PLUTONIUM

This page intentionally left blank.

APPENDIX C

TANK WASTE MASS RATIOS NORMALIZED TO PLUTONIUM

CSER 94-001, *Criticality Safety of Single Shell Waste Storage Tanks*, (Rogers 1994) develops the argument that tanks 241-C-106 (C-106) and 241-AY-102 (AY-102) are safe from criticality based on both plutonium concentration as well as the concentration of neutron absorbing elements and chemical compounds (i.e., poisons) also present in the waste. Section 9 of that document, which analyzes the tanks involved in Project W-320, is reproduced at the end of this Appendix.

This document simply furthers the argument that based on the same principles, the sum total of wastes in AY-102 will also remain safe after all the wastes in C-106 have been transferred into it. For this calculation, it is assumed that at the completion of sluicing operations, all the wastes in C-106 have been retrieved and transferred to AY-102 (about 200 kgal) and that an additional 600 kgal of supernatant has been added to AY-102 as a result of the sluicing operation. This results in a volume of waste in AY-102 that is composed of 200 kgal of C-106 solids, 30 kgal of AY-102 solids, and 600 kgal of AY-101 liquids (assumed to be equivalent to AY-102 liquids) for a total of 830 kgal.

The absorbers of greatest concern reported herein are aluminum, chromium, iron, sodium, nickel, nitrate, and natural uranium. The final mass ratios of these species are calculated as follows:

$$\text{solids mass ratio} = \frac{[30*(\text{AY-102 solids}) + 200*(\text{C-106 solids})]}{[30*(\text{AY-102 solids}) + 200*(\text{C-106 solids})]} \text{ for absorber}$$

$$\text{liquid mass ratio} = \text{ratio in AY-102 liquid where the plutonium concentration, reported at 0.0000 g/L, is assumed to be 0.000005 g/L.}$$

The results or the absorber-to-plutonium mass ratios are as follows:

<u>Absorber</u>	<u>Mass Ratio in AY-102 Solids</u>	<u>Mass Ratio in AY-102 Liquids</u>
Al	$\frac{30(36.45)+200(37.80)}{30(0.054)+200(0.053)} = 708$	>26,000
Cr	$\frac{30(1.170)+200(3.740)}{30(0.054)+200(0.053)} = 64.1$	---
Fe	$\frac{30(58.10)+200(83.70)}{30(0.054)+200(0.053)} = 1510$	---
Mn	$\frac{30(7.970)+200(8.780)}{30(0.054)+200(0.053)} = 163$	---
Na	$\frac{30(76.40)+200(41.10)}{30(0.054)+200(0.053)} = 860$	>432,000

WHC-SD-WM-ES-290
Revision 2

<u>Absorber</u>	<u>Mass Ratio in AY-102 Solids</u>	<u>Mass Ratio in AY-102 Liquids</u>
Ni	$\frac{30(0.820)+200(3.050)}{30(0.054)+200(0.053)} = 7.00$	---
NO ₃	$\frac{30(1.130)+200(1.690)}{30(0.054)+200(0.053)} = 30.4$	>338,000
²³⁸ U	$\frac{30(0.200)+200(14.80)}{30(0.054)+200(0.053)} = 243$	---

Section 9 of CSER 94-001 follows.

9.0 TRANSFER OF WASTE FROM TANK C-106 TO AY-102

Waste stored in Tank C-106 generates considerable heat. Two methods are used to remove this heat: a ventilation system and the addition of cooling water. Over the past 10 years about 800,000 gal (3,000,000 L) of cooling water has been added at a rate of about 6,000 gal each month. A failure to continue water addition would eventually allow the waste to dry out.

In order to remove the need for cooling water, a plan has been devised to remove the heat-generating sludge. This plan calls for waste to be pumped from Tank C-106 and to Double-Shell Tank AY-102. Before the waste can be pumped it is necessary to sluice it into a pumpable liquid.

A device, called a "slurry distributor," will be installed in Tank 102-AY to spread the incoming slurry over a larger area of the tank to ensure a more uniform mixing of wastes.

The following criticality safety evaluation covers sluicing operations in Tank C-106 and the operations associated with transfer to Tank AY-102.

9.1 DESCRIPTION OF TANK C-106

Sluicing operations for Tank C-106 are described in the Functional Design Criteria (Bailey 1993). Much of the following description is taken from that document.

Tank C-106 is a 75-ft diameter single-shell tank with a capacity of 530,000 gal. It contains 197,000 gal (746,000 L) of sludge stratified in two layers, as follows:

- * The top layer consists of 173,000 gal (655,000 L) of high heat generating sludge. The heat generation is caused by ^{90}Sr , but neither the heat nor the ^{90}Sr influence the margin of criticality safety.
- * The bottom layer consists of 24,000 gal (91,000 L) of hardened coating waste from dissolution of aluminum fuel cladding.

Hanlon (1992) lists the volume of drainable liquid in Tank C-106 at 48,000 gal (183,000 L). Of this, 32,000 gal is supernate and 16,000 gal is interstitial liquid.

9.1.1 Characterization of Waste in Tank C-106

Harris (1993) compiled characterization data dating back to 1975 for Tanks AY-101, AY-102, and C-106. Eight (8) analytical samples are reported for Tank 106-C: 3 sludge (solids), 3 supernate (liquid), and 2 combination samples. Harris lists all of these samples and shows the high, low, and average value of each component concentration. Table 2 shows the high, low, and average

concentration of the individual components for the solids and the liquids in Tank C-106.

For this evaluation the term "sludge" is synonymous with "solids" and the term supernate is synonymous with "liquid."

A combination sample represents the configuration in which the solids and the liquids are homogenized within the analyzed sample. The average, high, and low values reported by Harris for the total waste are derived directly from the two combination samples. They do not represent a volume averaging obtained from independent sludge and supernate samples.

The concentration for solids is provided in units of g/kg. This can be converted to units of g/L by multiplying by the density. Harris reports the average value of the solids density to be 1.40 g/L, with the high and low reported values being 1.43 and 1.37 g/L. For this evaluation the high value of 1.43 g/L is used.

The high estimate of the plutonium concentration in solids is given as 0.089 g/kg. When multiplied by the density, the converted plutonium concentration becomes 0.127 g/L.

An estimate of the total plutonium content is obtained by multiplying the volume of waste, either solids or liquid, by the corresponding maximum concentrations. The total plutonium content in 197,000 gal (746,000 L) of solids is found to be 94.6 kg. For 48,000 gal of liquid at a plutonium concentration of 0.016 g/L, the total plutonium content is found to be 2.9 kg. The total plutonium for Tank C-106 is estimated to be 97.5 kg. This value is based upon the largest measured density and the largest measured plutonium concentration and is therefore considered to be an upper limit on the expected total plutonium content.

Agnew (1993) estimates the plutonium inventory of Tank C-106 as 63.7 kg.

9.1.2 Sluicing Operations

Two sluicers will be installed on opposite sides of Tank C-106. The process of sluicing will require that a stream of water under pressure be directed at the sludge to convert it into a slurry. This slurry will be pumped to DST AY-102 through a "new, temporary, above ground, shielded, encased transfer line." Supernate from Tank AY-102 will be recirculated back to Tank C-106 to be used in sluicing more waste.

Supernate will be sent through a 4-in. Schedule 40 transfer line to the sluicer nozzles. This pipe will be encased in a 6-in. diameter pipe for containment of liquid should a leak develop. The 1-in. diameter sluice nozzle will deliver a stream of water at a pressure of 180 psig and a temperature of 180°F.

Table 2. Composition of Solids and Liquids in Tank C-106.
(Some components less important to criticality safety are not included.)

Component	Concentration in Solids, g/kg			Concentration in Liquid, g/L		
	High	Low	Average	High	Low	Average
Plutonium	0.089	0.025	0.054	0.016	0.000	0.0036
Aluminum	40.90	30.00	36.45	0.76	0.03	0.27
Barium	4.89	4.89	4.89	0.005	0.005	0.005
Boron	0.019	0.019	0.019	0.010	0.010	0.010
Cadmium	0.210	0.001	0.111	0.026	0.026	0.026
Calcium	11.90	11.90	11.90	0.01	0.01	0.01
Chromium	1.35	0.98	1.17	0.33	0.01	0.17
Iron	64.10	52.10	58.10	0.01	0.01	0.01
Lead	1.06	1.06	1.06	1.68	0.08	0.64
Magnesium	6.56	0.46	3.51	0.01	0.01	0.01
Manganese	14.10	1.84	7.97	0.20	0.20	0.20
Mercury	---	---	---	0.02	0.02	0.02
Nickel	0.97	0.68	0.82	0.89	0.07	0.48
Phosphorus	9.21	9.21	9.21	0.34	0.34	0.34
Potassium	1.47	1.47	1.47	0.42	0.42	0.42
Silicon	71.00	20.60	45.80	2.58	0.11	1.34
Silver	0.53	0.53	0.53	0.01	0.01	0.01
Sodium	117.00	36.80	76.40	127.42	73.83	91.09
Uranium	0.41	0.00	0.20	0.96	0.16	0.56
Zirconium	2.17	0.74	1.45	0.29	0.29	0.29
TOC	4.62	4.62	4.62	20.00	2.52	11.26
Chlorine	---	---	---	0.80	0.15	0.25
CO ₂	---	---	---	91.90	18.60	44.86
NO ₂	---	---	---	13.25	2.99	9.75
NO ₃	1.33	0.93	1.13	112.20	1.40	67.15
PO ₄	93.70	93.70	93.70	11.10	0.85	4.04
SO ₄	4.85	0.94	2.89	6.47	3.52	4.99

9.2 DISCUSSION OF SLUICING

A conservative estimate of the plutonium concentration in Tank C-106 solids based upon 3 samples is 0.127 g/L. The minimum concentration of plutonium which can be made critical in conservatively defined waste was calculated to be 2.6 g/L. Therefore, the measured plutonium concentration is less than 5% of the minimum value which can be made critical under conditions of optimal moderation.

Although the actual water content of the waste has not been determined, it is very likely that the waste is overmoderated. As the level of moderation increases, so also increase the concentration of plutonium required to achieve criticality. In a solution of plutonium in full density water the minimum critical concentration is 7.2 g Pu/L. The presence of absorbers in the waste would increase the minimum concentration of plutonium required for criticality.

The use of water for sluicing actually increases the margin of safety. Allowing the waste to dry out, as it would eventually if no water were to be added, would actually increase the reactivity. However, the waste is so far subcritical that the increase would have no significance to safety. Even with complete drying, the waste would remain well subcritical.

A good way to show subcriticality is to compile the ratio of the concentration of selected waste components to the concentration of plutonium. A compilation of mass ratios for components in Tank C-106 waste is shown in Table 3. Subcritical mass ratios for iron, manganese, and uranium are specified in Section 6.1.

Table 3. Mass Ratios of Solids and Liquids in Tank C-106.
(Based on average and high concentrations from Table 1.)

Component	Solids Mass Ratio Component/Plutonium		Liquids Mass Ratio Component/Plutonium	
	Average/High	Avg./Average	Average/High	Avg./Average
Boron	0.213	0.352	0.625	2.78
Cadmium	0.529	2.06	1.63	7.22
Iron	652.8	1076.	0.625	2.77
Manganese	89.5	147.6	12.5	55.5
Silicon	514.6	848.2	83.7	372.2
Sodium	858.4	1,415.	5,693.	25,300.
Uranium	2.25	3.70	35.0	155.5
NO ₂	---	---	609.4	2,708.
NO ₂	12.7	20.9	4,197.	19,650.

The subcritical limit on the Pu/U mass ratio is 0.0013. When specified as a reciprocal, the U/Pu mass ratio becomes 770. The reciprocal ratio of the average uranium to the high plutonium concentration in Tank C-106 waste is found to be about 2 in solids and 35 in the liquids. These ratios are too small to prove subcriticality.

The subcritical limit of the Fe/Pu mass ratio is 160. The measured mass ratio of 653 is four times as large as the subcritical limit. Therefore, the concentration of iron in the solids is far more than required to ensure subcriticality.

The subcritical limit of the Mn/Pu mass ratio is 32. The measured mass ratio of 89 is almost three times as large as the subcritical limit. Therefore, the concentration of manganese in the solids is far more than required to ensure subcriticality.

The high estimate of the plutonium concentration in the supernate (liquid) is 0.016 g/L, as compared to the minimum critical concentration in water of 7.2 g/L. The plutonium concentration in the supernate would have to be increased by a factor of 450 to reach the minimum concentration at which criticality is possible in water. However, since the supernate consists of a large fraction of nitrate, the plutonium concentration at which criticality becomes possible would be larger than for water, and the margin of safety is even larger.

It can be seen from the above information that the margin of subcriticality for Tank C-106 waste is large. At the very least a 20-fold increase in the plutonium concentration would be required for criticality. However, the large contents of iron and manganese ensure that a far greater increase would be required.

9.3 SLURRY DISTRIBUTOR IN TANK AY-102

DST AY-102 was selected to receive waste from Tank C-106 based upon of the similarity and compatibility of the wastes. Both the solids and the liquids in these tanks are compatible.

A "slurry distributor" installed in Tank AY-102 will distribute the incoming slurry over a large area. Distribution of the slurry will be accomplished by spraying it from a rotating nozzle. Spraying the slurry ensures a higher degree of dispersal than would occur if the slurry were discharged at one location. This greater dispersal is intended to reduce the likelihood of regions of higher plutonium concentration. The incoming waste should form a layer on top of the original waste which is uniform in both thickness and composition.

Facility design will include provisions to monitor operations and to alarm on detection of radioactive particulate release, liquid and gaseous release, abnormal radiation levels, fire, overheating, and pressurization.

9.2.1 Description of Tank AY-102

Tank AY-102 is a 75-ft diameter double-shell tank with a capacity of 1,000,000 gal (3,785,000 L). Hanlon (1992) lists the inventory of Tank AY-102 as 565,000 gal of waste. Of this, 533,000 gal (2,018,000 L) is supernatant liquid and 32,000 gal (121,000 L) is sludge.

9.2.2 Characterization of Waste in Tank AY-102

Characterization data compiled by Harris (1993) for Tank AY-102 is shown in Table 4. Since he found only one solids and one liquid sample, he reports the same high, low, and average concentrations for each component.

The plutonium concentration in solids is reported as 3,306 $\mu\text{Ci/kg}$ and in liquid as 0.234 $\mu\text{Ci/L}$. Using the specific activity of 0.062 Ci/g for ^{239}Pu , this converts to 0.053 g/kg for the solids and 0.000004 g/L for the liquid.

Table 4. Composition of Solids and Liquids in Tank 102-AY.
(Some less important components are not included.)

Component	Concentration		Component	Concentration	
	Solids g/kg	Liquids g/L		Solids g/kg	Liquids g/L
Plutonium	0.053	0.0000	Potassium	1.44	0.04
Aluminum	37.80	0.13	Silicon	12.04	0.15
Barium	2.07	0.00	Silver	7.24	0.01
Boron	2.808	0.006	Sodium	41.10	2.16
Cadmium	0.414	0.000	Uranium	14.8	---
Calcium	14.00	0.00	Zirconium	0.59	0.00
Chromium	3.74	0.01	TOC	0.004	1.51
Iron	83.70	0.00	Chlorine	8.34	0.36
Magnesium	6.80	0.00	CO ₂	---	3.66
Manganese	8.78	0.00	NO ₂	2.94	1.15
Mercury	0.08	---	NO ₃	0.34	1.69
Nickel	3.05	0.00	PO ₄	1.71	0.16
Phosphorus	6.20	0.00	OH	---	5.03
			SO ₄	0.76	0.73

Table 5. Mass Ratios of Solids and Liquids in Tank AY-102.
(Based on concentrations from Table 4.)

Component	Solids Mass Ratio Component/Plutonium	Liquids Mass Ratio Component/Plutonium
Boron	53.	> 6
Cadmium	7.8	---
Iron	1,579.	---
Manganese	166.	---
Sodium	775.	> 2,000
Uranium	279.	---
NO ₂	55.5	> 1,100
NO _x	6.4	> 1,600

Harris reports a solids density of 1.36 g/L. When the plutonium concentration of 0.053 g/kg is multiplied by this density, the converted plutonium concentration becomes 0.072 g/L.

The total plutonium content in 121,000 L of solids is found to be 8.7 kg. No plutonium is found in the liquid. Therefore, the total plutonium for Tank AY-102 is estimated to be 8.7 kg.

9.3.3 Discussion

The plutonium concentration in Tank AY-102 solids is estimated to be 0.072 g/L. This is less than 3% of the minimum value which can be made critical under conditions of optimal moderation.

It is very likely that the waste is overmoderated. As the level of moderation increases, the concentration of plutonium required to achieve criticality also increases. A solution of plutonium in full density water requires a concentration of at least 7.2 g Pu/L to achieve criticality. Absorbers in the waste would increase the minimum concentration of plutonium required for criticality even more.

A compilation of mass ratios for components in Tank AY-102 waste is shown in Table 5. These mass ratios can be compared to subcritical mass ratios for iron, manganese, and uranium specified in Section 6.1.

The subcritical limit on the U/Pu mass ratio is 770. The U/Pu mass ratio for Tank AY-102 waste is found to be about 279 in the solids. By itself this value is not large enough to ensure subcriticality.

The subcritical limit of the Fe/Pu mass ratio is 160. The measured mass ratio of 1,579 is 9.8 times as large as the subcritical limit. Therefore, the

concentration of iron in the solids is far more than required to ensure subcriticality.

The subcritical limit of the Mn/Pu mass ratio is 32. The measured mass ratio of 166 is 5.1 times as large as the subcritical limit. Therefore, the concentration of manganese in the solids is far more than required to ensure subcriticality.

Cadmium and boron are both strong absorbers of moderated neutrons. If the ratio of hydrogen to plutonium atoms exceeds 250, subcriticality is assured when either the Cd/Pu atom ratio exceeds 0.5 or the B/Pu atom ratio exceeds 2.0 (Rogers 1993). The Cd/Pu mass ratio of 7.8 converts to an atom ratio of 16. The B/Pu mass ratio of 53 converts to an atom ratio of 1,100. The concentrations of both of these elements are far larger than required to ensure subcriticality for the plutonium present.

The plutonium concentration in the supernate (liquid) is found to be less than 0.001 g/L, as compared to the minimum critical concentration in water of 7.2 g/L. The plutonium concentration in the supernate would have to be increased by a factor greater than 7,200 to reach the minimum concentration at which criticality is possible in water.

It can be seen from the above information that the margin of subcriticality for Tank AY-102 waste is large. At the very least a 49-fold increase in the plutonium concentration would be required for criticality. However, the large contents of iron and manganese ensure that a far greater increase would be required.

The slurry distributor is designed to spread the incoming slurry over the surface of the waste. This ensures that the composition of the incoming waste is uniform within its layer. However, the waste is found to be well subcritical in comparison to mass ratios for several different components. It is extremely unlikely, if not impossible, that a process would be capable of separating plutonium from all the other components. For criticality to occur the plutonium would have to be concentrated more than 50-fold and at the same time separated from the iron, manganese, boron, and cadmium. This would have to occur over a fairly large region. In addition to this, the presence of water, or other hydrogenous compounds, would increase the required plutonium concentration by a factor of nearly 3. On the other hand, if water, or some other hydrogenous liquid, is not present, it would be very unlikely that the chemical processes required for separating the components would be possible. For these reasons subcriticality is not dependent upon the distribution of the waste. No criticality safety requirements need be placed on the slurry distributor.

The margins of safety for waste in Tank C-106 and in Tank AY-102 are very large. No mechanism capable of causing criticality as the result of mixing these wastes can be found. A sizeable margin of safety will be maintained throughout the process of sluicing waste from Tank C-106 and pumping it into Tank AY-102.

REFERENCES

Rogers, C. A., 1994, *CSER 94-001: Criticality Safety of Single-Shell Waste Storage Tanks*, WHC-SD-SQA-CSA-20363, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

This page intentionally left blank.

APPENDIX D

TANK 241-C-106 WASTE HEAT GENERATION PROFILES

This page intentionally left blank.

APPENDIX D

TANK 241-C-106 WASTE HEAT GENERATION PROFILES

Concerns about the location of the majority of the high-heat-producing radionuclides in tank 241-C-106 (C-106) wastes have been raised. If the majority of the decay heat content lies in waste that cannot be retrieved by Project W-320, the tank cannot be interim stabilized. However, an accident scenario could be envisioned where the majority of the heat-producing radionuclides remains in C-106 after sluicing activities have stopped, and the tank waste is inadvertently allowed to evaporate to dryness. In this case, there is some concern that the dried waste could overheat and initiate an uncontrolled exothermic waste energetic. By the waste reactivity model applied in this compatibility study, no inherent characterization of the waste could provide assurance against an uncontrolled energetic if the waste temperature is allowed to exceed 149 °C (Turner 1993).

However, this appendix demonstrates a defense-in-depth argument as to why the above postulated accident is considered highly unlikely. This defense is based on two points: (1) it is unlikely that the majority of the decay heat is located in the hardened lower layers of the sludge, and (2) if the waste characteristics could support the accident scenario, it is highly unlikely that the initiating conditions would be allowed to occur. In fact, there is nothing on which to base any relationship between this postulated accident and Project W-320--the issue is generic to all Hanford Site waste tanks.

The works of C. M. Walker and J. D. Anderson allow a history of C-106 to be reconstructed (Walker 1977; Anderson 1990). The tank was placed in service in 1947 and received metal waste (MW) from the bismuth phosphate process. Beginning in 1953, the tank was sluiced during the uranium recovery operation. From 1954 through 1963, the tank received tributyl phosphate (TBP) waste that resulted from the uranium recovery operation. From 1957 through 1969, the tank received Plutonium-Uranium Extraction (PUREX) acid waste (P) supernatant from A-Farm, and aluminum cladding waste (CW) from 1958 through 1963. No solids levels were reported until 1955. From 1955 through 1957, 12 kgal of solids were reported; from 1957 through 1962, 29 kgal; from 1963 through 1964, 24 kgal; and from 1963 through 1969, 62 kgal.

From late 1969 through 1974, the tank received PUREX sludge wash waste (PSS) and by 1971 the solids level was reported at 150 kgal. From 1974 through 1978, the tank received B-Plant complexed waste. A new solids level measurement was made when the tank was removed from service in early 1979 and showed 197 kgal of solids. The waste status summary for C-106 (Anderson 1990) is reproduced.

Thermal analyses performed on C-106 (Bander 1993) treated the sludge as three distinct layers. Layer 1 was the sludge in the tank before 1970. Layer 1 was deposited in roughly three-step-volume increases and includes some PSS. Layer 2 comprised the PSS solids settled from 1969 through 1974. Layer 3, roughly 50 kgal, comprised the B-Plant complexed solids deposited from 1974 through 1978.

"Figure 8 shows the total heat generation over time based on a total heat load of 110,000 Btu/h in 1992. The three step-increases in heat generation from 1947 to 1970 relate to the three increases in volume of layer 1. The three step-increases in layer 1 from 1971 to 1975 are due to the convective mixing between layers 1 and 2 due to the high thermal load. The two step-increases in layer 3 from 1977 to 1979 are associated with the increases in the volume of layer 3. A peak heat load of 153,300 Btu/h occurred toward the end of 1970 and another peak of 150,700 Btu/h occurred at the beginning of 1979" (Bander 1993).

Figure 8 (Bander 1993), which graphically illustrates the heat loading, is attached at the end of this appendix. This analysis shows that the waste present in the tank before 1969 contributes only about 15% of the total heat load in the tank.

Weiss and Schull (1988) report on the 1986 core sampling performed on the tank. A profile of 4, 48-cm (19-in.) core segments through the sludge was obtained. The first three segments were taken in push mode, but 15 cm (6 in.) into the last segment, the drill bit required operation in rotary mode with 15,170 kPa (2,200 lbf/in²) pressure. The soft sludges on top were aptly described as wet, dark brown mud. The hard layer on the bottom had large, coarse, white-colored granules.

The sum of the above references indicate that it is unlikely that the high-heat radionuclides are predominantly located in the lower, hard sludge layer. If sluicing operations are not successful in removing all the sludge from the tank, a process test involving psychometry or some other energy balance will be required to determine the status of project completion. A successful outcome of this test will be a prerequisite for eliminating water addition to this tank. Until it is definitely proven otherwise, it is a given that any sludge in C-106 must be kept wet.

In regards to the postulated sludge/dry-out accident, there is no relationship between Project W-320 and the wastes in C-106.

106-C-1

WHC-MR-0132

Waste Status Summary of 106-C Tank-Capacity 530,000 Gallons

<u>Qtr.- Year</u>	<u>Type Waste</u>	<u>Total Vol.</u>	<u>Liquid in Storage</u>	<u>Solids in Storage</u>	<u>Remarks</u>
1-1947	---	---	---	---	
2	---	---	---	---	
3	MW	368	---	---	3rd in Cascade, began filling July 1947
4	MW	528	---	---	Full in November 1947
1-1948	MW	528	---	---	
2	MW	528	---	---	
3	MW	528	---	---	
4	MW	528	---	---	
1-1949	MW	528	---	---	
2	MW	528	---	---	
3	MW	528	---	---	
4	MW	528	---	---	
1-1950	MW	528	---	---	
2	MW	528	---	---	
3	MW	528	---	---	
4	MW	528	---	---	
1-1951	MW	551	---	---	23 water from hose
2	MW	551	---	---	
3	MW	551	---	---	
4	MW	551	---	---	
1-1952	MW	519	---	---	
2	MW	519	---	---	
3	MW	519	---	---	
4	MW	519	---	---	

106-C-2

WHC-MR-0132

Waste Status Summary of 106-C Tank-Capacity 530,000 Gallons

Qtr.- Year	Type Waste	Total Vol.	Liquid in Storage	Solid in Storage	Remarks
1-1953	MW	---	---	---	1507 in 101 thru 106-C. 1651 removed thru CR 1213
2	MW	76	---	---	Supernatant supply
3	MW	439	---	---	Rec'd MW supernatant from 103-C
4	MW	143	---	---	MW supernatant blend tank
1-1954	MW	50	---	---	MW supernatant blend tank
2	MW	50	---	---	MW supernatant blend tank
3	TBP	538	---	---	Rec'd TBP waste during August
4	TBP	538	---	---	
1-1955	TBP	538	526	12 (TBP)	
2	TBP	538	526	12	
3	TBP	538	526	12	
4	TBP	538	526	12	
1-1956	TBP	538	526	12	
2	TBP	538	526	12	
3	TBP	538	526	12	
4	TBP	538	526	12	
1-1957	TBP	519	507	12	Latest electrode reading, enough for 171 TU
2	P	37	25	12	Rec'd 234 from 101-A & 77 from 102-A, 476 scvg during month
3	TBP-P	524	31-481	12	Rec'd 170 from 102-A (CW)
4	TBP-P	106	14-63	29	New electrode reading, 456 to 103-3Y
1-1958	TBP-P	106	14-63	29	
2	TBP-P-CW	232	14-63-126	29	
3	TBP-P-CW	519	14-63-413	29	7 to 110-EX, SS 294-CW rec'd
4	TBP-P-CW	535	14-63-429	29	Latest electrode reading
1-1959	TBP-P-CW	510	14-63-429	29	
2	TBP-P-CW	510	14-63-429	29	
3	TBP-P-CW	510	14-63-429	29	
4	TBP-P-CW	510	14-63-429	29	
1-1960	TBP-P-CW	510	14-63-429	29	
2	TBP-P-CW	527	14-63-421	29	SS 17 CW rec'd
3	TBP-P-CW	527	14-63-421	29	
4	TBP-P-CW	527	14-63-421	29	

106-C-3

WHC-MR-0132

Waste Status Summary of 106-C Tank-Capacity 530,000 Gallons

<u>Qtr.- Year</u>	<u>Type Waste</u>	<u>Total Vol.</u>	<u>Liquid in Storage</u>	<u>Solids in Storage</u>	<u>Remarks</u>
1-1961					
2	TBP-P-CW	527	14-63-421	29	[6 months report
3					
4	TBP-P-CW	527	14-63-421	29	[6 months report
1-1962					
2	TBP-P-CW	527	14-63-421	29	[6 months report
3					
4	TBP-P-CW	527	14-63-421	29	[6 months report
1-1963					
2	TBP-P-CW	530	19-63-421	24	[6 months report
3					
4	P	538	514	24	427 from 102-A
1-1964					
2	P	522	498	24	New electrode [6 months
3					report
4	P	505	481	24	[6 months report
1-1965					
2	P	541	479	62	36 from CR vault
3	P	546	484	62	
4	P	549	487	62	
1-1966					
2	P	549	487	62	
3	P	519	457	62	New electrode
4	P	519	457	62	
	P	527	465	62	New electrode
1-1967					
2	P	527	465	62	
3	P	527	465	62	
4	P	527	465	62	
1-1968					
2	P	66	4	62	461 PSN to 105-C
3	P	72	10	62	
4	P	70	8	62	
	P	70	8	62	
1-1969					
2	P	124	62	62	54 from 002 AR (101-A sludge was
3	P	244	182	62	120 from 002 AR sludge washes
4	P	293	231	62	50 from 002 AR sludge washes
	P(PSS)	167	110	57	52 from 002 AR, 176 to 105-C

106-C-4
Waste Status Summary of 106-C Tank-Capacity 530,000 Gallons

Qtr.- Year	Type Waste	Total Vol.	Liquid in Storage	Solids in Storage	Remarks
1-1970	P (PSS)	222	165	57	55 from 002 AR
2	P (PSS)	379	313	57	149 from 002 AR
3	P (PSS)	517	438	79	216 from 002 AR, 69 to 103-C
4	PSS	530	385	145	303 from 002 AR, 99 to 103-C, 194 to 102-A
1-1971	PSS	212	62	150	131 from 002 AR, 444 from 103-C, 194 from 102-A, 257 to 103-C, 827 to 105-C
2	PSS	212	62	150	
3	H ₂ O-PSS	239	63-25	150	63 water
4	H ₂ O-PSS	235	59-26	150	16 water, 22 condensate
1-1972 *	PSS	233	83	150	
2	PSS	235	110	125	
3	PSS	244	119	125	
4	PSS	248	123	125	
1-1973	PSS	255	130	125	
2	PSS	249	124	125	
3	PSS	241	116	125	
4	PSS	238	113	125	
1-1974 **	PSS	237	112	125	
2	PSS	250	125	125	
3	PSS-BL	324	45-154	125	238 from 3 Plant, 15 from 154-B catch tank, 3 water, 221 to 103-A
4	BL	420	314	106	506 from 3 Plant, 1 water, 409 to 103-C
1-1975	BL	373	267	106	356 from 3 Plant, 404 to 103-C
2	BL	345	239	106	236 from 3 Plant, 7 from 302-CT, 258 to 103-C
3	BL	469	363	106	242 from 3 Plant, 101 to 104-C
4	BL	288	182	106	414 from 3 Plant, 595 to 104-C
1-1976	BL	329	223	106	581 from 3 Plant, 477 to 104-C
2	BL	499	393	106	319 from 3 Plant, 148 to 104-C
3	Sr. Sludge	422	316	106	B Plant Waste Recovery
4	Sr. Sludge	233	127	106	B Plant Waste Recovery
1-1977	Sr. Sludge	373	228	145	B Plant Waste Recovery
2	Sr. Sludge	480	335	145	" " " "
3	Sr. Sludge	398	253	145	" " " "
4	—	384	228	156	

* Dry Wells 30-06-02, 30-06-04, 30-06-10 drilled.

** Dry Wells 30-06-03, 30-06-09, 30-06-12 drilled.

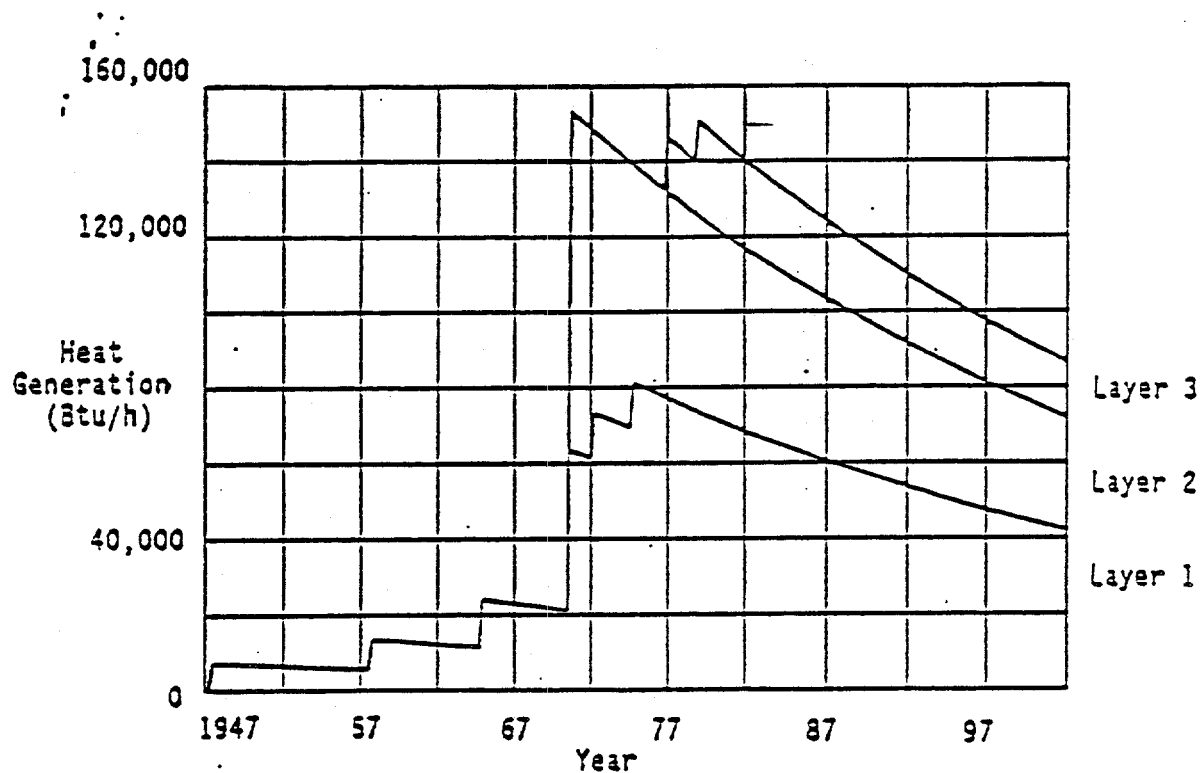
106-C-5

WHC-MR-0132

Waste Status Summary of 106-C Tank-Capacity 530,000 Gallons

<u>Qtr.- Year</u>	<u>Type Waste</u>	<u>Total Vol.</u>	<u>Liquid in Storage</u>	<u>Solids in Storage</u>	<u>Remarks</u>
1-1978	CPLX	255	99	156	Active-Receiving 8 Plt. Wst.
2-	CPLX	356	200	156	
3-	CPLX	444	288	156	
4-	CPLX	422	280	142	Solids level evaluated 11/3/78
1-1979	NCPLX	202	5	197	Solids level 3/31/79 Inactive
2-	CPLX	219	22	197	New photo 4/5/79
3-	CPLX	219	22	197	
4-	CPLX	219	22	197	
1-1980	CPLX	219	22	197	
2-	CPLX	219	22	197	
3-	CPLX	219	22	197	
4-	CPLX	219	22	197	

Figure 8. Total Heat Generated in the sludge Layers.



REFERENCES

- Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.
- Bander, T. J., 1993, *Revised Thermal History of Tank 241-C-106*, WHC-SD-WM-ER-200, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Turner, D. A., 1993, *Interim Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-EP-0681, Westinghouse Hanford Company, Richland, Washington.
- Walker, C. M., 1977, *History and Status of Tanks 241-C-105 and 241-C-106*, ARH-CD-948, Atlantic Richfield Hanford Company, Richland, Washington.
- Weiss, R. L., and K. E. Schull, 1988, *Data Transmittal Package for 241-C-106 Waste Tank Characterization*, WHC-SD-RE-TI-205, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

This page intentionally left blank.

APPENDIX E

SELECTION OF PROJECT W-320 RECEIVER TANK AND WASTE TYPE

This page intentionally left blank.

Westinghouse
Hanford Company

Internal
Memo

From: Waste Tanks Process Control 7E310-94-020
Phone: 373-2461
Date: April 20, 1994
Subject: SELECTION OF PROJECT W-320 RECEIVER TANK AND WASTE TYPE

To: K. G. Squires S6-12

cc: J. W. Bailey S6-12 D. A. Reynolds R2-11
N. W. Kirch *NWK* R2-11 J. P. Sederburg R2-11
T. H. May S6-12 SDE File/LB

- Reference(s): (1) Carothers, K. G., 1991, "Tank Farm Waste Compatibility Program," WHC-SD-WM-OCD-015, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- (2) Estey, S. D., 1993, "241-C-106 to 241-AY Tank Farm Waste Transfer Compatibility Study (Preliminary)," WHC-SD-WM-ES-244, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- (3) Bork, S. W., and Harrington, R. A., 1993, "Project W-320 Tank 106-C Waste Retrieval Study Analysis Session Report," KEH Letter W-320-04, Kaiser Engineers Hanford, Richland, Washington.

SUMMARY

This memo documents the process by which Project W-320, "Tank 241-C-106 Waste Retrieval," chose dilute complexed waste as the preferred working fluid for use in the waste recovery sluicing system (WRSS), and tank 241-AY-102 as the preferred receiving tank. The requirements of the Tank Farm Waste Compatibility Program (Reference 1) were first applied to the analysis of Project W-320 operations, as documented by References 2 & 3. This process was more rigorous than earlier attempts at analysis of waste compatibility for the retrieval project, and the results, which differ from the earlier studies, are more technically defensible.

DISCUSSION

In February of 1993, Project W-320 initiated a dedicated waste compatibility study with hopes of identifying a receiver tank for the wastes to be transferred by the retrieval project. This study (Reference 2) applied the criteria of Reference 1 in analyzing the proposed waste transfer to either tank 241-AY-102 or -101, using dilute non-complexed waste, process water, or a combination of both. At that time, use of dilute complexed waste was not considered an option due to the desire to keep it segregated from wastes with the non-complexed designation, which included tank 241-C-106 wastes.

K. G. Squires
Page 2
April 20, 1994

Reference 2 performed a thorough survey of available historical laboratory analyses for the tank wastes in question, processed the data, and applied it to the requirements contained in Reference (1), and other known operational requirements. The major conclusion of Reference 2 was that the available historical characterization data was insufficient to completely satisfy the analysis requirements contained in Reference 1 (hence the term "Preliminary" in its title), and that a defensible waste compatibility study would have to be performed prior to actual waste transfer.

However, Reference 2 did uncover some clear characteristics of the tank wastes. The most significant finding indicated that the non-complexed designation of tank 241-C-106 wastes was not sufficiently descriptive. The historical analysis data clearly indicated that the liquids in tank 241-C-106 were both transuranic (TRU) and complexed. The waste compatibility rules indicated that the dilute complexed supernatant in tank 241-AY-101, which is also TRU, would be the logical choice for a sluicing supernatant. This choice complies with the complexed/non-complexed segregation criteria and avoids the creation of additional TRU waste, which would result if non-complexed liquids or process water were used in the WRSS.

Reference 3 documents the study analysis session which was conducted to determine the impact that the findings of Reference 2 would have on Project W-320. Many of the waste compatibility findings were judged to be sufficient for use in influencing project planning. The applicable waste compatibility issues were considered with other issues in making a decision about the designation of a receiver tank and the sluicing media to be used by the project. These issues included schedule, likelihood for success, program interfaces, initial cost, minimization of liquid TRU waste, supporting waste minimization, life cycle costs, and tank configuration. The results were that tank 241-AY-102 was preferred to tank 241-AY-101 and that dilute complexed supernatant was preferred to dilute non-complexed supernatant or process water.

S. D. Estey

S. D. Estey, Engineer
Waste Tanks Process Control

mjg

APPENDIX F

CHEMISTRY OF MIXING TANKS 241-AY-101 AND 241-AY-102

This page intentionally left blank.

APPENDIX F

CHEMISTRY OF MIXING TANKS 241-AY-101 AND 241-AY-102

Tank 241 AY-101 supernatant data calculations			
Specific gravity = 1,100 g/L		Volume = 2,044,138 L	
Component	Composition (g/L)	Molecular weight (g/mol)	Moles (gmoles)
Cl	0.462	35.5	26602.58
CO ₃	16.965	60	577980
F	0.559	19	60140.69
NO ₂	11.696	46	519744.3
NO ₃	50.763	62	1673654
OH	7.608	17	914811.9
PO ₄	0.974	95	20957.79
SO ₄	6.277	96	133656.8
Al	1.778	27	134610.3
Na	56.748	23	5043511
H ₂ O	88.4 wt%	18.02	1.10 E+08

WHC-SD-WM-ES-290
Revision 2

Tank 241-AY-102 solids data calculations			
Specific gravity = 1,350 g/L		Volume = 121,134 L	
Component	Composition (g/kg)	Molecular weight (g/mol)	Moles (gmoles)
Cl	8.343	35.5	38432.06
F	2.66	19	22894.33
NO ₂	2.944	46	10465.98
NO ₃	0.682	62	1798.84
PO ₄	1.71	95	2943.556
Al	37.8	27	228943.3
Ba	2.055	137.34	2446.891
B	2.808	10.8	42518.03
Ca	14	40.08	57121.57
Cr	3.744	52	11774.22
Fe	83.7	55.85	245076.7
La	4.031	138.9	4745.81
Mg	6.804	24.3	45788.65
Mn	8.784	54.9	26164.94
Ni	3.052	58.71	8501.044
P	6.2	30.97	32737.86
K	1.443	39.1	6035.169
Si	12.04	28.09	70092.99
Ag	7.236	107.9	10966.72
Na	41.4	23	294355.6
H ₂ O	60.2 wt%	18.02	5463130

Resultant feed streams to model		
Component	Tank 241-AY-101 supernatant (gmoles/h)	Tank 241-AY-102 solids (gmoles/h)
H ₂ O	11,000	546.313
NaNO ₃	167.3654	0.179884
NaNO ₂	51.97443	1.046598
NaAlO ₂	13.46103	22.89433
NaOH	91.48119	1.78138
Na ₃ PO ₄	2.095779	0.294356
Na ₂ SO ₄	13.36568	0
Na ₂ CO ₃	57.798	0

COMP	AY-101 (MOLES/HR)	AY-102 (MOLES/HR)	RESULT (MOLES/HR)
H2O	1.09735E+04	5.00523E+02	1.14740E+04
NAH03	1.67377E+02	1.79881E-01	1.67557E+02
NAH02	5.19710E+01	1.04642E+00	5.30175E+01
NAALO2	1.34615E+01	1.76506E+00	3.63557E+01
NAOH	9.14912E+01	2.29107E+01	9.32728E+01
NA3PO4	2.09588E+00	0.00000E+00	2.39025E+00
NA2SO4	1.33665E+01	0.00000E+00	1.33665E+01
NA2CO3	5.51053E+01	0.00000E+00	5.05263E+01
ALOH3	5.01202E-07	2.11291E+01	1.36727E-06
CO2	4.10456E-11	0.00000E+00	4.11169E-11
HNO2	5.04076E-03	1.86008E-04	5.22033E-03
HNO3	0.00000E+00	0.00000E+00	0.00000E+00
NAHC03	1.53532E-03	0.00000E+00	1.55312E-03
AL2SO43	0.00000E+00	0.00000E+00	0.00000E+00
ALOOH	0.00000E+00	0.00000E+00	0.00000E+00
ALP04	0.00000E+00	0.00000E+00	0.00000E+00
NA2C03.1	2.69349E+00	0.00000E+00	7.27247E+00
NA2C03.1	0.00000E+00	0.00000E+00	0.00000E+00
NA2C03.7	0.00000E+00	0.00000E+00	0.00000E+00
NA2SO4.1	0.00000E+00	0.00000E+00	0.00000E+00
NA3PO4.1	0.00000E+00	2.94362E-01	0.00000E+00
NAH2P04.	0.00000E+00	0.00000E+00	0.00000E+00
NAH2P04.	0.00000E+00	0.00000E+00	0.00000E+00
NAH2P04	0.00000E+00	0.00000E+00	0.00000E+00
NAHS04	0.00000E+00	0.00000E+00	0.00000E+00
TOTAL (GMOL)	1.13711E+04	5.47849E+02	1.18978E+04
MASS (GM)	2.29121E+05	1.19257E+04	2.41046E+05
TEMP (C)	23.000	18.000	22.766
PRES (ATM)	1.0000	1.0000	1.0000
ENTH (CAL)	-8.09441E+08	-4.42169E+07	-8.53658E+08
DENS (GM/L)	1107.5333	1144.7974	1109.3868
PH	13.6733	13.5525	13.6733
VOL (M3)	0.206875	1.041731E-02	0.217279

INPUT

=====

H2OIN
NAO3IN
NAO2IN
NAALO2IN
NAOHIN
NA3PO4IN
NA2SO4IN
NA2CO3IN
ALOH3IN
CO2IN
HNO2IN
HNO3IN
NAHCO3IN
AL2SO43IN
ALOOHIN
ALPO4IN
NA2CO3.10H2OIN
NA2CO3.1H2OIN
NA2CO3.7H2OIN
NA2SO4.10H2OIN
NA3PO4.12H2OIN
NAHSO4IN

SPECIES CONSIDERED

=====

H2O
ALOH3AQ
CO2AQ
HNO2AQ
HNO3AQ
NAHCO3AQ
ALION
ALOH2ION
ALOH4ION
ALOHION
CO3ION
H2P2O7ION
H2PO4ION
H3P2O7ION
HCO3ION
HION
HP2O7ION
HPO4ION
HSO4ION
NACO3ION
NAION
NASO4ION
NO2ION
NO3ION
OHION
P2O7ION
PO4ION
SO4ION
AL2SO43PPT
ALOH3PPT
ALOOHPPT
ALPO4PPT
NA2CO3PPT
NA2SO4PPT
NA3PO4PPT
NAHCO3PPT
NAHSO4PPT
NANO2PPT
NANO3PPT
NA2CO3.10H2O
NA2CO3.1H2O
NA2CO3.7H2O
NA2SO4.10H2O
NA3PO4.12H2O

EQUILIBRIUM EQUATIONS CONSIDERED

=====

AL2SO43PPT=2ALION+3SO4ION
ALOH2ION=ALION+2OHION
ALOH3AQ=ALION+3OHION
ALOH3PPT+OHION=ALOH4ION
ALOH4ION=ALION+4OHION
ALOHION=ALION+OHION
ALOOHPPT+OHION+H2O=ALOH4ION
ALPO4PPT=ALION+PO4ION
CO2AQ+H2O=HION+HCO3ION
H2O=HION+OHION
H2P2O7ION=HION+HP2O7ION
H2PO4ION=HION+HPO4ION
H3P2O7ION=HION+H2P2O7ION
HCO3ION=HION+CO3ION
HNO2AQ=HION+NO2ION
HNO3AQ=HION+NO3ION
HP2O7ION=HION+P2O7ION
HPO4ION=HION+PO4ION
HSO4ION=HION+SO4ION
NA2CO3.10H2O=2NAION+CO3ION+10H2O
NA2CO3.1H2O=2NAION+CO3ION+1H2O
NA2CO3.7H2O=2NAION+CO3ION+7H2O
NA2CO3PPT=2NAION+CO3ION
NA2SO4.10H2O=2NAION+SO4ION+10H2O
NA2SO4PPT=2NAION+SO4ION
NA3PO4.12H2O=3NAION+PO4ION+12H2O
NA3PO4PPT=3NAION+PO4ION
NAC03ION=NAION+CO3ION
NAHCO3AQ=NAION+HCO3ION
NAHCO3PPT=NAION+HCO3ION
NAHSO4PPT=NAION+HSO4ION
NANO2PPT=NAION+NO2ION
NANO3PPT=NAION+NO3ION
NASO4ION=NAION+SO4ION

APPENDIX G

**EVALUATION OF 241-C-106 SLUICING FLUID OPTIONS
FOR PREVENTING FLAMMABLE GAS RETENTION**

This page intentionally left blank.

APPENDIX G

EVALUATION OF 241-C-106 SLUICING FLUID OPTIONS FOR PREVENTING FLAMMABLE GAS RETENTION

EXECUTIVE SUMMARY

Tank 241-C-106 (C-106), a high-heat single-shell tank, is planned to be retrieved into double-shell tank 241-AY-102 (102-AY). This paper evaluates issues regarding the planned sluicing approach and whether tank 102-AY will exhibit the behavior of Flammable Gas Watch List tanks during or after completion of C-106 retrieval.

It has been theorized that solid compounds of aluminum oxides, existing in certain pH ranges (hydroxide concentrations), can form an amorphous structure (e.g., a gel) with a sufficiently low viscosity to create the potential for trapping gasses. The C-106 solids contain aluminum. The concentration of aluminum and hydroxide for the C-106 solids, 102-AY solids and the resulting combined streams are evaluated against aluminum phase chemistry information. The evaluation is performed for four different sluicing alternatives:

- Case 1: Sluicing with 101-AY liquid (current plan)
- Case 2: Sluicing with 2.5 molar hydroxide
- Case 3: Sluicing with dilute waste
- Case 4: Sluicing with inhibited raw water.

In all sluicing alternatives, the resulting waste combinations are in the dilute aluminum region of the phase chemistry information. The Flammable Gas Watch List double-shell tanks are more concentrated in aluminum and/or hydroxide. In the current plan of Case 1 and Cases 3 and 4, the final combined streams are in the insoluble aluminum region. In this region, no new aluminum solids are expected to precipitate. In Case 2, the 2.5 molar hydroxide alternative, the resulting stream is in the dissolved aluminum region. The dissolution is expected to be very slow.

Although all sluicing fluid alternatives are not expected to result in gas retention behavior in tank 102-AY, Case 2 offers flexibility to introduce sodium hydroxide for dissolution of aluminum. Accepting Case 2, sluicing with 2.5 molar hydroxide, allows the C-106 retrieval project to proceed while analysis and mixing studies are completed.

**EVALUATION OF 241-C-106
SLUICING FLUID OPTIONS FOR
PREVENTING FLAMMABLE GAS RETENTION**

INTRODUCTION

Tank 241-C-106 (C-106) is a high-heat, single-shell tank (SST). The current heat load of C-106 is greater than 100,000 BTU/hr and plans are to retrieve C-106 to double-shell tank (DST) 241-AY-102 (102-AY) as part of Project W-320, Tank 241-C-106 Waste Retrieval Sluicing System.

The compatibility of C-106 waste material with the sluicing fluid (241-AY-101 supernate) and 102-AY solids has been evaluated (Sederburg 1994). Additional issues have been raised regarding the planned sluicing approach and whether tank 102-AY will exhibit the behavior of Flammable Gas Watch List tanks during or after completion of C-106 retrieval. This paper presents an evaluation of flammable gas retention for the planned sluicing operation and alternative sluicing scenarios. Additionally, the planned and alternative scenarios are evaluated for other possible Tank Waste Remediation System (TWRS) impacts, such as impact to Project W-320 or waste tank operations. This paper is supplemental to Sederburg 1994. Sederburg 1994 will be revised to incorporate the results of this evaluation.

FLAMMABLE GAS WATCH LIST TANK CHARACTERISTICS

Flammable Gas Watch List tanks generate and trap gases (hydrogen, nitrogen, nitrous oxide, ammonia) until the buoyant forces overcome the trapping forces and result in a gas release. The ability of the waste matrix to trap gases is related to the viscosity and shear strength. Only DSTs containing concentrated waste slurries called Double-Shell Slurry or Double-Shell Slurry Feed have exhibited the cyclic gas trapping and release behavior. The SSTs have shown evidence of gas entrapment but not the cyclic release behavior.

It has been proposed that the aluminum solids that exist in certain pH ranges create gels which trap gases. At lower hydroxide concentrations, aluminum is insoluble and may be in the form of gibbsite $[\text{Al}(\text{OH})_3]$. As hydroxide ion concentration is increased, aluminum becomes soluble until at high hydroxide concentrations, aluminum is again insoluble as sodium aluminate (NaAlO_2).

The aluminum and hydroxide concentrations for the tanks to be used in C-106 sluicing are shown in Table 1 and the volumes to be used during sluicing are in Table 2. The concentrations are converted to moles per liter (M). For solids, the values represent the moles per liter of sample. The detailed description of the sluicing operation is discussed later. The general concept is to use liquid from 101-AY to sluice C-106 solids into 102-AY.

Table 1
Current Status of Tanks

Tank	Solid Phase		Liquid Phase		Solid Phase		Liquid Phase	
	OH ⁻	Al mg/kg	OH ⁻ mg/l	Al mg/l	OH ⁻ M	Al M	OH ⁻ M	Al M
C-106	0	35450	0.176	270.1	0	1.84	1.04E-5	0.010
102-AY	0	37800	5032	68.2	0	1.89	0.296	0.0025
101-AY	N/A	N/A	7608	1778	N/A	N/A	0.4473	0.0659

N/A - not applicable

Table 2
Waste Volumes for C-106 Sluicing Evaluation

Tank	Solids, l	Liquid, l	Solid, gal	Liquid, gal	Solid, tank inch	Liquid, Tank Inch
C-106	746,000	182,000	197,000	48,000	71.6	17
101-AY	0	2,040,000	0	585,000	0	200
102-AY	121,000	0	32,000	0	11.6	0
Final	867,000	2,222,000	229,002	633,000	85.20	219

The tanks used for sluicing of C-106 are compared with the double-shell tanks on the Flammable Gas Watch List in Figure 1. Included in Figure 1 are the aluminum solubility lines from Barney 1976 (upper line) and Herting 1986 (lower line). The Barney curve is for very concentrated solution such as found in the evaporators. Herting's curve is for dilute solution similar to what has been found in this study. The left hand zone represents an area that has gibbsite solids present. The zone above and to the right of the lines represents an area where sodium aluminate (NaAlO_2) is present. Below the lines is a zone where no aluminum solids should be present. It should also be pointed out that the boundary lines represent a case where the solution was saturated with five different chemical species, ie. the solution was a very concentrated solution. In actuality, this line is a rather broad region and the solubilities of the aluminum species will depend on common ion effects, pH or hydroxide concentration, buffers, and competing solubilities.

In Figure 1, the tanks used for sluicing all cluster near the origin. This shows that the sluicing will take place with dilute solutions. The Flammable Gas Watch List tanks are all greater than 2 M hydroxide, represent very concentrated slurries, and lie nearer to the aluminate line.

The region of interest for C-106 sluicing is shown on the phase diagram with an expanded scale to show the dilute hydroxide region (Figure 2). The aluminum versus hydroxide concentration from Table 1 is plotted for the various phases. The line in this graph is the gibbsite solubility boundary derived from Herting 1986. The area above the curve represent a zone that has gibbsite ($\text{Al}(\text{OH})_3$) present. The area below the line represents a zone that does not have solid gibbsite present.

It is clear that the solid phases in both C-106 and 102-AY have aluminum present. During analysis of the previous waste samples, the specific aluminum forms were not identified in the solid layer of either tank. All the liquid phases have been in contact with the solid phase long enough to equilibrate. Because the aluminum concentration in the liquid phase is low, it can be assumed that the solid phase aluminum is not soluble in the liquid to be used in this sluicing operation.

If the mineral species is gibbsite and the liquid is in equilibrium with the gibbsite, the aluminum concentration of the liquid should be at the Herting line. Since the aluminum concentrations are below the gibbsite line, the aluminum is present in a more insoluble species than gibbsite such as an aluminum silicate.

EVALUATION OF ALTERNATIVE SLUICING FLUIDS

Four different fluids for sluicing C-106 are evaluated here. The first case is the base case 101-AY liquid currently planned for sluicing. The second case would be to use the 101-AY liquid and add sodium hydroxide to bring it up to 2.5 M hydroxide. The third case would be to use another waste for sluicing instead of 101-AY. The fourth case would be to use raw water with caustic added to meet tank corrosion specifications.

Each of the sluicing scenarios are evaluated using a graphical simulation and a computer simulation using ProChem, a chemical equilibria model. With the graphical simulation, each stream is plotted on the aluminum-hydroxide phase diagram and the combined streams are plotted using the inverse lever rule. Using ProChem individual stream chemical compositions and masses are input and a resulting stream composition is calculated. The input streams must have cations and anions balanced; this was achieved by varying hydroxide and sodium. The equilibrium composition of the mix is calculated for 30°C (86°F) and 1 atmosphere.

CASE 1: SLUICING WITH 101-AY LIQUID

Case 1 is the current base case. The goal is to transfer (sluice) the solid and liquid layers in C-106 to an aging waste tank, 102-AY. To do this the liquid currently in 102-AY will be moved. This will leave behind the solid layer in 102-AY. A portion of the liquid in 101-AY will be transferred to 102-AY for the sluicing medium. When sluicing is completed, liquid from 101-AY, liquid from C-106, and solids from both C-106 and 102-AY will be commingled in 102-AY.

Combination of 102-AY Solids and 101-AY Liquid

The first sequence will be by adding liquid from 101-AY to the solids left in 102-AY prior to sluicing. Figure 3 shows the resulting mix. The "MIX" represents the average composition of mixing the solids from 102-AY and the liquid from 101-AY. The resulting composition lies below the gibbsite boundary. This would indicate that the aluminum would be in solution. However, because 101-AY solution is already saturated in aluminum, (at least it has been in contact with solids in 101-AY which contain aluminum) it is not anticipated that aluminum would be dissolved. Most likely, neither the solids nor the liquid would change composition.

The ProChem model results indicate that 96% of the aluminum would remain in the solid phase as gibbsite. Other solids present would be iron hydroxide, barium sulfate, calcium carbonate, chromium hydroxide, calcium phosphate, calcium fluoride and lanthanum phosphate. The hydroxide in solution would be 0.278 M and the estimated pH would be 13.2. The aluminum in solution would be 0.023 M. The solution density is estimated at 1.1 g/ml.

Combination of C-106 Solids in 102-AY

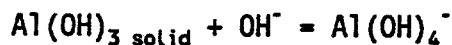
This sequence assumes that all of C-106 solids are transferred into 102-AY along with the liquid from 101-AY and solids already present in 102-AY. Figure 4 shows the final mix above the gibbsite boundary. This means that the aluminum solids that were in C-106 would be brought over to 102-AY but not dissolved. This is an average composition for the tank and not for the supernate. The aluminum in the C-106 solids would not be dissolved to any appreciable amount because the sluicing liquid from 102-AY would be near saturation when contacting that material. Instead the mineral form from C-106 would be transported to 102-AY unchanged.

The ProChem result for this step indicates that the liquid would be low pH, 11.7. Essentially all of the aluminum would be in the solid phase. The solution density is estimated at 1.16 g/ml.

CASE 2: SLUICING WITH 2.5 MOLAR HYDROXIDE

The second case involves adding sodium hydroxide to the 101-AY liquid in 102-AY to control the solubility of aluminum and prevent the formation of gibbsite.

Figure 5 plots the addition of 250,000 liters (66,000 gallons) of 50% sodium hydroxide to the 101-AY/102-AY mixture. Note that the mixtures do not fall on a straight line between the two points being mixed. This is because the hydroxide concentration was corrected for the reaction:



The consumption of hydroxide by this reaction moves the mixture point to the left of the straight line. Also included in Figure 5 are both the Herting gibbsite solubility curve and the Barney solubility curve. The combined stream

(Final Mix) is approximately on the Herting gibbsite boundary. This assumes that all of the aluminum is in solution. To have the final mix be at 2. M hydroxide, approximately 400,000 liters (106,000 gallons) of 50% sodium hydroxide would need to be added.

The ProChem model estimated that the final hydroxide concentration would be 1.83 M and the concentration of aluminum in solution would be .33 M. The estimated pH is 14.3 and the liquid density is 1.23 g/ml. About 60% of the aluminum would still remain in the solid phase as gibbsite $[Al(OH)_3]$.

Sluicing with 2.5 M caustic has the additional benefit of testing pretreatment technology for in-tank washing. The goal of this technology is to dissolve aluminum and chromium in a caustic stream from waste sludges which reduces high-level waste glass.

CASE 3: SLUICING WITH DILUTE WASTE

Case 3 would use other dilute waste in place of 101-AY liquid. The contents of tank 101-AY are classed as dilute complexed due to the relatively high total organic carbon (TOC). This waste was originally chosen because the contents of C-106 also is relatively high in TOC.

Two other wastes, a dilute non-complexed waste or waste which has been concentrated through the evaporator, are evaluated for sluicing, a liquid waste would be desirable and very concentrated evaporator bottoms would not be acceptable. Waste similar to the end product of the recent evaporator campaign would be acceptable. This waste, which is currently in tank 106-AN, was chosen for Case 3a with the understanding that a similar waste would be used, not necessarily this waste. The waste currently in 102-AY is dilute non-complexed waste and was chosen for Case 3b as an example of that waste type. For this study, the volumes of these waste used was 2,000,000 liters (528,000 gallons).

Figure 6 shows the way these two wastes would combine with the waste in tank C-106. Notice that the starting material is clearly below the aluminum saturation line. After blending with the waste from C-106, the mixture is above the aluminum saturation line. In both cases, the hydroxide concentrations are low enough that the driving force to dissolve aluminum is modest. The aluminum species present in C-106 would most likely be moved to 102-AY without any change in form. The aluminum in C-106 would be in the same form in 102-AY.

Case 4: SLUICING WITH INHIBITED RAW WATER

Case 4 uses 2,000,000 liters (528,000 gallons) of 0.01M hydroxide solution as the sluicing medium. This stream will go into 102-AY on top of the existing solids. Figure 7 shows the resulting combination. The water with very little hydroxide would not have the driving force to bring the aluminum into solution. The aluminum would remain in the solid form that is currently in C-106.

COMPARISON OF SLUICING FLUID ALTERNATIVES

A comparison of all the sluicing alternatives is shown on Figure 8. Cases 1, 3b, and 4 are all clustered in the dilute hydroxide and aluminum region with very little difference between alternatives. Case 3a is more concentrated in hydroxide and Case 2 is sufficiently high in hydroxide so that the aluminum is in the soluble region.

OTHER CONSIDERATIONS

Impact on Waste Storage

One of the concerns with adding caustic is that the impact that would have on waste volumes. To bring the waste up to 2.5 M hydroxide, about 66,000 gallons of 50% caustic would be used. The added caustic has an impact on how far the waste can then be evaporated for final storage. Figure 9 shows the impact on adding caustic. The evaporation lines are extended to the edge of the Barney diagram. This is equivalent of making Double-Shell Slurry Feed. The waste with caustic added (Case 2) had a significantly lower waste volume reduction factor, 77% vs 93%. This results in additional tank space required for storage.

Impact on Low Level Glass

The 66,000 gallons of 50% caustic needed could make an additional 1.5 million pounds of glass or about 9,000 ft³ of glass. Although this is an additional waste, it is a small additional contribution to the total sodium salts in the tank wastes.

Speculation on Aluminum Solids

Aluminum has a fairly complicated chemistry in the waste tanks. The previous work (Barney 1976, Herting 1986) assumed that the aluminum would be compared with gibbsite mineral form. Gibbsite can be written as $\text{Al}(\text{OH})_3$. Boehmite can also be represented by that formula. In addition, there is an amorphous form of the same formula which does not have crystalline properties. The exact form of aluminum in 106-C is not known. It is doubtful that the aluminum is in the amorphous form as that is the thermodynamical unstable form. The amorphous form spontaneously converts to one of the crystalline forms with time. The waste has been in C-106 long enough (years) to have converted to the crystalline form. Only the amorphous form is a "gel" -- the crystalline forms are well behaved solids.

In addition to the hydrated oxide forms of solids, aluminum forms a large family of clay type minerals with silicate. An example of this is cancrinite ($2\text{NaAlSiO}_4 \cdot 0.52\text{NaNO}_3 \cdot 0.68\text{H}_2\text{O}$). The aluminum silicate minerals are very hard to dissolve in either acid or base. The waste in C-106 has approximately equal amounts of aluminum and silicon. This may be an indication of an aluminum silicate type clay material. A recent study by Battelle Pacific Northwest Laboratory (Colton 1994) suggests that none of the aluminum in C-106 would be dissolved in 3 M hydroxide.

Speculation on Solutions

The aluminum solids in the tanks are not expected to change form but to remain in the form that they are in now. The following speculation was made to determine how many additional solids would form if the aluminum in solution were to precipitate.

Gibbsite has a density of 2.42 g/ml (Dean). Table 3 shows the greatest amount of solids if all of the aluminum in solutions were to precipitate out as gibbsite. The aluminum would not all precipitate out but this is a bounding calculation

Table 3 Speculation on Amount of Gibbsite Formed			
Tank	Volume, liter	Al, mg/l	Al(OH) ₃ solids, liter
C-106	182000	270.1	20
102-AY	0	68.2	0
101-AY	2040000	1778	1480
Total	2222000		1500

Physical Considerations

There are major differences between the resulting 102-AY waste after C-106 retrieval and 101-SY waste. The physical properties of the wastes and the configuration of the tanks are significantly different. These differences will be shown in this section.

Table 4 shows the differences in configuration between the two tanks. The values in 102-AY column are after the material from 106-C has been transferred to 102-AY. The physical properties of the wastes and calculated physical properties for the different sluicing scenarios are shown in Table 5.

Table 4
Physical Configuration Differences

Attribute	101-SY	102-AY
Total Depth, inches	400+	278
Depth of "solids"	~200	65
Volume of dome space, ft ³	41,000	85,800

Table 5
Comparison of Physical Properties

Attribute	101-SY	101-AY	C-106	Case #1	Case #2	Case #3
Liquid Density	1.53	1.1	1.16	1.16	1.23	1.1/1.2
Solid Density	1.7		1.4	1.4	1.4	1.4
Percent Water in Liquid Phase	37%	90%	77.43%	90%	84%	85+%

The densities are important for calculating hydrostatic head under which the gas is trapped. Notice that the 101-SY has greater densities. The percent water in the liquid shows that 101-SY is a very concentrated liquid. There is more dissolved salts in a kilogram of this liquid than water. This affects the viscosities, densities, activity of water, etc. Notice that in all cases, the sluicing cases have very dilute liquid streams.

RECOMMENDATIONS

It is recommended that the project proceed without delay on the assumption that the sluicing material will be 101-AY liquid with enough caustic added to bring the waste up to 2.5 M hydroxide.

The process for adding the caustic to the waste will be determined by the project. However, one alternative is to add caustic through the 204-AR facility to 102-AY after the liquid from 101-AY has been transferred. At that time, some or all of the air lift circulators could be turned on to mix the waste. The blending two liquid streams of different density requires less mixing energy than suspending solids and the air lift circulators should be adequate to do the job.

It has been calculated that between 60,000 and 90,000 gallons of 50% caustic may be needed depending on the amount of buffering in the 101-AY waste. This amount of caustic is not a trivial amount. Lesser quantities of 101-AY may be used and still have adequate sludge media. For example, to keep the total liquid amount in 102-AY the same (571,000 gallons), then 64,000 gallons of 50% caustic would have to be added to 507,000 gallons of 101-AY waste.

It is not expected that the viscosity of the sludge media would increase substantially by the addition of the caustic. For instance, 2.5 M sodium hydroxide is approximately 17% sodium hydroxide. This has a density of approximately 1.18 g/ml and a viscosity at 30°C of 2.5 centipoise (Fleming 1958). The other dissolved ions in the 101-AY material will not add significantly to the density and viscosity.

FURTHER WORK

Actual wastes will be retrieved from the tanks in questions and will be available for testing. The following tests are proposed to verify the conclusions in this study.

Additional Analysis

The solids from C-106 should be examined microscopically (optical and X-Ray diffraction) to identify the form of the aluminum. If large amounts of aluminum are attached to silicon as a clay type mineral, then very little of the aluminum will be available for dissolution. It should be noted that since aluminum accounts for a small fraction of the solids, the other solids fractions may prevent identification of aluminum species.

Dilution Test

The C-106 waste material should be mixed with the liquid waste from 101-AY and agitated. Three different aliquots should be removed at different times to see if aluminum will dissolve in the liquid. Two cases are possible:

1. Aluminum will increase in solution, ie. aluminum dissolves in the solution. If aluminum is dissolving in the solution, then the equilibrium concentration should be found.

The equilibrium solution should be tested to see if aluminum gel will precipitate by a minor adjustment in pH as might be expected if carbon dioxide were used.

2. Aluminum does not increase in solution, ie. aluminum does not dissolve. This would mean that there would not be enough aluminum in solution (only the small amount already present) to cause a gel formation. This would mean that the base case (Case #1) should be the preferred case.

Caustic Addition Test

Similar tests would be performed as above except that the 101-AY waste would have added sodium hydroxide to bring the hydroxide concentration up to 2.5 M. The same two cases would apply.

1. If the aluminum increased in the solution, that would be an indication that the aluminum solids in C-106 sludge are soluble in the higher caustic material. The solution would be allowed to equilibrate and then there would be an attempt to form an aluminum gel.
2. If the aluminum does not dissolve in the higher concentration hydroxide solution, then the benefit of adding the caustic would not be great.

Essentially the case for adding caustic would be made if: 1) not adding caustic, the dissolved aluminum may precipitate and 2) addition of caustic prevented the precipitation. There would be no benefit to adding the caustic under other combinations.

REFERENCES

- Barney, G. S., 1976, *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford*, ARH-ST-133, Atlantic Richfield Hanford Company, Richland, WA.
- Colton, N. G., 1994, *Sludge Pretreatment Chemistry Evaluation: Enhanced Sludge Washing Separation Factors*, TWRSP-94-053, Westinghouse Hanford Company, Richland, WA.
- Fleming, R. F., 1958, *A Compilation of Physical and Chemical Properties of Materials and Streams Encountered in the Chemical Processing Department*, HW-57386, General Electric Company, Richland, WA.
- Herting, D., Welsh, T., Reynolds, D., 1986, *Gibbsite Equilibrium in Simulated Liquid Waste*, SD-WM-TI-211, Rockwell International Company, Richland, WA.
- Dean, John A., Lange's Handbook of Chemistry, McGraw-Hill Book Company, 11th Edition,
- MacLean, G. T. to J. W. Bailey, 1994, *Caustic Sluicing of Waste Tank C-106*, IM 7E330-94-005, Westinghouse Hanford Company, Richland, WA.
- Sederburg, J. P., 1994, *Chemical Compatibility of Tank Wastes in Tanks 241-C-106, 241-AY-101, and 241-AY-102*, WHC-SD-WM-ES-290, Westinghouse Hanford Company, Richland, WA.

Figure 1. Comparison of Sluicing Process Wastes to Watch List Tanks.

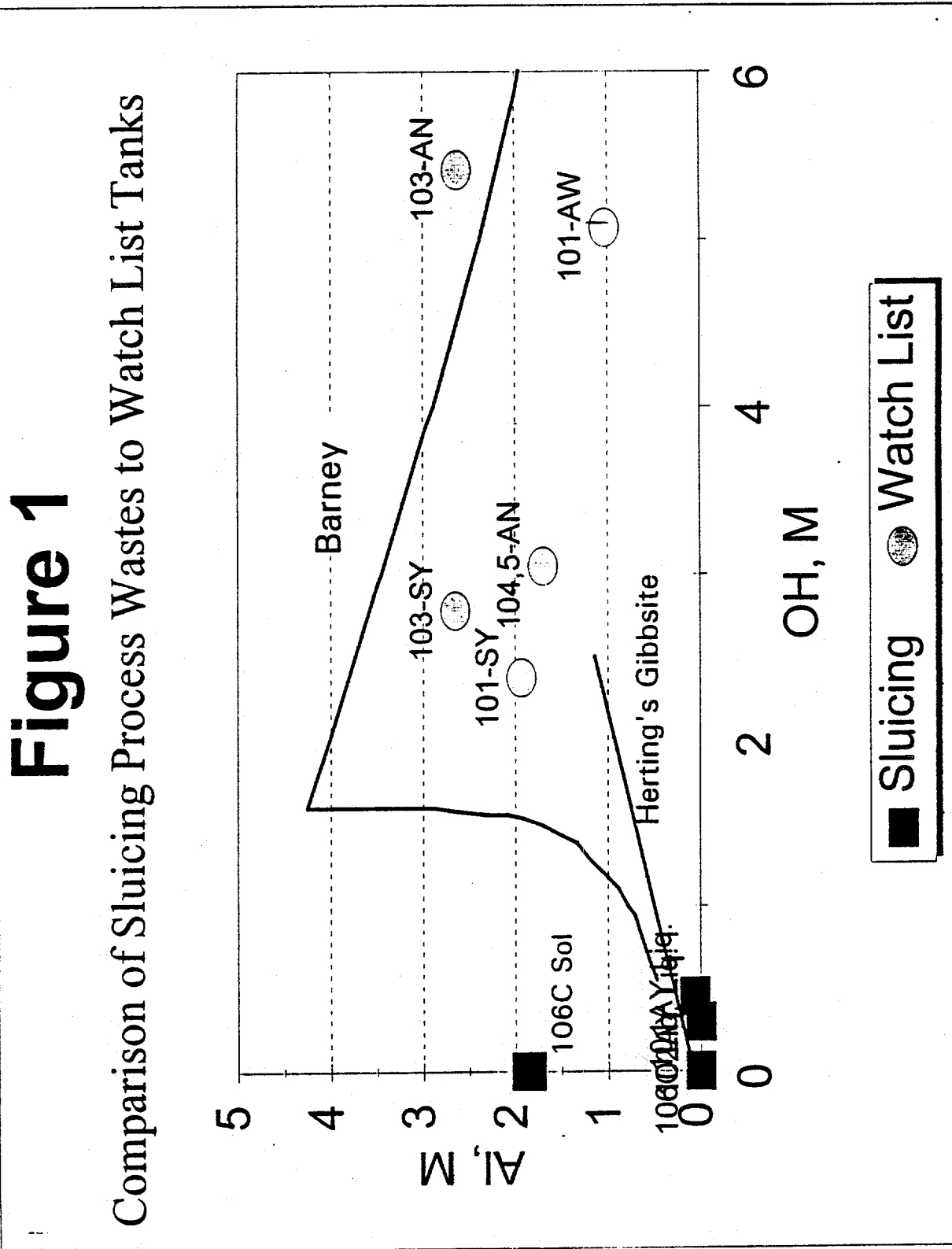


Figure 2. Current Composition of Wastes.

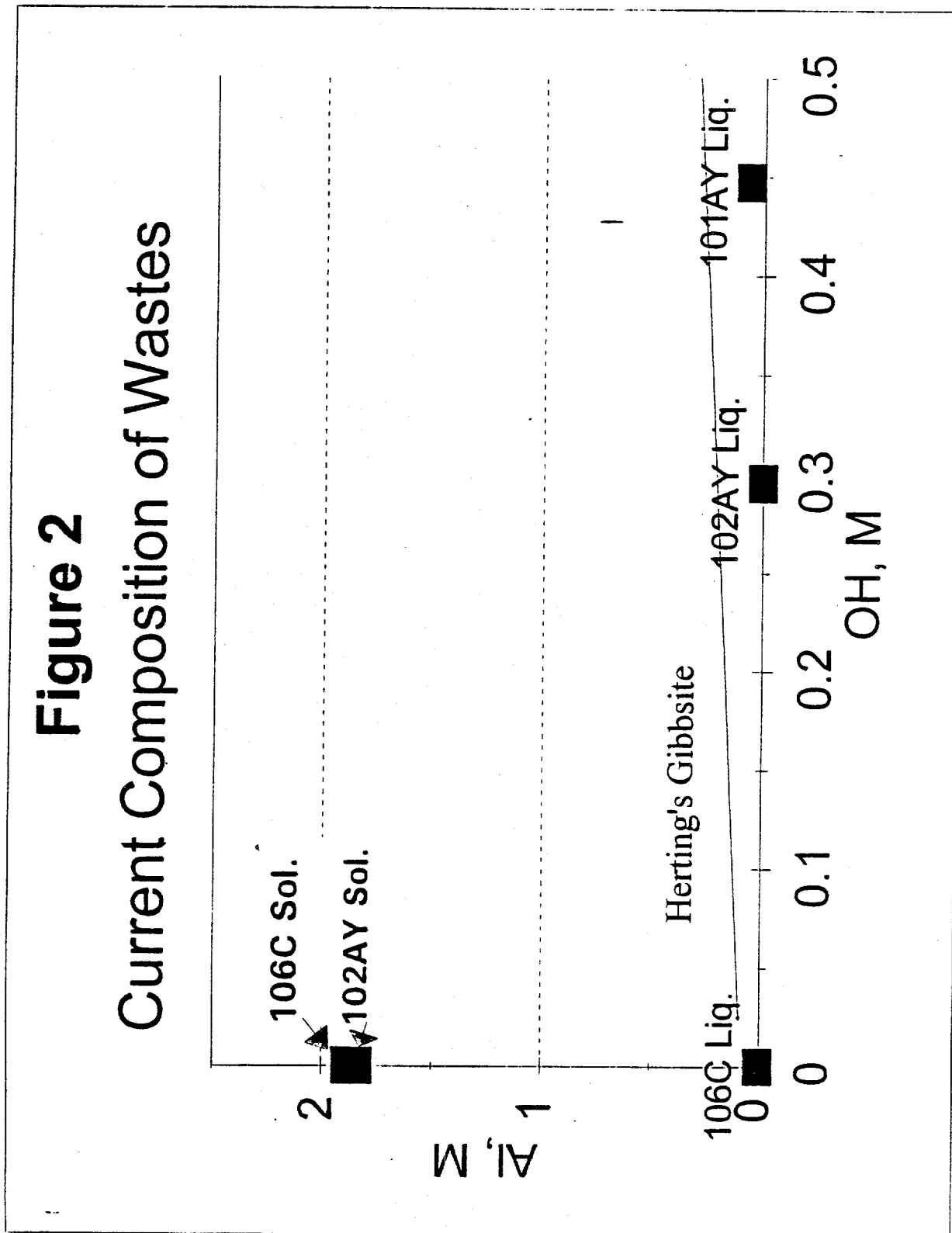


Figure 3. Combination of 101-AY Liquid and 102-AY Solids.

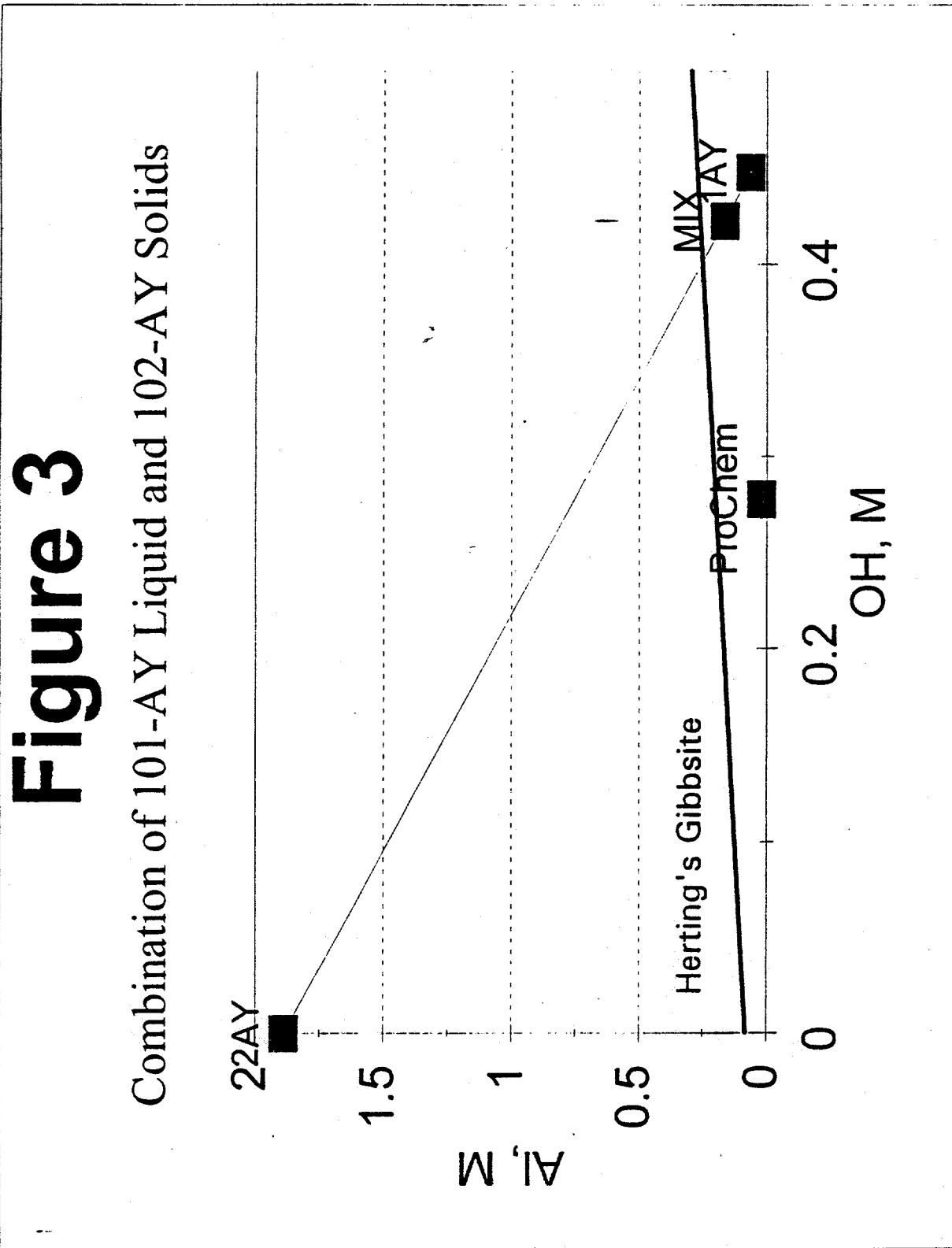


Figure 4. Combination of 106-C and 102-AY.

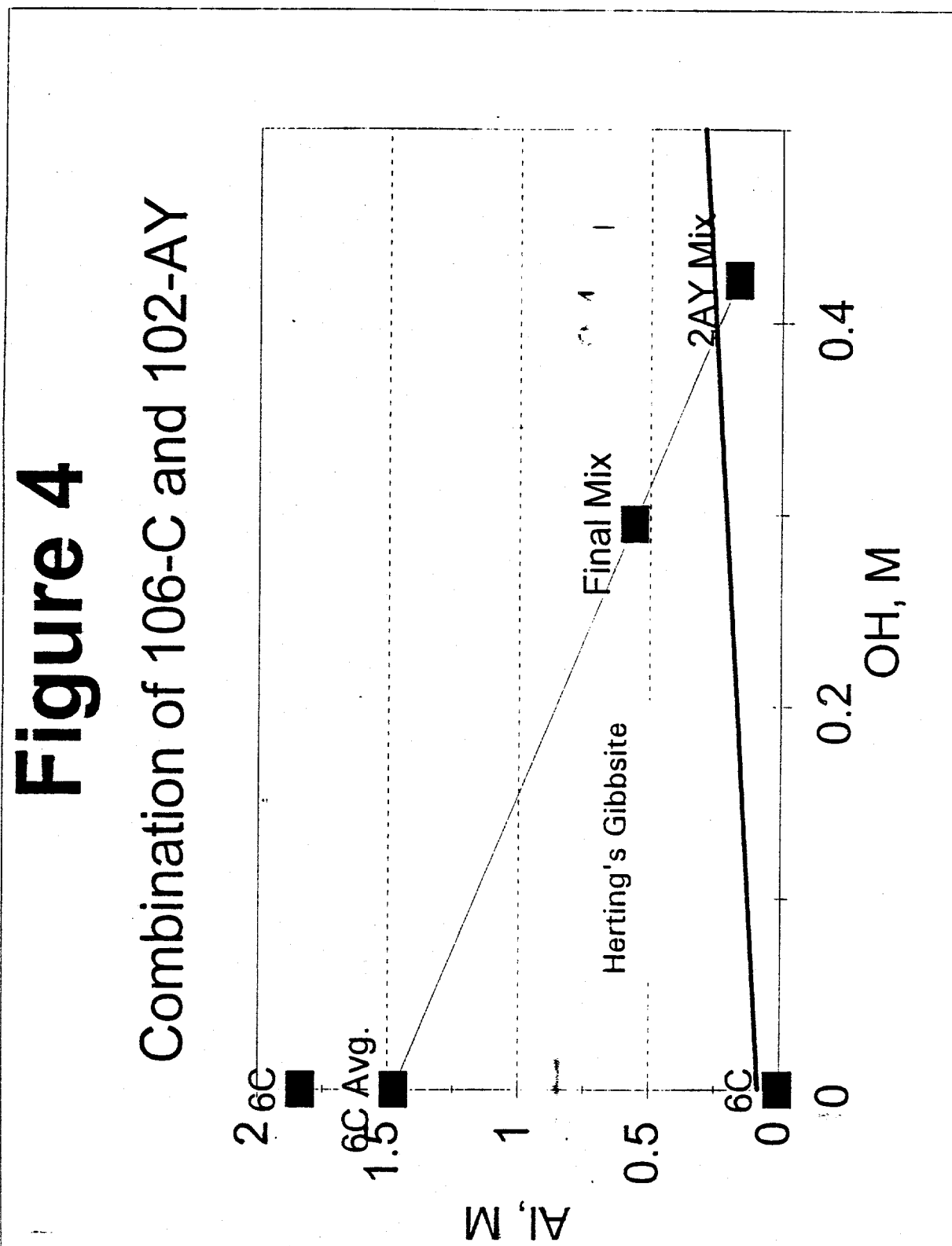


Figure 5. Case 2: Sluicing with 2.5 Molar Hydroxide.

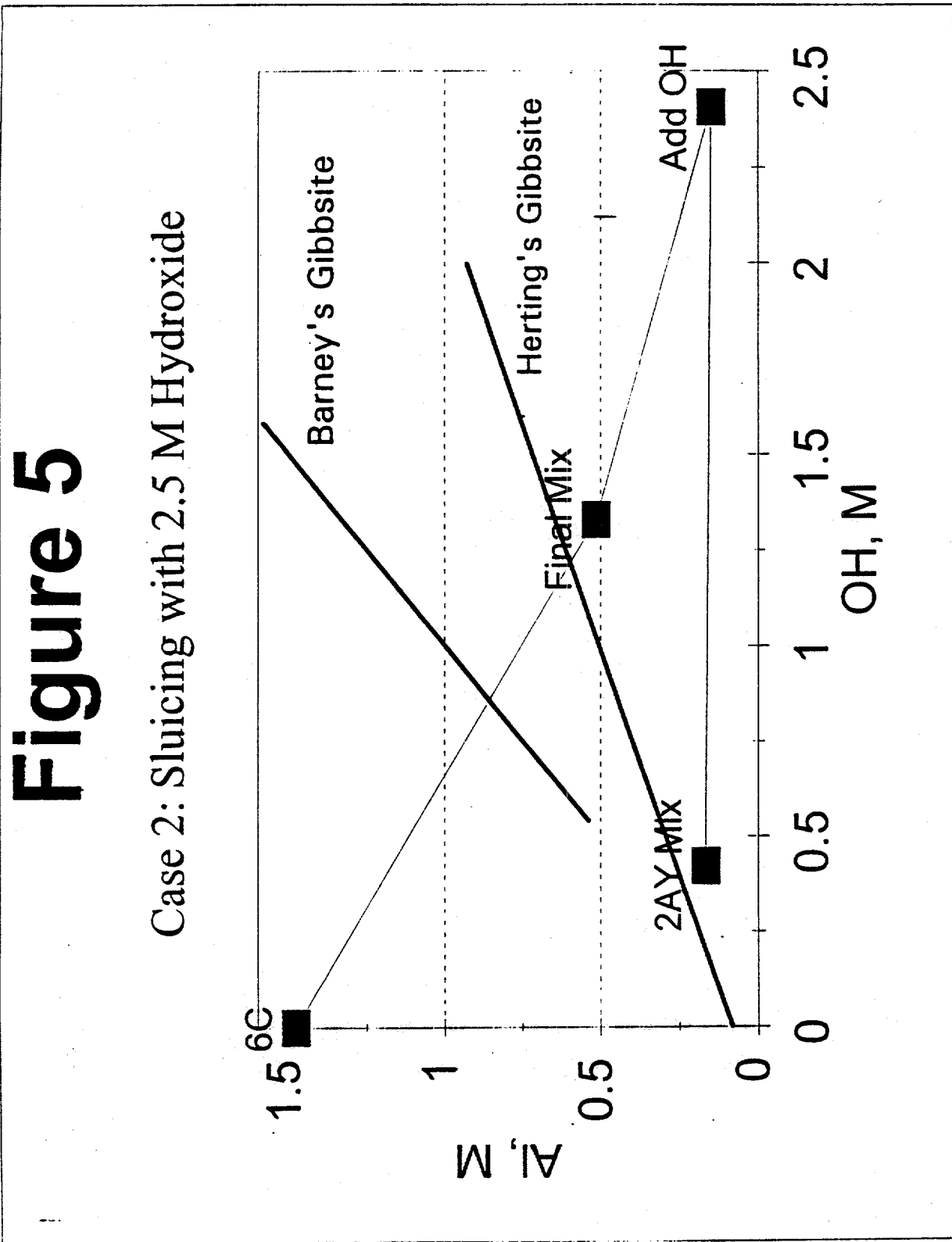


Figure 6. Case 3: Sluicing with Dilute Waste.

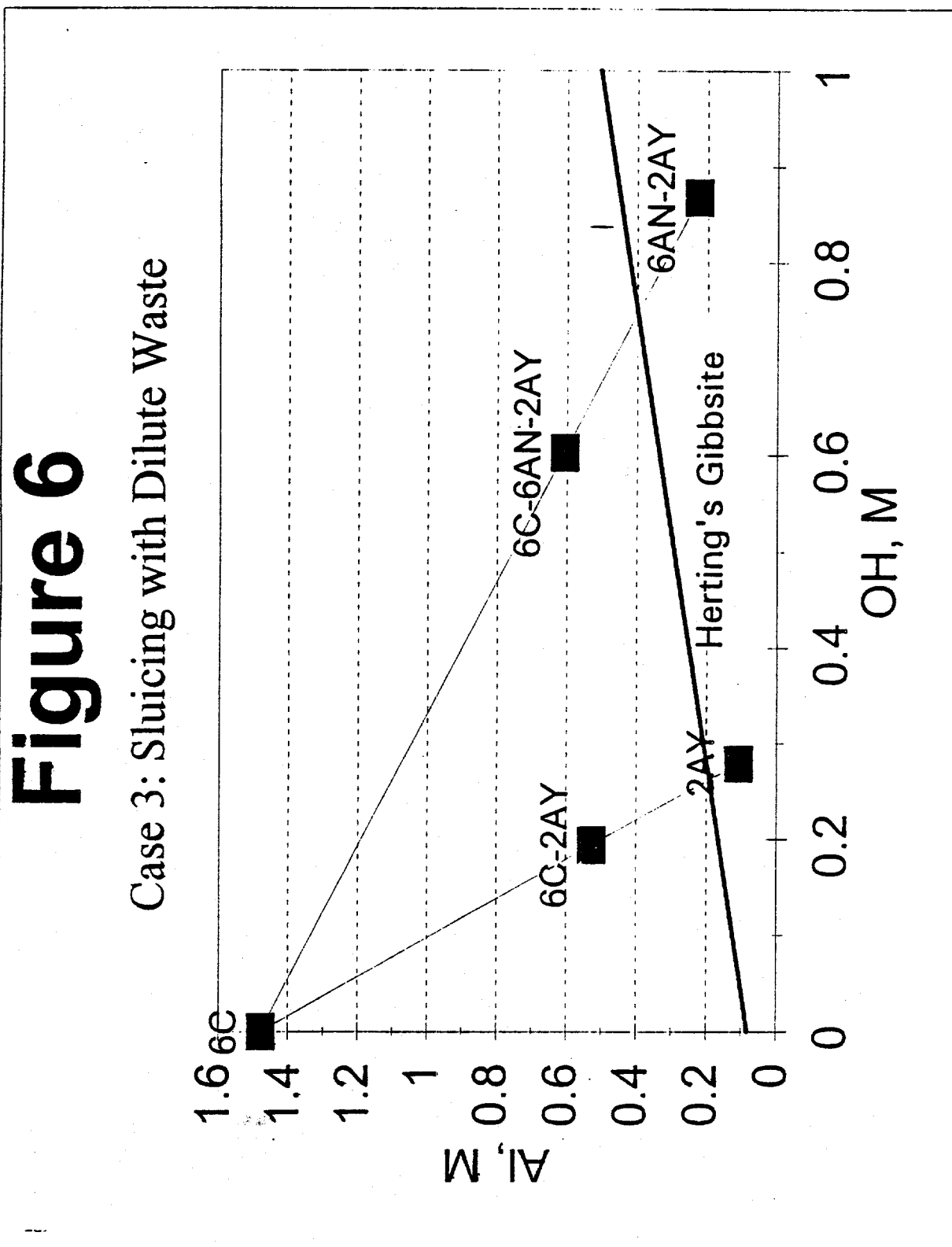


Figure 7. Case 4: Sluicing with Inhibited Water.

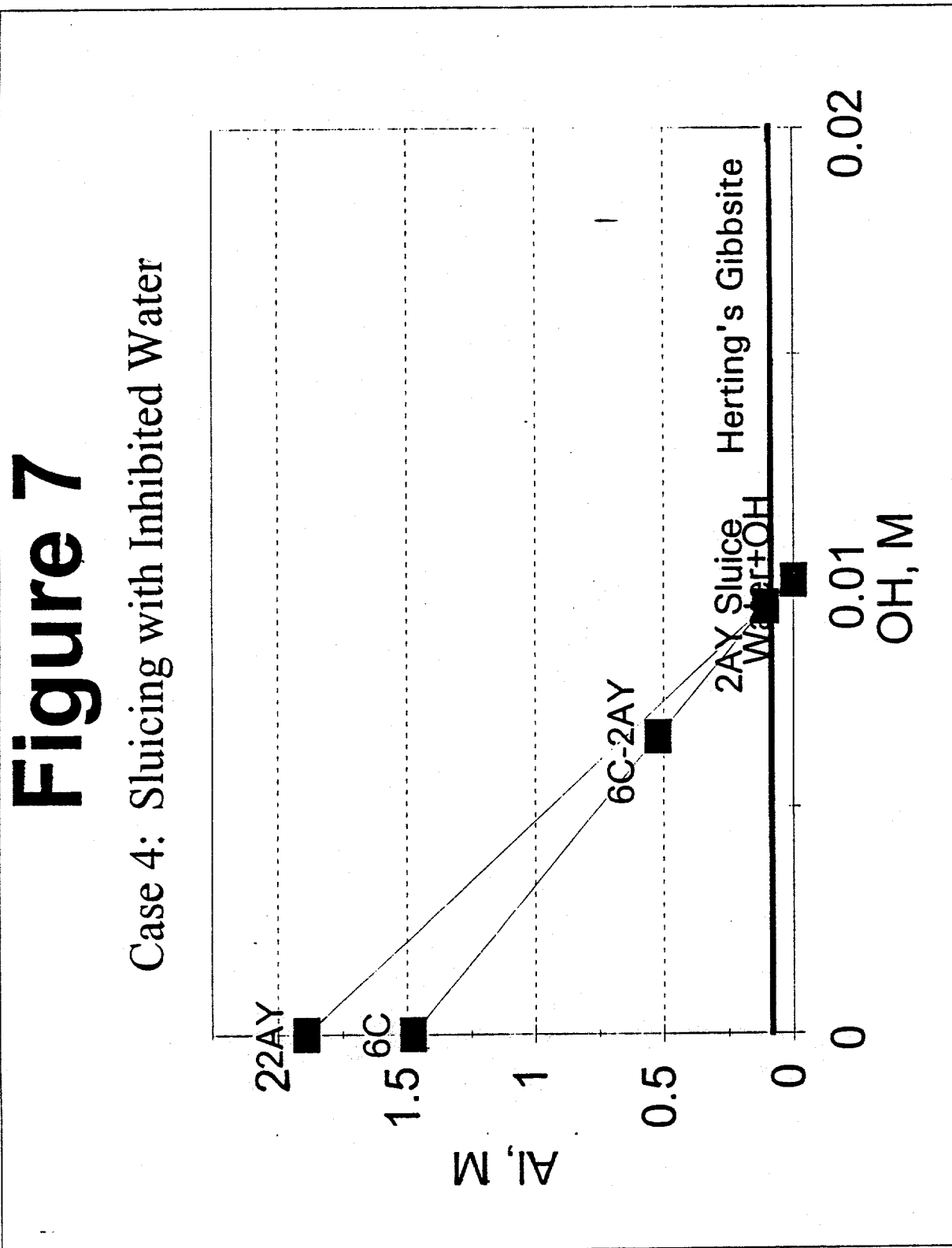


Figure 8. Comparison of Sluicing Alternatives.

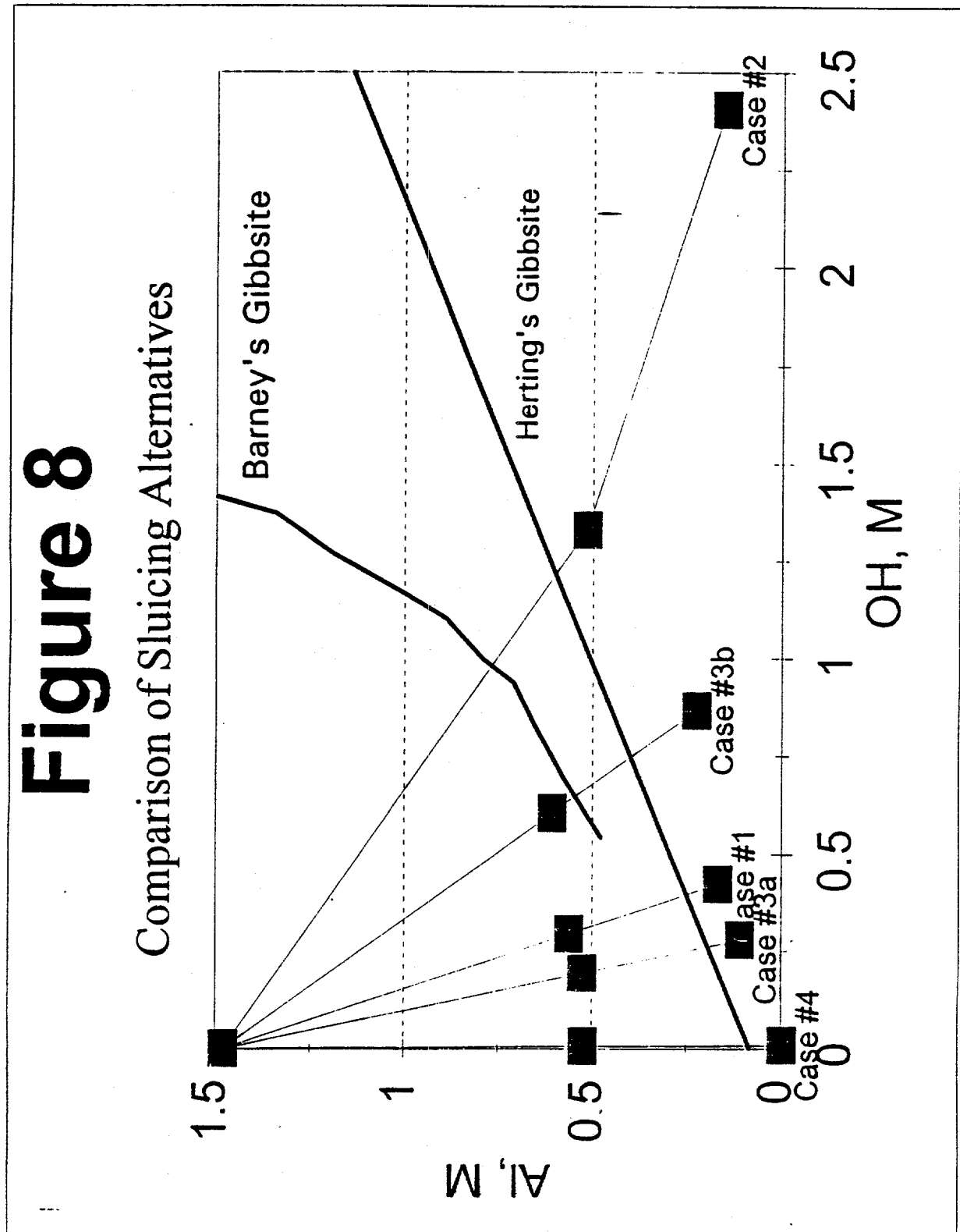
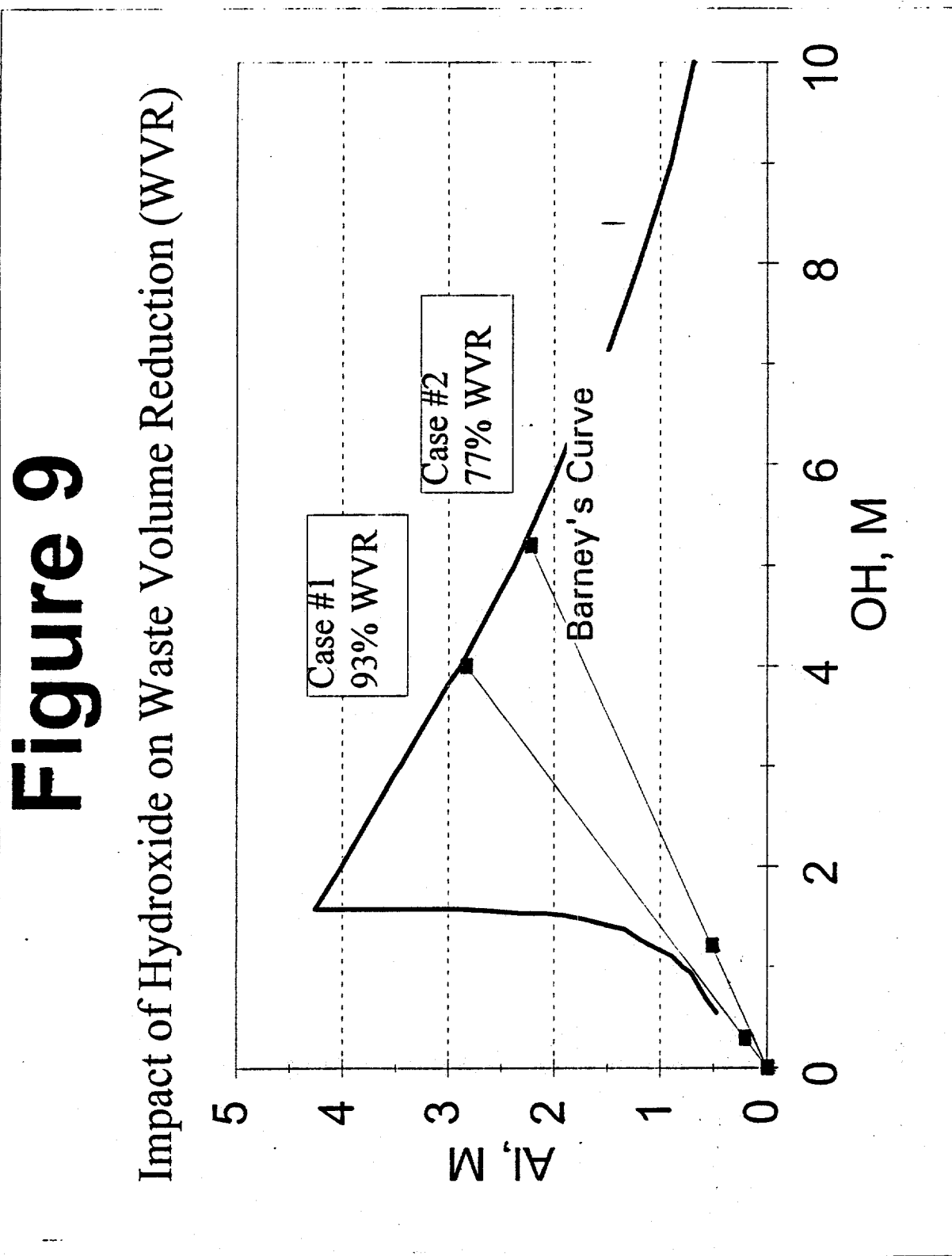


Figure 9. Impact of Hydroxide on Waste Volume Reduction (WVR).



This page intentionally left blank.