

Key Words: PUREX Waste
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Organic Waste
Organic Sorbents

Retention: Permanent

PUREX Waste Solidification (U)

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TABLE OF CONTENTS

TABLE OF CONTENTS	ii
LIST OF TABLES	v
LIST OF ACRONYMS AND ABBREVIATIONS	vi
1.0 EXECUTIVE SUMMARY	1
2.0 INTRODUCTION	2
2.1 Background	2
2.2 Objective.....	3
2.3 Approach	3
2.3.1 Disposal Requirements	3
2.3.2 Test Matrix	5
3.0 EXPERIMENTAL PROCEDURES	6
3.1 Sorbent and Waste Loading Selection.....	6
3.2 PUREX Simulant Preparation	7
3.3 Sorbent Characterization.....	7
3.4 Waste Form Preparation	8
3.5 Waste Form Characterization.....	8
3.5.1 Waste Form Properties.....	8
3.5.1.1 Visual Appearance and Bulk Densities.....	8
3.5.1.2 Paint Filter Test	8
3.5.1.3 Liquid Release Test	8
3.5.1.4 Processing Properties	8
3.5.2 PUREX-Sorbent Interaction.....	9
3.5.3 Transportation and Storage Properties.....	10
3.5.3.1 Vibration Testing.....	10
3.5.3.2 Effects of Temperatures.....	10
3.5.4 Leaching Properties.....	11
3.5.4.1 TCLP Extraction and Analyses for Regulatory Classification	11
3.5.4.2 I-129 Kd Determination	11
3.5.4.2.1 Calculation of Distribution Ratios.....	12
3.5.4.3 ANSI 16.1 Testing.....	12
3.5.4.3.1 Calculation of Effective Diffusion Coefficients and Leach Indices.....	13
3.5.5 Durability/Aging Properties.....	14
3.5.5.1 Exposure to Cobalt-60 Radiation.....	14
3.5.5.2 Exposure to Ultraviolet Light.....	15
3.5.6 Microbial Degradation	17
4.0 RESULTS	18
4.1 Sorbent Characterization.....	18
4.2 Waste Form Characterization.....	24
4.2.1 Waste Form Appearance.....	24
4.2.2 Waste Form Processing	24
4.2.2.1 Unit Weight Determination	28
4.2.2.2 Solid Property Determination (Paint Filter Test).....	32
4.2.2.3 Liquid Release at 50 psi.....	32
4.2.3 Waste Form-PUREX Interactions.....	32
4.2.4 Storage and Transportation Properties.....	37

4.2.4.1	Vibration Testing.....	37
4.2.4.2	Storage Temperature Effects.....	37
4.2.5	Leaching Properties.....	38
4.2.5.1	TCLP Results.....	38
4.2.5.2	I-129 Distribution Coefficients.....	40
4.2.5.3	Organic and Radionuclide Leaching Results.....	40
4.2.6	Durability/Aging Properties.....	45
4.2.6.1	Short-Term Aging Effects.....	45
4.2.6.2	Degradation Effects from Co-60 Irradiation.....	45
4.2.6.3	Degradation Effects from Ultraviolet Light Exposure.....	53
4.2.6.4	Hydration of Fresh and Aged Waste Forms.....	56
4.2.7	Microbial Degradation.....	57
5.0	Discussion.....	58
5.1	Regulatory Classification of the PUREX Waste and Solidified Waste Forms ..	58
5.2	Disposal Options.....	60
5.3	Comparison of Sorbents Tested for Solidification of Organic PUREX Waste..	60
5.4	Sorbents for Waste Treatment versus Spill Control.....	62
5.5	Review of Leaching Techniques for Hydrophobic Organic Waste Forms.....	63
5.6	Accelerated Aging of Sorbents and Sorbent Waste Forms.....	63
6.0	CONCLUSIONS.....	64
7.0	RECOMMENDATIONS.....	65
8.0	ACKNOWLEDGEMENTS.....	65
9.0	REFERENCES.....	66
10.0	APPENDIX A. Analyses of Spent PUREX waste in tanks 33 and 35.....	A1
11.0	APPENDIX B. Dose Calculations for Cobalt-60 irradiation.....	B1
12.0	APPENDIX C. TGA/DTA for Simulated Spent PUREX-sorbeNt waste forms .	C1
13.0	APPENDIX D GEL, Inc. Results.....	D1
14.0	APPENDIX E Microbial Degradation Reports.....	E1

LIST OF FIGURES

Figure 2-1. Summary of SRS and NTS low-level radioactive waste disposal criteria.	4
Figure 3-1. Liquid Release Test apparatus. Blue absorbent paper is used to collect liquid expressed from the waste forms.	9
Figure 3-2. Fritsch Laboratory Vibrator.	10
Figure 3-3. ANSI 16.1 leach test configuration.	13
Figure 3-4. Absorbed dose versus time plot for Tank 33 and 35 PUREX waste.	16
Figure 4-1. Micrographs of the Sorbent Materials. (RL indicates reflected light. X indicates the magnification)	19
Figure 4-2. Imbiber Bead FTIR spectra and compound identification.	21
Figure 4-3. Nochar A610 and A650 FTIR spectra and compound identification.	21
Figure 4-4. Petroset II FTIR spectra (top) and reference pattern for the effect of expanded basal spacings (due to cations) on the wave number.	22
Figure 4-5. X-ray diffraction pattern of Petroset II sorbent.	23
Figure 4-6. Simulated PUREX waste forms with 1:1 absorbent:PUREX waste loadings. ...	25
Figure 4-7. Simulated PUREX waste forms with 1:2 absorbent:PUREX waste loadings. ...	26
Figure 4-8. Samples prepared with actual PUREX waste for leaching tests.	27
Figure 4-9. FTIR spectra of Imbiber Beads – Simulated PUREX waste form.	34
Figure 4-10. FTIR spectra of Nochar A610 – Simulated PUREX waste form. No interactions between the Nochar A610 and the simulated PUREX waste.	35
Figure 4-11. FTIR spectra of Nochar A650 – Simulated Purex waste form. No P=O or P-O-C shift is seen, and therefore no interaction between TBP and Nochar 650.	35
Figure 4-12. FTIR spectra of Petroset II– Simulated PUREX waste form.	36
Figure 4-13. FTIR spectra of Petroset II Granular waste form and simulated PUREX waste.	36
Figure 4-14. Imbiber Beads and Imbiber Beads –PUREX waste forms exposed to Co-60 gamma radiation.	48
Figure 4-15. Imbiber Bead NG and Imbiber Bead NG – PUREX waste forms exposed to Co- 60 gamma radiation.	49
Figure 4-16. Nochar A610 and Nochar A610 –PUREX waste forms exposed to Co-60 gamma radiation.	50
Figure 4-17. Nochar A650 and Nochar A650 –PUREX waste forms exposed to Co-60 gamma radiation.	51
Figure 4-18. Petroset II Granular and Petroset II Granular –PUREX waste forms exposed to Co-60 gamma radiation.	52
Figure 4-19. Weight change of the sorbent:PUREX waste forms as a function of exposure to gamma irradiation.	53
Figure 4-20. Degradation of the PUREX waste forms after exposure to 254 nm ultraviolet light for 90 hours.	55

LIST OF TABLES

Table 2-1. Solidified PUREX waste form test plan.	5
Table 3-1. List of sorbents and waste loading tested in the PUREX organic waste scoping study.	6
Table 3-2. Composition of simulated organic PUREX waste based on Tank 33 and 35 averages [1].	7
Table 3-3. Relation between Co-60 exposure time, dose, and approximate years of aging or the PUREX waste forms.	16
Table 4-1. Physical descriptions of the sorbents tested.	18
Table 4-2. Summary of phases identified in the sorbent materials evaluated for PUREX solidification and temperatures at which these phases decompose.	20
Table 4-3. Description of the solidified waste forms prepared with simulated PUREX.	24
Table 4-4. Processing observations for laboratory-scale samples.	28
Table 4-5. Bulk density and volume relations for 1:1 solidified PUREX waste forms.	30
Table 4-6. Bulk density and volume relations for 1:2 solidified PUREX waste forms.	31
Table 4-7. Summary of the chemical interactions between the simulated PUREX waste and the sorbents.	33
Table 4-8. Thermal decomposition of the sorbents with and without absorbed simulated PUREX waste.	38
Table 4-9. TCLP results and total volatile organic analyses for the organic PUREX waste forms.	39
Table 4-10. Leachate results for organics for the 24 hour interval.	41
Table 4-11. Leaching data and I-129 K_d values for actual Tank 35 PUREX.	42
Table 4-12. Short-term aging effects based on FTIR spectra.	45
Table 4-13. Chemical changes in simulated PUREX waste forms as the result of Co-60 irradiation.	46
Table 4-14. Description of solidified PUREX waste forms exposed to Co-60 irradiation.	47
Table 4-15. Weight change as a function of exposure to Co-60.	53
Table 4-16. Description of solidified PUREX waste forms exposed to ultraviolet light.	54
Table 4-17. FTIR spectra for waste forms exposed to UV light.	56
Table 4-18. FTIR spectra for waste forms hydrated after exposure to Co-60 radiation.	56
Table 5-1. Summary of the analytical results related to RCRA classification.	59
Table 5-2. Comparison of sorbents for PUREX waste solidification.	61
Table 5-3. Properties of spill control sorbents versus waste treatment reagents.	62

LIST OF ACRONYMS AND ABBREVIATIONS

ADS	Analytical Development Section, Savannah River Technology Center
ANSI	American Nuclear Society Institute
ASTM	American Society for Testing and Materials
BNFL	British Nuclear Fuel Limited
CIF	Consolidated Incinerator Facility
DOE	Department of Energy
DSSI	Diversified Scientific Services, Inc.
DTA	Differential Thermal Analysis
EPA	Environmental Protection Agency
EST/SRTC	Environmental Science and Technology Division/Savannah River Technology Center
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas chromatography- mass spectroscopy
GEL	General Engineering Laboratory Inc.
ICP	Induction coupled plasma spectroscopy
ICP-ES	Induction coupled plasma emission spectroscopy
ICP-MS	Induction coupled plasma mass spectroscopy
K_d	Distribution coefficient (concentration in/on solid divided concentration in liquid)
LLW	Low-level waste
LLWAC	Low-level waste acceptance criteria
MS	Mass Spectroscopy
MSDS	Material Safety Data Sheet
MWFA	Mixed Waste Focus Area
NA	not applicable or not available
NFPA	National Fire Prevention Association
NG	Nuclear Grade
NRC	Nuclear Regulatory Commission
NSST	New Solvent Storage Tank
NTS	Nevada Test Site
PCE	Perchloroethene = Tetrachloroethene
psi	pounds per square inch
PUREX	Plutonium Uranium Extraction
RCRA	Resource Conservation and Recovery Act
R_d	Distribution Ratio (Approximated to be K_d)
RL	reportable limit
SpG	specific gravity
SRS	Savannah River Site
SRS (E-Area)	Savannah River Site E-Area
SRTC	Savannah River Technology Center
SRTC/SR&D	Savannah River Technology Site/Strategic Research and Development
SVOCs	semivolatile organic compounds
SW	Solid Waste
SWE	Solid Waste Engineering
TBD	To Be Determined
TBP	tributylphosphate
TCE	Trichloroethene
TCLP	Toxicity Characterization Leaching Procedure
TGA	Thermal Gravimetric Analysis
TMFA	TRU and Mixed Waste Focus Area
TRU	Transuranic Waste
TTP	Technical Task Plan
UHC	Underlying Hazardous Constituents
USA	United States of America
USDOE	U. S. Department of Energy

UTS	Universal Treatment Standards
UV	ultra violet light (radiation)
VOCs	volatile organics compounds
WAC	Waste Acceptance Criteria
WSRC	Westinghouse Savannah River Company
WSRC-RP	Westinghouse Savannah River Company Report
XRD	X-ray diffraction
%	per cent
>	greater than
<	less than

1.0 EXECUTIVE SUMMARY

Approximately 38,000 gallons of PUREX waste is currently stored in H-Area at the New Solvent Storage Facility (NSST). About 25,000 gallons of this waste is an organic liquid containing solvents from the PUREX process. Since the Consolidated Incinerator Facility (CIF) is not currently operational to treat this waste, waste treatments other than thermal oxidation are under investigation. The goal of waste treatment is to produce a waste form for final disposal at the SRS low-level waste landfill in E-Area or at the Nevada Test Site (NTS).

This report summarizes the results of a feasibility study that evaluated solidification as an alternative treatment for organic waste. Six sorbents (four organic polymers and two clay products) were tested for solidification of simulated PUREX waste. Waste forms containing actual PUREX waste from Tank 35 were prepared to confirm the simulant and for the I-129 leaching experiments. Mixing and general appearance of the waste forms prepared with the simulant and the actual waste were indistinguishable in the laboratory experiments. Waste forms were prepared with two waste loadings, 50 and 66 weight percent PUREX, referred to as 1:1 and 1:2 waste loadings, respectively.

Waste forms were evaluated for processing, storage and transportation, leaching and durability /aging properties. The sorbent materials and the waste forms were characterized by: gravimetric, thermal, spectroscopic, and X-ray diffraction techniques in an attempt to understand the mechanisms of sorption, the PUREX-sorbent interactions, and the long-term degradation effects.

All of the six sorbents resulted in waste forms that meet the basic criteria for disposal at the SRS E-Area disposal facility and at the Nevada Test Site. However, environmental transport of I-129 must be analyzed further to determine the acceptability of E-Area disposal for the solidified PUREX material.

Four of the six sorbents, Imbiber Beads, Nochar A610, Petroset II and Petroset II Granular are recommended for further testing which should include additional laboratory-scale testing with actual waste and scale-up testing with an acceptable simulated waste.

Imbiber Beads Nuclear Grade was eliminated for further testing because it contains a wicking agent that is hydrophilic and swells upon absorption of water. This feature is undesirable from the standpoint of packaging, storage and transportation. The Nochar A650 sorbent was eliminated because it reacts with the organic components in the PUREX and undergoes physical and chemical changes upon aging. (This polymer is plasticized by the PUREX waste.)

Further selection of a material for solidifying the spent PUREX waste will depend on optimizing the waste form properties and on scale-up test results using simulated and actual waste. The two organic sorbents Imbiber Beads and Nochar A610 result in light weight particulate waste forms that may offer some processing advantages not apparent in laboratory-scale batches. The Petroset II and Petroset II Granular products resulted in similar waste forms and had the best long-term performance. The consistency of these solid waste forms was that of damp clay (stiff paste). Scoping tests indicate that the paste can be modified to a rigid solid by the addition of portland cement. Additional formulation studies are required to optimize this waste form if a rigid solid is desired.

2.0 INTRODUCTION

2.1 Background

Currently about 38,000 gallons of legacy PUREX waste are stored in two tanks, Tank-33 and -35, at the New Solvent Storage Tank (NSST) Facility at Savannah River Site (SRS). These tanks contain approximately 25,000 gallons of spent PUREX solvent (organic liquid) and about 13,000 gallons of aqueous waste. The PUREX solvent was used in organic-aqueous isotope separation processes in F- and H-Areas. The aqueous fraction is primarily wash water generated when the organic liquid was transferred from old underground storage tanks in E-Area to the new tanks in H-Area. An additional 100,000 gallons of PUREX solvent are currently included in the F-Area process chemical inventory. This material will also require treatment for final disposal at some point in the future.

The spent PUREX waste consists of two immiscible phases, a lower density organic liquid containing n-paraffins and tributyl phosphate in addition to aromatic hydrocarbons and amine compounds and an aqueous phase containing water and dibutyl phosphate. Analyses of the Tank 33 and 35 samples are provided in Appendix A. This waste is classified as low-level radioactive mixed waste because analyses of some samples from the old tanks indicated several hazardous constituents, such as, mercury, chromium lead, silver, benzene, and trichloroethylene were present in concentrations above the limits for RCRA characteristically hazardous waste.

Thermal oxidation in the CIF is currently identified as the treatment of the spent PUREX waste. However, at the present time the CIF is not operating, and SRS is pursuing alternatives to treatment in the CIF because of the high cost of restarting the facility to treat the PUREX waste. Consequently, the DOE TRU and Mixed Waste Focus Area (TMFA) is funding alternative technologies for hazardous organic waste treatment.

This report describes solidification/stabilization technologies that result in solid, non-hazardous waste forms suitable for low-level shallow land disposal at SRS (E-Area) or at the Nevada Test Site (NTS). Details of the task plan are described elsewhere [1]. Another alternative technology that was evaluated at SRTC for treatment of spent PUREX involves decontamination/removal of radionuclides to the extent that the spent PUREX can meet the Waste Acceptance Criteria (WAC) for a commercial low-level radioactive mixed waste incinerator such as the one operated by DSSI [2]. A third treatment strategy, microbial destruction, was funded by SRTC/SR&D and is being evaluated by M. A. Heitkamp, EST/SRTC, [3].

Solidification/stabilization was also evaluated as an alternative treatment for the aqueous fraction. The reference saltstone formulation was used as the baseline for this evaluation, and results are presented elsewhere [4].

This work was requested by M. G. Looper, Solid Waste Engineering, and was funded by the TRU and Mixed Waste Focus Area, TTP-SR18MW44.

2.2 Objective

The objectives of this study were to evaluate solidification/stabilization as an alternative treatment technology for the SRS spent PUREX waste using simulated waste and to evaluate waste forms prepared with actual spent organic PUREX waste for regulatory classification. The objective of the waste treatment is to produce a waste form that meets the requirements for final shallow land disposal at SRS or at the NTS. More specifically, the task included the following:

- Prepare simulated waste based on analyses of the Tank 33 and 35 material.
- Identify potential solidification/stabilization reagents for treatment of the organic PUREX waste.
- Conduct scoping studies to evaluate potential solidification/stabilization reagents using simulated PUREX waste.
- Develop a test matrix for evaluating solidified waste forms for processing, storage, transportation, and disposal.
- Confirm that the simulated waste approximates the actual waste with respect to waste form testing.
- Evaluate PUREX waste-sorbent interactions.
- Evaluate leaching properties for waste forms prepared with actual spent PUREX waste.

2.3 Approach

The approach was to conduct scoping studies using simulated spent PUREX waste and commercially available organic sorbents to produce solid waste forms for disposal. Both organic polymer sorbents and inorganic sorbents were included in the test matrix. This study focused on waste form processing, storage, transportation, leaching and durability. If the results of this testing are promising, scale-up studies (5 to 55 gallon) will be conducted to confirm processing properties and to obtain engineering data for process design. Additional testing with actual organic PUREX waste will also be conducted to confirm that the current simulant is suitable for process development.

2.3.1 Disposal Requirements

The Low-Level Waste Acceptance Criteria (WAC) for E-Area and for the Nevada Test Site were reviewed to identify required tests [5 and 6, respectively]. The E-Area WAC does not include solidified PUREX waste forms as accepted waste streams. Consequently, as a new waste stream, the solidified PUREX waste must undergo the SW Waste Certification Process to determine whether it is acceptable for E-Area disposal. This process is initiated by the waste generator and is performed by SW.

The NTS requires the approved waste generator to submit a waste profile (characterization) for consideration. In addition, packaging and transportation requirements for shipping waste from SRS to NTS must be identified and addressed if solidified PUREX waste is sent off-site. Some disposal issues and requirements for both the SRS and NTS low-level waste disposal sites are listed in Table 2-1.

Figure 2-1. Summary of SRS and NTS low-level radioactive waste disposal criteria.

Waste Form Requirement	SRS E-Area WAC [5]	Nevada Test Site WAC [6]
Regulatory Classification	RCRA non hazardous Waste must not exhibit characteristics of or be listed as hazardous waste per RCRA (Pass TCLP test)	RCRA non hazardous Waste must not exhibit characteristics of or be listed as hazardous waste per RCRA (Pass TCLP test)
Solid	Pass Paint Filter test	Pass Paint Filter test
Free Liquid	< 0.5 vol. % free liquid w/o additional absorbents 0 vol. % free liquids w/absorbents	< 0.5 vol. % of the waste processed to a solidified form i.e., w/o additional absorbents. Provisions for additional sorbent should be made to obtain 0 vol. % free liquids under storage, transportation, and disposal site conditions. Waste must be evaluated to determine potential to release liquid during handling, storage, and transportation.
Particulates		Fine particulate wastes shall be immobilized so that the waste package contains no more than 1 wt. Percent of <10 µm diameter particles or 15 wt % of less than 200 micrometer diameter particles. Secure packaging may be used in place of immobilization.
Physical Stabilization		Where practical, waste must be treated to reduce volume and to provide a physically stable form.
Chemically non reactive		Waste must not react with other waste or the packaging. Chemical stability and compatibility must be demonstrated.
Waste Form Type	Solidified Organic Waste (Spent PUREX solvent solidified with organic polymer sorbents or with inorganic reagents)	Solidified Organic Waste (Spent PUREX solvent solidified with organic polymer sorbents or with inorganic reagents).
Chelating Agent		LLW packages containing chelating or complexing agents in amounts greater than 1percent of the waste shall not be accepted unless stabilized or solidified.
Radionuclide Limits	Low-level waste Radionuclide concentrations are specific to disposal options (slit trench, engineered trench, low-activity vault) per 1S Manual, Attachment 2 Table 4A and B	Low-level waste Radionuclide concentrations per the NTS "Radionuclide Characterization and Reporting Requirements, Appendix E in the NTS WAC
Solidified Organic Liquid	Prepare Waste Characterization and Request Waste Certification	Prepare and submit Waste Profile

2.3.2 Test Matrix

A test matrix was prepared to evaluate processing, storage and shipping criteria, leaching, and degradation properties. The detailed test plan is presented elsewhere [1]. Tests, test methods, and parameters are summarized in Table 2-2.

Table 2-1. Solidified PUREX waste form test plan.

Test	Parameter/Method	Reference:
Starting Materials Characterization		
Sorbent Material	Appearance (macroscopic and microscopic examination) Composition (DTA/TGA, FTIR, and x-ray diffraction)	
Waste Form Properties		
Final Waste Form Physical Properties	Appearance (macroscopic and microscopic examination) Unit weight Free Liquids: EPA methods 9095 and 9096	[7 and 8, resp.]
Processing Considerations	Appearance, mixing properties,	
Waste-Sorbent Interactions	Composition (DTA/TGA, FTIR, and X-ray diffraction) DTA/TGA, FTIR	
Transportation/Storage Performance		
Vibration Cycling	Phase separation/liquid expression ASTM D-999	[9]
Thermal Stability up to 500° C	Changes in compounds as a function of temperature (DTA/TGA)	
Leaching		
Saturated water leaching: Leach Index	7 day ANSI 16.1	[10, 12]
	I-129 K _d ASTM D4319	[11, 12]
	Volatile and Semivolatile Organics	[12]
TCLP Extraction Procedure	Regulatory classification [12]	[13]
Exposure to water	Visual description of Waste Forms in 10 x volume of water	
Durability/Aging Behavior		
Time (7-14 days vs. 60-80 days)	Visual appearance and FTIR	
Radiation Stability Co-60 irradiation	Visual appearance and FTIR	
254 nm UV Exposure for 90 hr at 630 μWatt	Visual appearance and FTIR	
Effects of hydration (exposure to water after irradiation with Co-60)	Visual appearance and FTIR	
Microbial Degradation	ASTM G21-70 Fungi	[14]
	ASTM G22-76 Bacteria (plastic)	[15]
	ASTM G22-76 Bacteria (PUREX)	[15]

3.0 EXPERIMENTAL PROCEDURES

3.1 Sorbent and Waste Loading Selection

Solidification reagents for organic liquids were identified from vendor literature and from information obtained from personnel at Chem-Nuclear, SC, the Nevada Test Site, NV, Envirocare, UT and British Nuclear Fuels, Limited (BNFL), Sellafield UK. Materials used for solidifying organic liquids are commonly referred to as sorbents. These materials are used primarily for spill control in industrial applications.

Three vendors, Nochar, Inc., Imbibitive Technologies, Inc., and Fluid Tech, Inc. market sorbents for organic waste treatment in addition to spill control. The Nochar and Imbiber sorbents are organic polymers. The Fluid Tech, Inc. sorbents are modified inorganic clays (sodium montmorillonites). Product samples and technical information were obtained from each of these vendors. Nochar Inc. provided a technical representative to assist in the initial product screening. The sorbents/solidifying reagents tested in this study are listed in Table 3-1.

The waste loadings were selected to enable a simple comparison of the various sorbent/solidifying reagents. (Optimizing the waste loading for each sorbent was not an objective of this study.) The proportioning was conducted on a weight rather than a volumetric basis because weights were more accurate, consistent, and convenient for laboratory work.

Table 3-1. List of sorbents and waste loading tested in the PUREX organic waste scoping study.

Vendor/Product	Waste Loading Reagent : Simulated PUREX (by weight)	
	50 wt. % waste loading	66 wt.% waste loading
Imbibitive Technologies, Inc.		
Imbiber Beads™ (organic polymer) (alkylstyrene copolymer from MSDS)	1:1	1:2
Imbiber Beads NG™ (organic polymer in Imbiber Beads plus a polyethylene wicking agent)	1:1	1:2
Nochar, Inc.		
Nochar A-610 Petrobond™ (organic polymer)	1:1	1:2
Nochar A-650 Petrobond™ (organic polymer)	1:1	1:2
Fluid Tech, Inc.		
Petroset II™ (organo-clay intercalated with quatarnary ammonium amine)	1:1	1:2
Petroset II Granular™ (same as Petroset II)	1:1	1:2

3.2 PUREX Simulant Preparation

Simulated PUREX waste was prepared from reagent chemicals and was used for most of the testing. The simulant composition was based on analyses of the actual waste. See Appendix A. The ingredients and proportions of the simulant used in most of this testing are shown in Table 3-2.

A satisfactory method of simulating the addition of I-129 in non-radioactive surrogate was not found. Therefore, leaching samples were prepared with actual Tank 35 waste to assure representative leaching results for I-129. (Tank 35 material was chosen because it contained more I-129 than the Tank 33 material.)

Table 3-2. Composition of simulated organic PUREX waste based on Tank 33 and 35 averages [1].

Ingredients	Flash Point (°C)	Ignition Temp. (°C)	NFPA Chemical Hazards Rating*	SpG	Amount (wt. %)
Tributyl Phosphate	193		2/1/0	0.979	17.60
Aliphatic hydrocarbon (n-paraffin)					
Undecane	60			0.7402	8.45
Dodecane	71	200	2/2/1	0.748	8.45
Tridecane	79	201	2/2/0	0.757	8.45
Tetradecane	101	204		0.763	8.45
Aromatic hydrocarbon					
Diethylbenzene	57			0.870	21.00
Di-isopropylbenzene	76			0.857	21.00
Aliphatic amine					
Di-n-octylamine	>110		2/2/0	0.799	6.60
Total					100.00

* See SRS Asset Management Manual 3B Section 2-3 for the key to the hazard ratings [16].

3.3 Sorbent Characterization

Physical and chemical properties of the six sorbents were measured to obtain information on raw materials handling, waste form processing, and PUREX waste-sorbent interactions.

Macroscopic and microscopic descriptions were recorded and bulk densities were measured. Data generated from Thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Fourier Transform Infrared (FTIR) Spectroscopy were used to obtain approximate polymeric compositions and structures of the organic reagents. X-ray diffraction (XRD) was used to obtain information on the mineralogy and basal spacing of the inorganic clay sorbent.

3.4 Waste Form Preparation

The order of mixing and the need for stirring were evaluated. Vendors recommended the addition of the liquid to the sorbent without mixing. This technique resulted in very inhomogeneous products that were not appropriate for comparison testing. Consequently for the purpose of this study, the waste forms were prepared by adding the sorbent to the organic liquid waste while mixing vigorously. The exception was the preparation of the leaching samples with Tank 35 waste. Mixing was performed after the sorbent was added to the waste. This technique resulted in the most even distribution of the liquid waste and the most uniform product. Laboratory batches ranged from 50 to 150 grams. The largest batches (150 grams) were equivalent to about 500 cubic centimeters.

After mixing, the waste forms were placed in sealed glass containers for curing/aging prior to testing. All test specimens were cured for a minimum of seven days at room temperature prior to evaluation.

3.5 Waste Form Characterization

3.5.1 Waste Form Properties

3.5.1.1 Visual Appearance and Bulk Densities

Photographs and visual descriptions were used to document the appearance of the waste forms. The bulk densities of the waste forms were estimated by weighing 100 ml of well-mixed (bulked) unpacked loose material.

3.5.1.2 Paint Filter Test

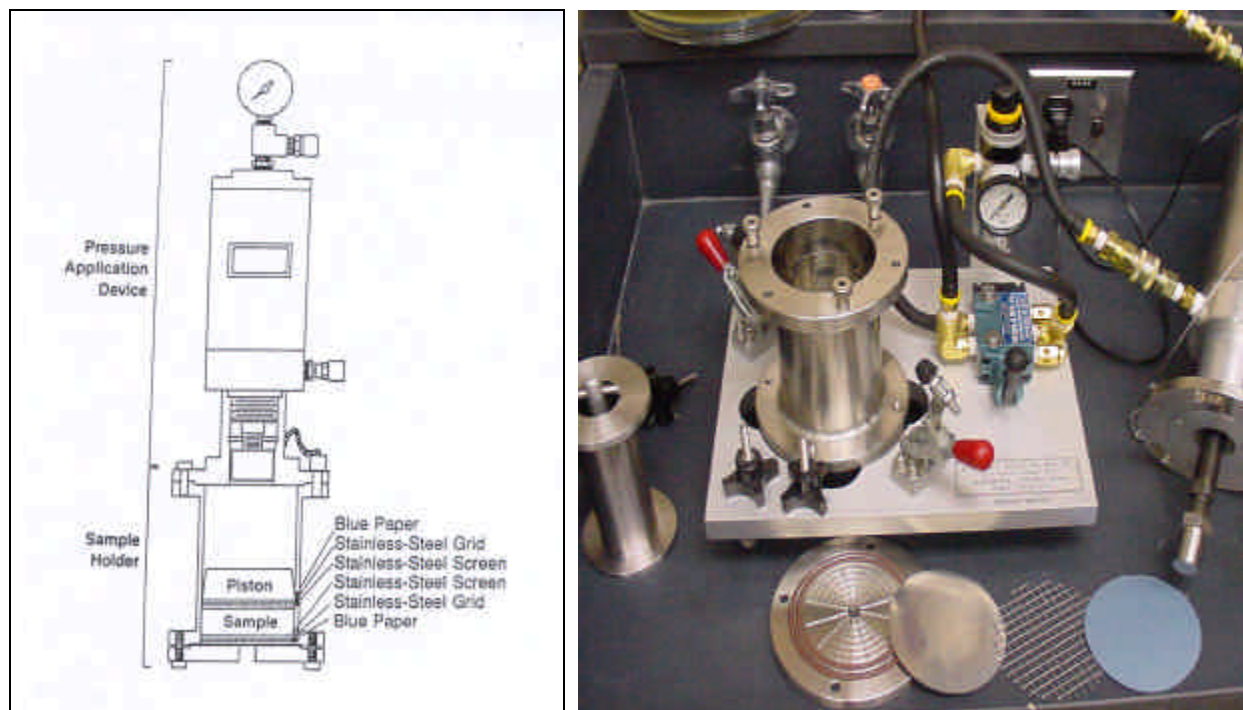
The Paint Filter Test (EPA SW-9095) is applied to a waste or waste form to determine whether the material meets the EPA definition of solid [7]. It is a pass/fail test for waste forms since only solid materials qualify for shallow land disposal. The material is placed in a paint filter identical to those used to remove lumps from paint. The amount of liquid that passes through the filter is recorded. If drainage is observed from the filter, the material fails the test for a solid waste form.

3.5.1.3 Liquid Release Test

The Liquid Release Test (EPA SW-9096) is intended to determine whether liquid is expressed from a waste or waste form in the shallow land-disposal environment under pressure corresponding to about 50 feet of overburden [8]. The apparatus used for this test is shown in Figure 3.1. The pressure is applied for 10 minutes and the expressed liquid is collected on absorbent paper placed under the sample. The amount of liquid release is determined gravimetrically by measuring the absorbent paper weight gain. See Figure 3-1.

3.5.1.4 Processing Properties

Direct observations of handling and mixing properties were recorded. Engineering data and processing parameters, which are necessary for designing a process, were beyond the scope of this initial study. However, the bulk densities and final volumes of the various waste forms were determined to estimate the volume increase resulting from the solidification process.



(a) Schematic

(b) Disassembled apparatus

Figure 3-1. Liquid Release Test apparatus. Blue absorbent paper is used to collect liquid expressed from the waste forms.

3.5.2 PUREX-Sorbent Interaction

TGA/DTA and FTIR spectroscopy data were used to determine the interactions between the sorbent materials and the simulated PUREX waste. TGA data provide weight changes as a function of temperature. Samples were evaluated up to 500°C in this study. Weight changes in these samples were due to volatilization of the PUREX waste components (below 200°C) and decomposition of the compounds in the sorbent at higher temperatures. Comparisons of the graphs for the waste forms and for the sorbents without PUREX provide information on the changes in the sorbent due to chemical interactions with the PUREX components. The DTA is generated by differentiation of the TGA results.

FTIR spectroscopy was used to identify the chemical components in materials by measuring the infrared absorption spectra of the material. The types of chemical bonds in the compounds that make up the sample are determined by the wavelengths of light absorbed in the infrared range.

X-ray diffraction was used to identify the inorganic components of the Petroset II and to determine modifications of the clay structure due to the presence of organic compounds. In particular, x-ray diffraction was used to measure increases in the basal spacing of the clay (degree of swelling of the clay structure) due to the intercalation of organic compounds.

3.5.3 Transportation and Storage Properties

3.5.3.1 *Vibration Testing*

Segregation of liquid from the solid waste form during transportation is a concern if the solidified PUREX is shipped to the NTS for disposal. The effects of vibration can be severe and can result in release/segregation of liquid held by capillary forces under static conditions. Consequently, the waste forms were subjected to a cyclical vibration test. Although it is not possible to precisely duplicate the vibratory regime that a waste form will experience during truck or rail transportation, SRTC has correlated vibration test results on resins to the effects of truck transportation [17]. The test protocol used for this correlation was used for the PUREX waste forms.

The laboratory test involves vibrating the PUREX waste forms on a Fritsch Laboratory Vibrator at an amplitude of 2 mm. Absorbent paper under the sample collected any moisture released during vibration. The paper was weighed at ten-minute intervals. Testing was continued until no further change in weight was measured. The test was terminated after no further weight gain (if any) was measured. The vibration apparatus is illustrated in Figure 3.2.



(a) Illustration of blue absorbent paper for collection of expressed liquid.



(b) Configuration during testing.

Figure 3-2. Fritsch Laboratory Vibrator.

3.5.3.2 *Effects of Temperatures*

Samples were subjected to TGA /DTA to determine the response of the waste form to elevated temperature. Samples were placed in a small platinum container and the temperature was increased at a rate of 10°C/min. The weight loss and heat responses were measured. The gas generated during this treatment was not collected for the present study.

3.5.4 Leaching Properties

3.5.4.1 TCLP Extraction and Analyses for Regulatory Classification

The TCLP extraction procedure is used to determine the soluble hazardous metals in a waste or waste form for the purpose of regulatory classification and determination of disposal options. For this test, the alkalinity of the sample must first be determined in order to select the extraction fluid. The PUREX waste forms are not alkaline so extraction Fluid #1, which is a sodium acetate solution with a pH of 4.93, was determined to be appropriate. (Samples with a high alkalinity use extraction Fluid #2, which is a dilute acetic acid solution with a pH of 2.8.) The samples were size reduced to pass a minus 3/8 inch sieve and then tumbled in the appropriate extraction fluid for 18 hours. The choice of extraction fluids does not apply to extracting the volatiles. Fluid #1 is always used and a Zero Headspace Extraction (ZHE) apparatus is used when analyzing for volatiles.

The radioactive PUREX waste forms were extracted by ADS/SRTC. The hazardous metals were analyzed by ICP-MS (Ag, Ba, Cd, Cr, Pb), atomic absorption spectroscopy (As and Se) and by mercury cold vapor extraction (Hg). The metals that make up the RCRA underlying hazardous constituents (UHC) were analyzed by ICP-ES with the exception of thallium, Tl, which was analyzed by ICP-MS. The detection limits for the methods used to analyze these metals were below the RCRA Universal Treatment Standard Limits (UTS). Therefore, the results are adequate for planning and engineering purposes. Certified analyses are required for regulatory purposes. One waste form, the Petroset II with a 66 wt. % loading was sent to GEL, Charleston for a certified analysis.

In addition, total benzene and total trichloroethylene concentrations were determined for the waste forms with 1:2 waste loadings. The benzene and TCE concentrations in the waste are 66 percent of the total concentrations in the waste form based on the 1:2 waste loadings. The Imbiber Beads and the Petroset II and Petroset II Granular waste forms had the most uniform distribution of waste in the waste form. Therefore, the results from these waste forms best represent the total concentrations in the waste. Volatile organic analyses were performed by gas chromatography-mass spectrometry (GC-MS) using ADS method 2656 [15]. Samples were concentrated using a Dynamic Headspace concentrator (purge and trap) that has a three stage trap. Internal standard and recovery surrogate compounds were added as specified in the contract laboratory program for volatile organics. The method detection limits for these organic components were well below the treatment standard values (UTS limits).

3.5.4.2 I-129 Kd Determination

I-129 distribution ratios, R_{ds} , assumed to approximate the equilibrium values, K_{ds} , were determined according to ASTM D-4319 [11]. The test configuration consisted of placing 20 g of each waste form (1:2 waste loading) in 200 mL of deionized water. Glass containers were used for this test and tumbled at 30 rpm for 6 hours and leached under static conditions for the remaining 72 hour test period. A 60 ml aliquot of each leachate was extracted, filtered through a 45-micron filter and submitted to ADS for I-129 analysis. The same procedure was followed with fresh samples except that the leaching was performed for 3, 6 and 16 days to assess changes with time (equilibrium evaluation).

ADS/SRTC performed the I-129 analyses. Each sample was spiked with stable iodide and was subjected to a silver iodide precipitation to separate any iodide in the matrix from other radionuclides. A blank DI water sample was analyzed along with the batch as a control. The precipitates were analyzed with a low energy HPGe gamma spectroscopy detector. After gamma analyses, the precipitates were analyzed by neutron activation analysis to determine the levels of stable iodide carrier in the precipitates. The recoveries of the iodide carrier were used to correct the gamma spectroscopy results for the I-129 recoveries. Uncertainties provided are one sigma.

3.5.4.2.1 Calculation of Distribution Ratios

The parameter known as the distribution coefficient, K_d , is used to quantify sorption reactions for the purpose of environmental transport modeling of ionic species. The distribution coefficient is used to assess the degree to which a chemical species will be removed from solution as a fluid migrates through a media. In other words, the distribution coefficient provides an indication of how rapidly an ion can move relative to the rate of ground water movement under the geochemical conditions tested.

Justification of the distribution coefficient concept is generally acknowledged to be based on expediency in modeling, averaging the effects of one or more attenuation reactions. Measured partitioning reactions may include adsorption, ion exchange, co-precipitation and filtration processes that cannot be easily described by equations.

In reference to partitioning in soils, equilibrium is assumed (although not always achieved) and the equilibrium value is referred to as the K_d . In these laboratory experiments, the distribution ratio, R_d , is calculated which may be used for estimating the value of the distribution coefficient for a given set of site specific geochemical conditions. Although attainment of equilibrium in the short-term laboratory tests is not presumed, the R_d values can be used as approximations of the equilibrium K_d values. Iodine-129 distribution ratios were calculated for the absorbed PUREX waste forms based on the following equations:

$$(4) \quad R_d = \frac{\text{(mass of the solute on the solid phase per unit mass of the solid phase)}}{\text{(mass of the solute in solution per unit volume of the liquid phase)}}$$

where:

$$R_d = \text{distribution ratio, mL/g,}$$

3.5.4.3 ANSI 16.1 Testing

The PUREX waste forms were leached according to the accelerated ANSI 16.1 test protocol [10]. This test is conducted over 7 days and has 10 leach intervals. Actual Tank 35 waste was used because a satisfactory method of incorporating I-129 into the organic simulant was not determined.

This test is designed for monolithic samples. The PUREX waste forms were prepared as cylinders, but they did not hold their shape after immersion in water. Consequently, diffusion of contaminants from a monolithic material is not the controlling release mechanism. However, diffusion from the individual organic polymer grains is a likely mechanism and leaching the granular, non monolithic samples in this way gives conservative results because of the increased waste form surface area.

Glass leaching vessels were used because the tributylphosphate component in the PUREX reacts with most plastics. Deionized water was used as the leachate and the volume of the leachate was fixed at 850 ml. The amount of waste form used in the test was determined by molding the waste form into a cylinder with a surface area of 85 cm². The waste form surface area to leachate volume ratio was approximately 10cm per the ANSI test. Fresh waste form samples were used for each leach interval.

The leachates were analyzed for the Tank 50 rad-screen constituents, total gamma, I-129, VOCs and SVOCs by SRTC/ADS [12]. The leach Index for I-129 was calculated according to the ANSI 16.1 protocol [10]. The leaching sample configuration is illustrated in Figure 3.3. For the purpose of calculating the I-129 K_d values, less than values were used. The result is that the K_ds are reported as greater than values and are therefore conservative.



(a) Waste forms mixed and molded for leaching.

(b) Waste forms leaching in deionized water in glass containers.

Figure 3-3. ANSI 16.1 leach test configuration.

3.5.4.3.1 Calculation of Effective Diffusion Coefficients and Leach Indices

The diffusion coefficients are calculated from the leach data generated in the ANSI 16.1 test according to equation (1):

$$(1) \quad D = p \left[\frac{a_n / A_0}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T$$

where:

- D = effective diffusivity (effective diffusion coefficient), (cm²/s)
- V = volume of leachate, (cm³)
- S = geometric surface area of the specimen as calculated from the measured dimensions, (cm²)

$$T = \left[\frac{1}{2} (t_n^{1/2} + t_{n-1}^{1/2}) \right]^2$$

- leaching time representing the “mean time” of the leaching interval, (s)
- a_n = amount of the species released from the specimen during the leaching interval n, (g)
- A_0 = total amount of a given species in the specimen at the beginning of the first leaching interval (g). The concentration in the initial wash off is not included in A_0
- t_n length of time of the leach interval, n
- t_{n-1} length of time for the leach interval before t_n
- n leach intervals 1 to 10.

If more than 20 % of the leachable species was removed by any time, t, the calculation for the effective diffusivity must take into account a reduction in source term, A_0 . The ANSI procedure provides tables for making the required corrections for cylindrical samples. These tables could not be used for the waste forms leached in this study because the waste forms did not retain a cylindrical shape during the leach testing.

3.5.5 Durability/Aging Properties

Long-term properties of the solidified PUREX waste forms were evaluated by:

- Comparing DTA/TGA data and FTIR spectra of samples cured for 7 to 14 days with those of samples cured for 60 to 80 days in sealed containers at ambient conditions.
- Accelerating aging with gamma radiation and with ultraviolet light. The irradiated samples were evaluated by: visual examination, free liquid testing, and response to immersion in water (hydration testing). DTA/TGA, and FTIR spectroscopy were also used to identify the chemical and structural changes that occurred as the result of these forms of aging.

The rate of degradation and the relative proportions of the degradation products generated during exposure to Co-60 gamma radiation and UV exposure are difficult to correlate to years of aging. However, the types of degradation products obtained by these methods approximate those formed as the result of time dependent aging [18].

3.5.5.1 Exposure to Cobalt-60 Radiation

Cobalt-60 gamma rays were used to irradiate the starting materials (simulated PUREX and sorbents) and the solidified PUREX-sorbent waste forms. Exposure times were based on dose rate and time. The Co-60 dose was correlated to the dose delivered by the radionuclides in the actual spent PUREX. The radionuclide analyses for the PUREX waste is provided in Appendix A. The correlation calculations are provided in Appendix B. The samples were examined after receiving doses that corresponded to aging from 50 to 10,000 years. See Table 3.3.

Dose calculations were performed for both the organic and aqueous liquids in Tanks 33 and 35. The detection limits for Cm-245 and Cm-246 are about 10X higher in the organic waste compared to the aqueous waste in both tanks. Plutonium, cesium and tritium were significant contributors to the calculated absorbed doses for all samples. All of the radiochemical data were

converted from dpm/mL and converted to values of curies/g using an assumed density of 1 g/cc for aqueous and 0.82 g/cc for organic. Tables 1-4 in Appendix B provide the radionuclide data necessary for estimating absorbed dose contributed by each radionuclide.

Literature data for the radionuclides [19] and standard calculation routines for absorbed dose [20] were employed. The calculations conservatively assumed that 100% of the energy from all radionuclides in the PUREX waste is absorbed in the waste and in the waste form, i.e., no energy loss due to escape from the material. The calculated absorbed doses for the waste or waste form were then extrapolated out to 50, 500, 1000, 5000 and 10,000 years. The dose for 500 years was used to calculate the long-term dose rates because the shortest lived radionuclides decay away at earlier times. The results for the Tank 35 organic waste are plotted in Figure 3-4. The calculated dose for the organic fraction is significantly higher at longer times than the calculated doses for the aqueous fractions. This is due to the higher detection limits associated with the long-lived Cm-245 and Cm-246. Consequently the doses from the radionuclides in the organic waste are somewhat over estimated for longer times. *The highest calculated dose, i.e., the dose from the Tank 35 organic waste was used in the final calculation of the exposure times for waste forms evaluated in this study (simulated spent PUREX waste).*

The Co-60 irradiation times needed to simulate the radiation exposure in the aqueous and organic fractions were calculated using the doses calculated for the waste (Appendix B) and the dose determined for the Co-60 source. The dose rate of the SRTC Co-60 source that was used in this study was $9.9\text{E}+5$ rad/hr in July 2001. This value was calculated from a measured dose rate of $2.2\text{E}+06$ rad/hr determined in May 1995.

Table 3-3 shows the irradiation times, the expected doses and the equivalent time of irradiation expected for the samples. The shortest irradiation time of approximately 30 minutes in the Co-60 source equates to a calculated sample exposure of about 50 years. The longest irradiation time of approximately 90 hrs equates to a calculated sample exposure of 10,000 years.

Irradiated samples were weighed to determine weight gains (oxidation or hydration) and losses (volatilization of PUREX and/or organic polymer components, dehydration and/or decarbonization of inorganic components in the sorbents). Irradiated samples were also examined by TGA/DTA and FTIR and the degradation products were recorded.

3.5.5.2 Exposure to Ultraviolet Light

Unlike Co-60 irradiation exposure, the effects of ultraviolet light exposure can not be equated/extrapolated to actual years of aging or exposure. However the 254 nm UV light is a relatively high-energy wavelength and is known to generate ozone in the ppm range. Since ozone is a very aggressive oxidizer, this test served as a screening evaluation for combined degradation effects from exposure to light and oxygen.

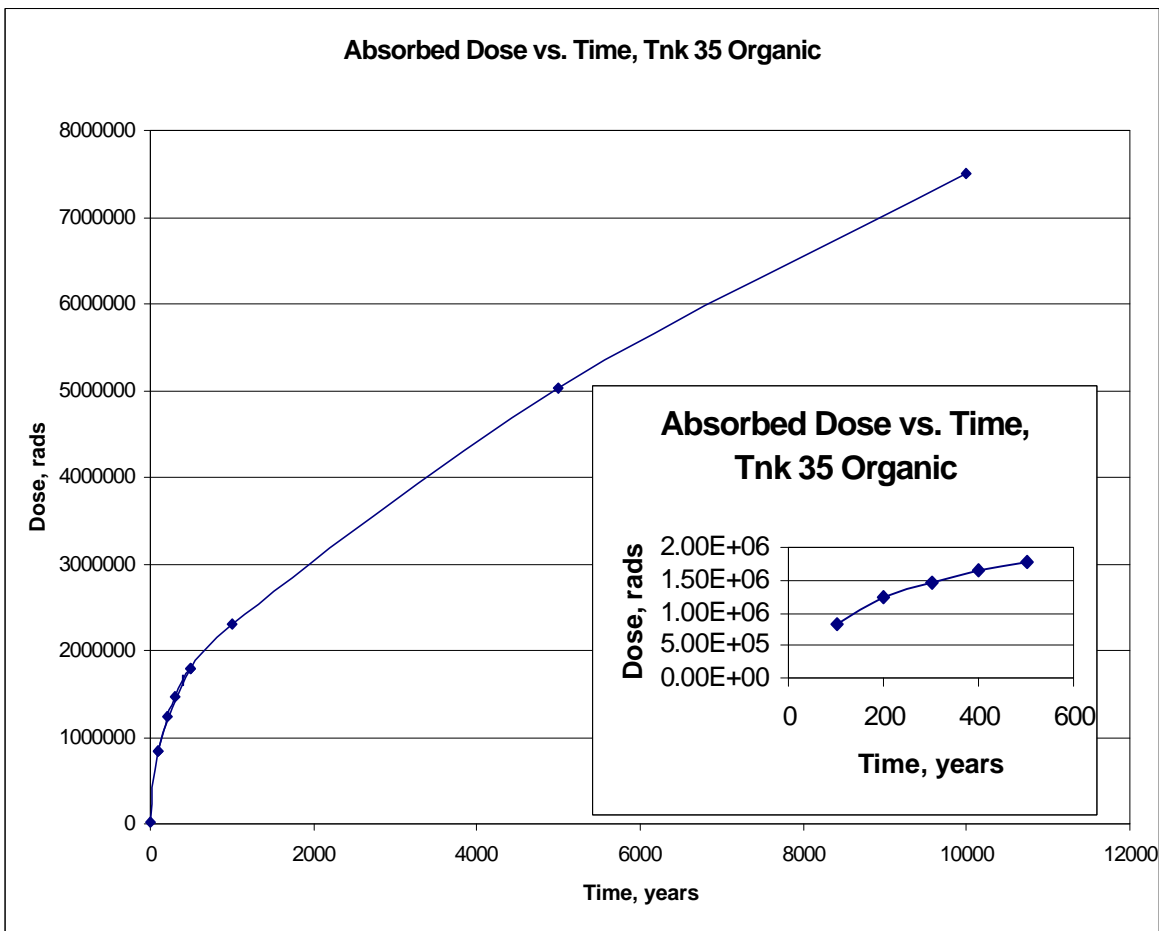


Figure 3-4. Absorbed dose versus time plot for Tank 33 and 35 PUREX waste.

Table 3-3. Relation between Co-60 exposure time, dose, and approximate years of aging or the PUREX waste forms.

Exposure Time (hours)	Co-60 Dose (total) (Rads)	Approximate aging time of PUREX Waste Forms (years)
0.5	3.7 E+04	50
4.5	1.9E+05	500
9	3.7E+05	1000
45	1.7E+06	5000
90	3.2E+06	10,000

Samples of the solidified PUREX waste forms were cured for 7 days prior to exposure to ultraviolet light, which is known to degrade many organic compounds. Approximately 10 grams of each waste form were spread out in individual glass dishes to a thickness of at least 2 mm and placed under an ultraviolet lamp. Aluminum foil was used to make a light-tight enclosure around the samples and the lamp to address eye safety issues. Samples were examined after varying times up to 90 hours of exposure. The flux at 2 cm from the bulb was 2400 microwatts per cm², and 254 nm wave length light was used. (The lamp manufacturer, UVP, Inc. measured the flux at 7.6 cm as 1200 microwatts per cm² with a radiometer.) The experimental set up for this testing placed the lamp 5 cm above the samples. Since the bulb was 37.5 cm long rather than a point source, flux delivered to the samples was inversely proportional to the distance rather than the square of the distance from the bulb.

In addition to visual observations of color and physical property changes, FTIR spectra were obtained from samples exposed to the UV light. The waste form degradation products were recorded for waste forms exposed to UV radiation for 90 hours.

3.5.6 Microbial Degradation

Resistance of the sorbent materials, the simulated PUREX waste, and the solidified PUREX waste forms to microbial degradation was also evaluated. The ASTM G21 [14] and G22 [15] methods were used to determine the extent of degradation caused by fungi and bacteria, respectively. These tests are included in the Nuclear Regulatory Commission (NRC) certification criteria for disposal of low-level waste forms.

Microbial testing was subcontracted to Celsis Laboratory, Inc., St. Louis, MO, which specializes in biodegradation testing. Dr. R. Rogers, INEEL, an expert on microbial degradation of radioactive waste forms in shallow land disposal environments, reviewed the approach and provided modified test protocols for granular and non monolithic samples.

The bacteria and fungi specified in the ASTM methods are targeted for decomposition of the polymer waste form substrates as well as the simulated PUREX waste. The ASTM specified fungi are: *aspergillus niger*, *penicillium pinophilum*, *chaetomium golbosum*, *gliocladium virens*, and *aureobasidium pullulans*. The ASTM G-22 bacterium is *pseudomonas Aeruginosa*. Dr. R. Rogers and Dr. M. Heitkamp, SRTC, both approved the substitution of the bacteria *Klebsiella* for *pseudomonas Aeruginosa* in the test program since the latter is a pathogen.

In addition, Dr. Heitkamp isolated over 35 microbes from the interface between the organic and aqueous phases in Tank 33. Dr. Heitkamp provided one of the bacteria, currently designated as # 17-3, to be included in the microbial degradation testing at Celsis Laboratory.

4.0 RESULTS

4.1 Sorbent Characterization

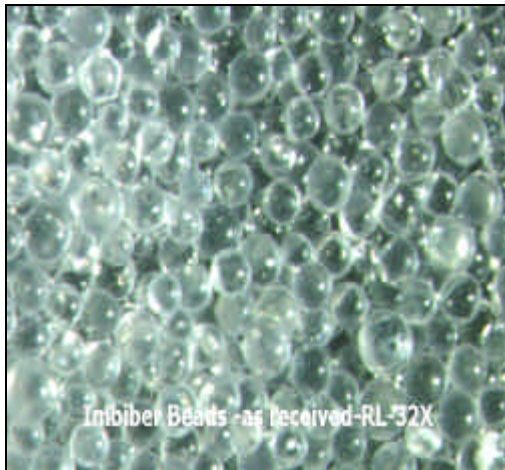
The physical properties of the various sorbents are described in Table 4-1. Micrographs of the sorbents are provided in Figure 4-1. Catalogue price information was obtained for some sorbents.

The basic compounds in the sorbents were identified in general terms to provide base line information for understanding the sorption properties/limitations of the sorbents and for predicting the effects of degradation and long-term performance of the waste forms. Techniques used to identify the sorbents included FTIR spectroscopy and TGA/DTA. The results are summarized in Table 4-2. The FTIR spectra for the sorbents are provided in Figures 4-2 to 4-4.

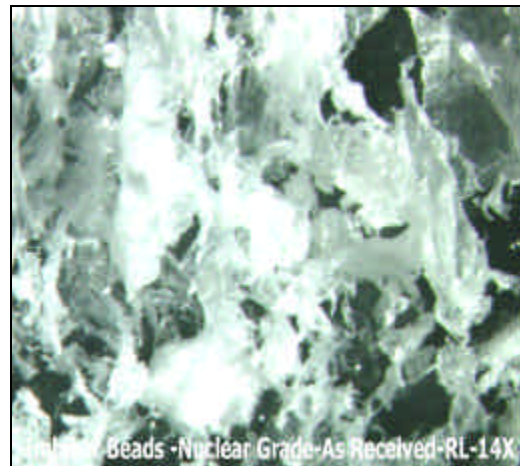
Table 4-1. Physical descriptions of the sorbents tested.

Vendor/Product	Estimated Price	Bulk Density (g/cc)*	Particle Size (mm)	Visual Description
Imbibitive Inc./Imbiber Beads™ (alkylstyrene copolymer)	\$3.55/lb (bulk)	0.70 +/-0.06	125-420 um. from MSDS	Spheres (clear)
Imbibitive Technologies Inc./Imbiber Beads NG™ (alkylstyrene copolymer plus polyethylene wicking agent)		0.27 +/-0.05	Spheres same as Imbiber beads Film material (polyethylene) is very thin and hydrophilic	At least 3 materials, spheres wrapped in shredded (feathery/lacy) material plus a 3 rd material present as angular chunks (may be the same material as the film) Some phase separation of the spheres from the other material.
Nochar Inc./Nochar A-610™	\$8/lb (\$304/40lb)	0.24 +/-0.03	Nodular material 0.1 to > 2mm in size and stringers up to 1mm	Irregular shaped particles made up of connected nodules (white, opaque)
Nochar Inc./Nochar A-650™		0.38 +/-0.02	<0.1 to 0.5 mm	Irregular grains, (colliform, nodular) (white, opaque)
Fluid Tech Inc./Petroset II™	\$1.75/lb	0.52 +/-0.04	< 0.01 to > 0.03 mm	Small agglomerates of particles (gray to brown)
Fluid Tech Inc./Petroset II Granular™		0.65 +/-0.15	0.05 to 0.2 mm	Agglomerated particles (dark olive black)

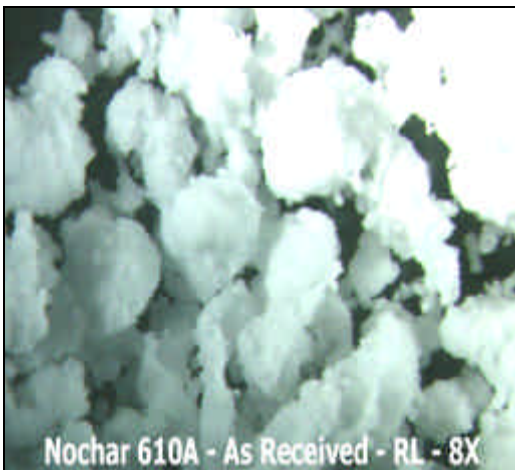
* Relatively small samples were used for the bulk density determinations. On this small-scale, sample preparation technique (sampling, degree of packing, etc.) for these compressible materials effects the results.



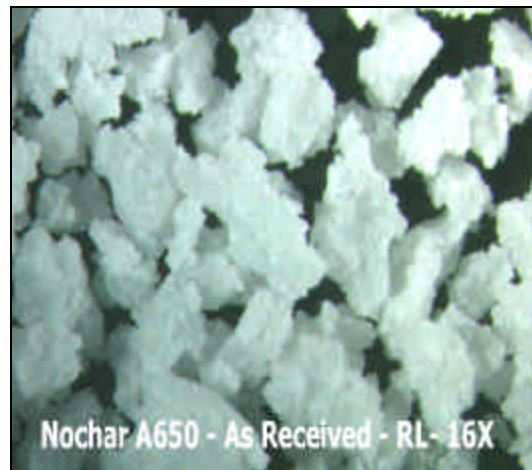
Imbibed Beads



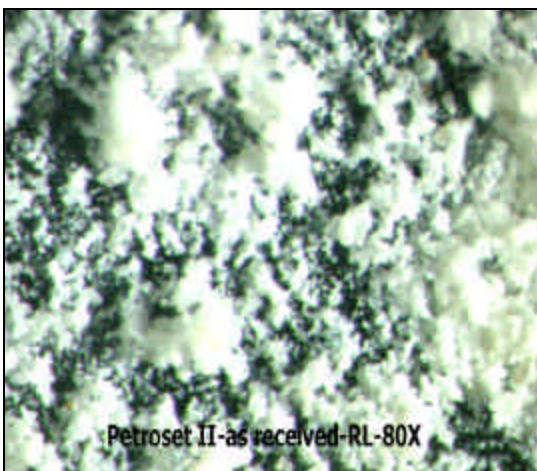
Imbibed Beads Nuclear Grade



Nochar A610



Nochar A650



Petroset II



Petroset II Granular

Figure 4-1. Micrographs of the Sorbent Materials. (RL indicates reflected light. X indicates the magnification)

Table 4-2. Summary of phases identified in the sorbent materials evaluated for PUREX solidification and temperatures at which these phases decompose.

	Components	Component identification via three analytical methods		
		Thermal Gravimetric Analysis	Fourier Transform Infrared Spectroscopy	X-Ray Diffraction
Nochar/ A-610 Petrobond	Copolymer of styrene, butadiene and possibly acrylates and phthalates	300 – 350°C: acrylic acid and styrenic acid volatilization 525°C: carbonization of the polymer backbone	Styrene: 1610, 1498, 755 and 698 cm ⁻¹ , butadiene: 2924, 2856, 1047, 1033, 560 and 1450 cm ⁻¹ and possibly acrylates (or phthalates) 1723, 1183 cm ⁻¹	NA
Nochar/ A-650 Petrobond	Similar to A610 plus calcium carbonate	400 – 450°C: acrylic acid styrenic acid volatilization 500°C: carbonization of polymer backbone	Same as Nochar A610, plus calcium carbonate: 1457 and 877 cm ⁻¹	NA
Imbibitive Technologies Inc./ Imbiber Beads	Styrene, ethylene and probably acrylate copolymer	225 – 450°C: acrylic and styrenic acids volatilization >500°C: carbonization of polymeric backbone	Cross linked polystyrene resin with carbonyl functional groups, (possibly acrylate groups)	NA
Imbibitive Technologies Inc./ Imbiber Beads Nuclear Grade	Same as Imbiber beads plus polyethylene as a separate phase	225 – 400°C: acrylic and styrenic acids volatilization 450 – 500°C carbonization of polyethylene >500°C: carbonization of polymeric backbone	Same as Imbiber beads plus polyethylene as a second phase	NA
Fluid Tech/Petroset II and Petroset II Granular	Mixture of sodium montmorillonite and sodium montmorillonite intercalated with a quaternary amine, plus mineral impurities (quartz, gypsum, halite)	181 – 300°C: hydrocarbon volatilization 300 - >400°C: hydrocarbon volatilization >600°C: NO ₂ volatilization	Montmorillonite clay plus tetra hydrocarbons (C14) attached to a nitrogen (amine).	Sodium montmorillonite, modified sodium montmorillonite, plus (quartz, gypsum, halite, etc.)

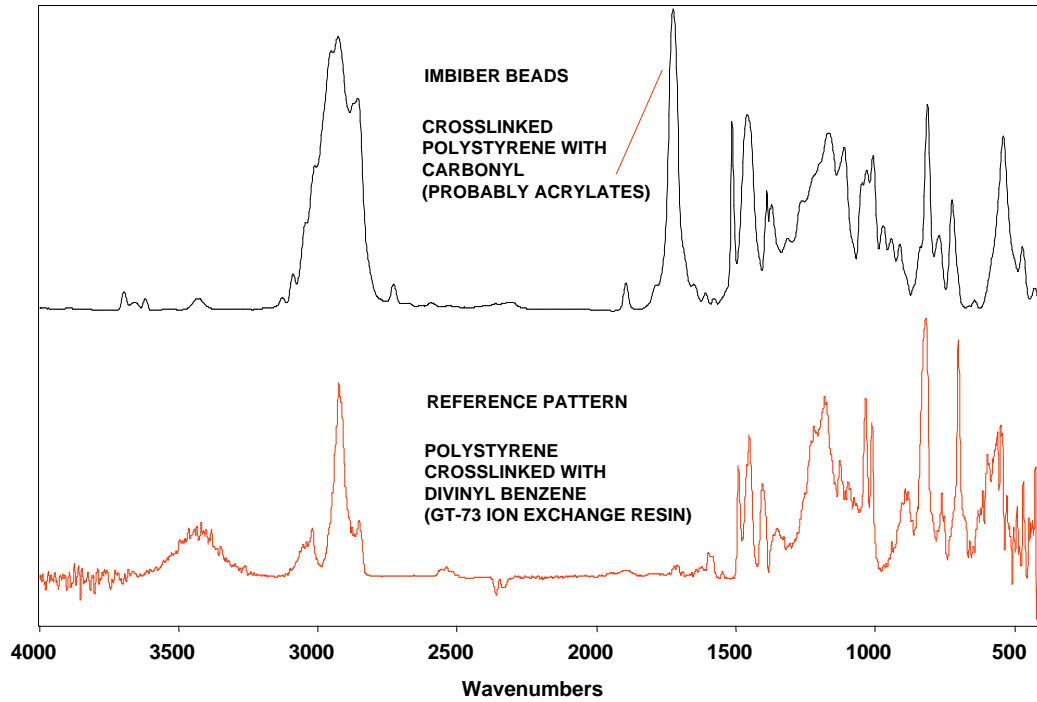


Figure 4-2. Imbiber Bead FTIR spectra and compound identification.

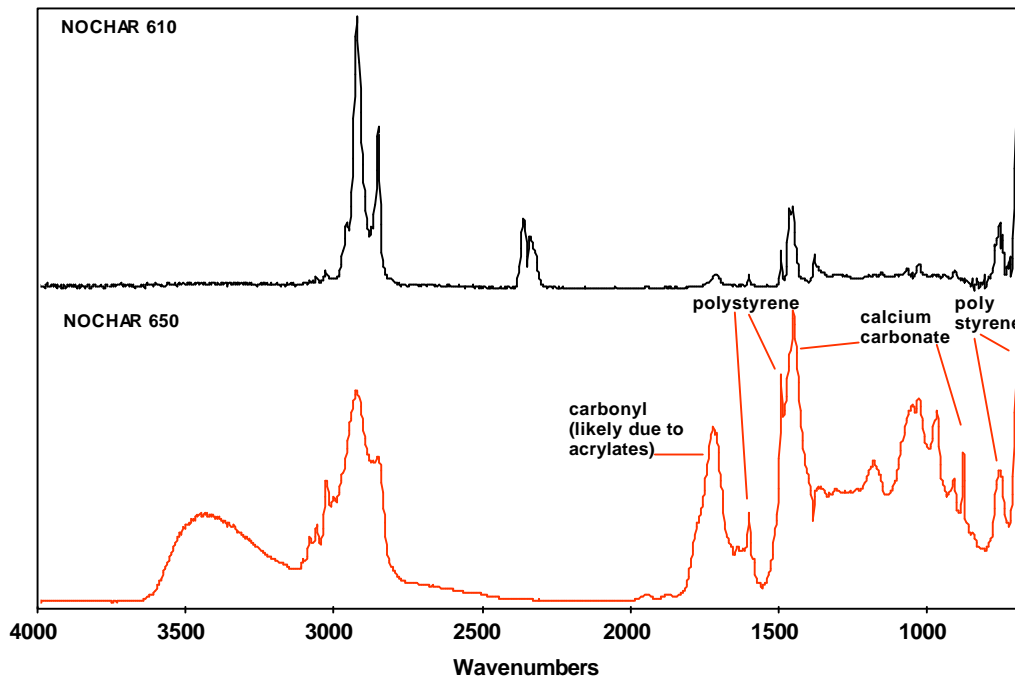
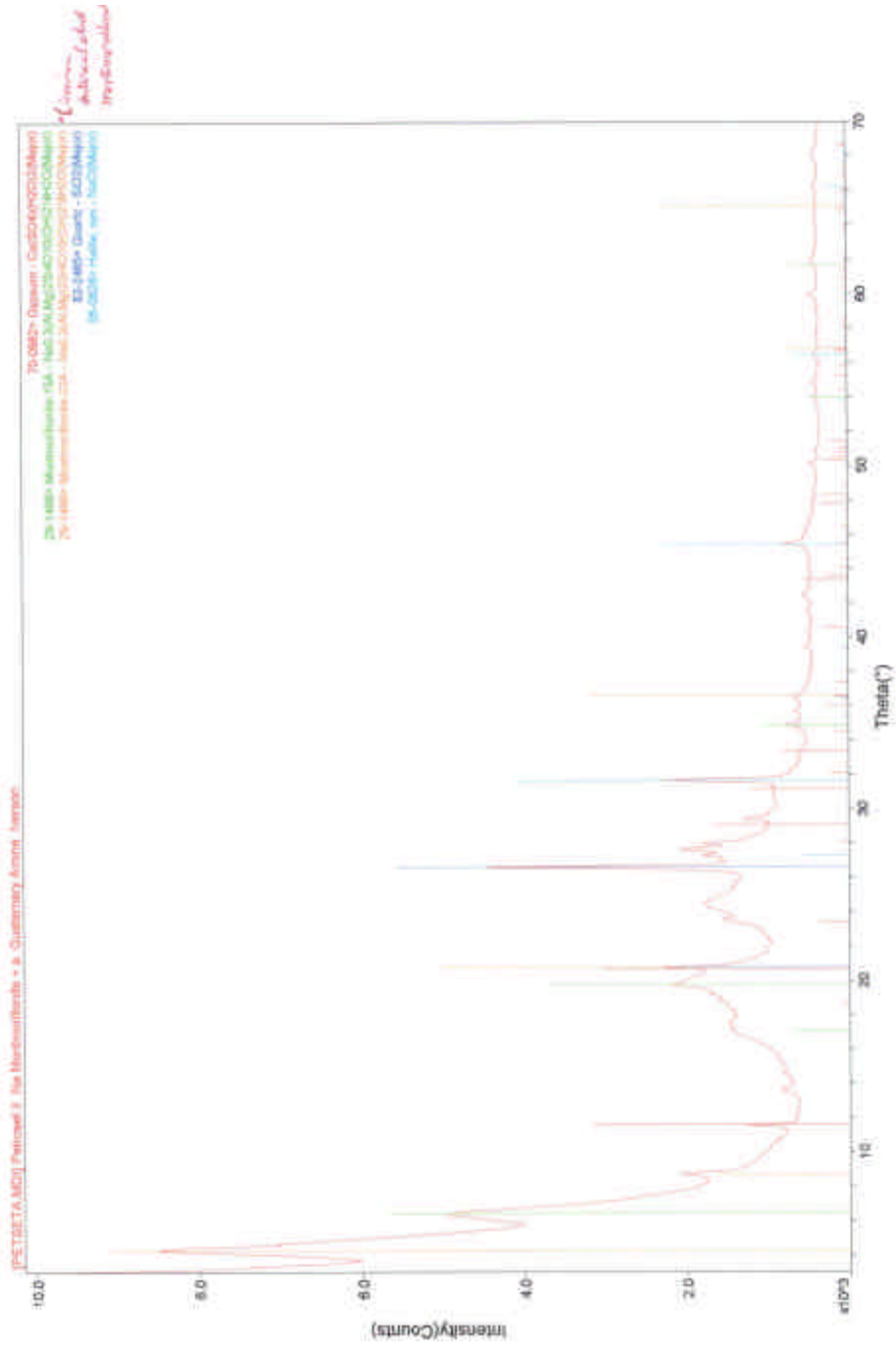


Figure 4-3. Nochar A610 and A650 FTIR spectra and compound identification.



Savannah River Site

Figure 4-5. X-ray diffraction pattern of Petrosel II sorbent.

4.2 Waste Form Characterization

4.2.1 Waste Form Appearance

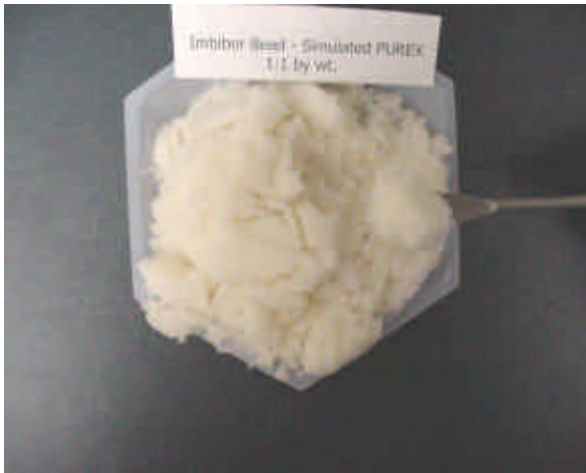
The waste forms described in Table 4-3 were prepared with simulated PUREX waste. Photographs of the 1:1 and 1:2 waste loadings are shown in Figures 4-6 and 4-7, respectively. Photographs of some of the waste forms made with actual waste are shown in Figure 4-8. Waste forms prepared with actual Tank 35 waste appeared to be similar to those prepared with the simulated waste except for the color. The actual PUREX waste was medium to dark brown in color and resembled the simulated PUREX after it was irradiated with Co-60 gamma rays in the laboratory. The Tank 35 PUREX waste is yellow to brown in color as are the waste forms made from actual spent PUREX liquid. The simulated PUREX was clear and consequently the waste forms retain the color of the sorbent.

Table 4-3. Description of the solidified waste forms prepared with simulated PUREX.

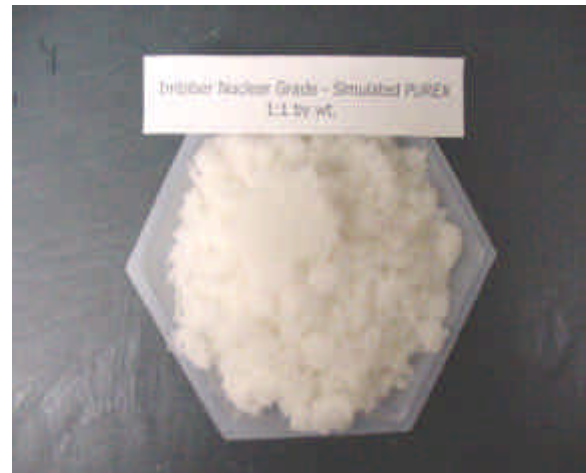
Waste Form	Waste Loading by Wt.	Final Waste Form Description
Imbiber Beads™	1:1	White, opaque to translucent, beads that stick to any surface. Material with 1:2 loading is more translucent and looks “wetter”
	1:2	
Imbiber NG™	1:1	White, opaque, soft material. Clear beads are distributed throughout a white shredded polymer material. Material with 1:2 loading is more translucent and looks “wetter”
	1:2	
Nochar A-610™	1:1	White, opaque, soft spongy particles. Dry appearance and feel. Resembles ground up styrofoam cups. Material with 1:2 loading contains lumps of more “solidified” translucent material that is sorbing more waste.
	1:2	
Nochar A-650™	1:1	White, opaque mass. Some portions display grain boundaries others do not.
	1:2	White, opaque, sticky gel that flows. No grain boundaries visible.
Petroset II™	1:1	Clay-like, sticky. Consistency feels like peanut butter
	1:2	
Petroset II Granular™	1:1	Clay-like, sticky. Consistency feels like peanut butter. Few inclusions of original material.
	1:2	

4.2.2 Waste Form Processing

Observations made during processing the various waste forms are tabulated in Table 4-4. The sorbents were added to the waste and mixed vigorously to obtain even distribution of the waste. The materials that had rapid, high absorption capacities required the most vigorous mixing to obtain a relatively uniform product. Otherwise, a large amount of the sorbent was not exposed to the liquid waste.



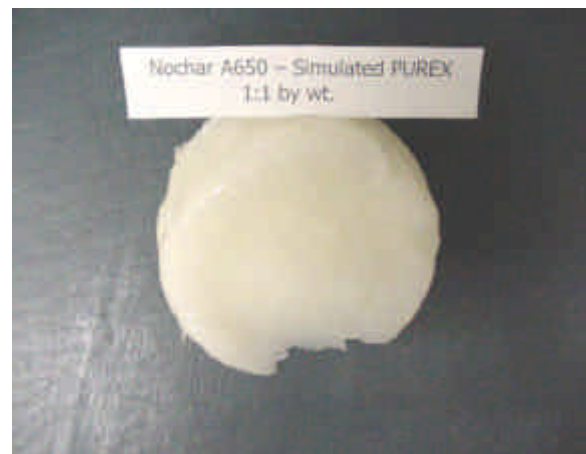
Imbiber



Imbiber Nuclear Grade



Nochar A610



Nochar A650

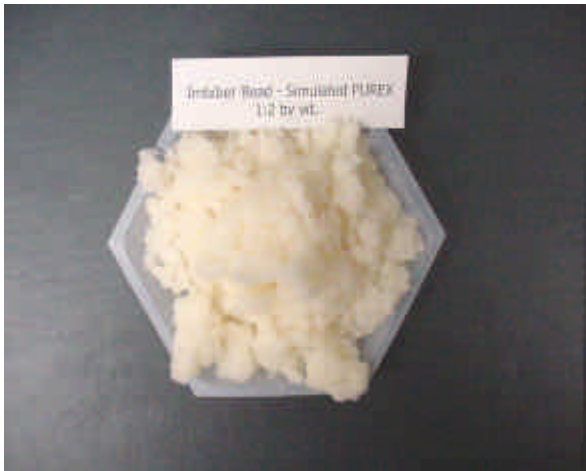


Petroset II

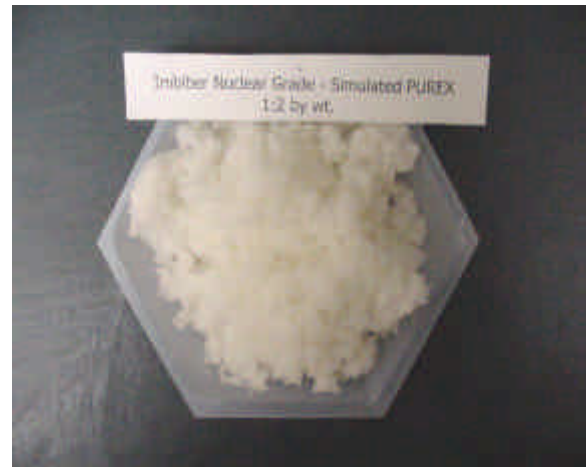


Petroset II Granular

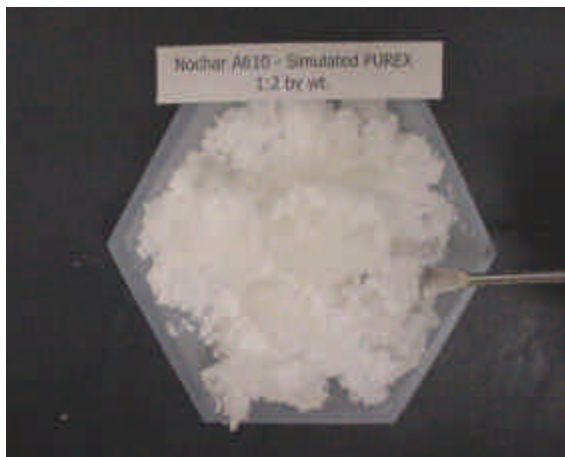
Figure 4-6. Simulated PUREX waste forms with 1:1 absorbent:PUREX waste loadings.



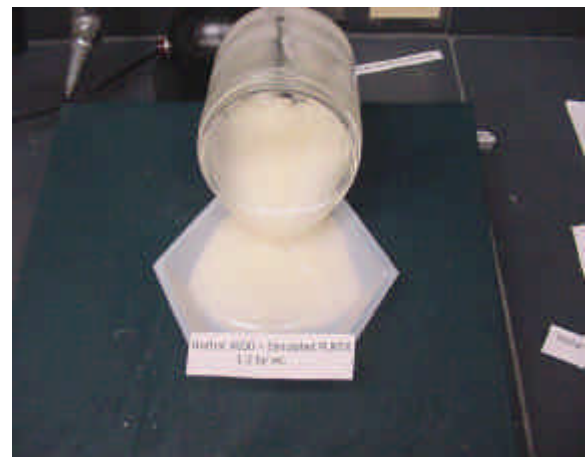
Imbiber



Imbiber Nuclear Grade



Nochar A610



Nochar A650



Petroset II



Petroset II Granular

Figure 4-7. Simulated PUREX waste forms with 1:2 absorbent:PUREX waste loadings.



(a) Before Mixing Imbiber NG and Tank 35 Waste (1:2)



(b) After Mixing Imbiber Beads and Tank 35 Waste (1:2)



(c) After Addition but Before Mixing Nochar A610 and Tank 35 Waste (1:2)



(d) After Mixing Nochar A610 and tank 35 Waste (1:2)



(e) After Addition but Before Mixing Nochar A650 and tank 35 Waste (1:1)



(f) After Mixing Nochar A650 and Tank 35 waste (1:1)



(g) While Mixing Petroset II and Tank 35 Waste (1:1)



(h) After Addition but Before Mixing Petroset II Granular and Tank 35 Waste (1:2)

Figure 4-8. Samples prepared with actual PUREX waste for leaching tests.

Table 4-4. Processing observations for laboratory-scale samples.

Waste Form	Waste Loading by Weight	Laboratory-Scale Observations
Imbiber Beads™	1:1	No dusting. Beads are easily scattered when dry like tiny ball bearings. Minimal mixing is required.
	1:2	
Imbiber NG™	1:1	No dusting. Sorbent is easy to handle. Minimal mixing is required.
	1:2	
Nochar A-610™	1:1	No dusting. Sorbent is easy to handle, fluffy and v. absorbent. Vigorous mixing is required especially at higher waste loadings to assure even distribution. Otherwise, rapid sorption results in regions w/ and w/o waste
	1:2	
Nochar A-650™	1:1	No dusting. Sorbent is easy to handle, light weight and fluffy. Minimal mixing is required.
	1:2	
Petroset II™	1:1	Dusty (like cement). High-shear (not necessarily rapid) mixing is required.
	1:2	
Petroset II Granular™	1:1	Dusty (like cement). High-shear (not necessarily rapid) mixing is required.
	1:2	

Some of the radioactive waste forms shown in Figure 4-8 were photographed after the addition of the Tank 35 waste but prior to mixing. These samples were prepared in a radioactive hood and it was not possible to mix and combine ingredients simultaneously given the limited hood constraints. Uneven distribution of the waste is evident on the small laboratory scale. Even distribution of the waste throughout the waste form was considered a processing objective in addition to being necessary for laboratory testing and comparisons.

One important consideration that was applicable to all of these waste forms is that the vapor pressures of the components in the simulated PUREX waste are low and result in the off-gassing of volatile and semivolatile organic compounds. The legacy PUREX waste is expected to have less off gassing but this must be considered in design of the process ventilation and in containerization of the solidified waste forms. The simulated PUREX waste also had a strong odor. All laboratory work with the simulated waste and waste forms was performed in well-ventilated hoods. The laboratory waste forms were stored in sealed containers.

4.2.2.1 Unit Weight Determination

Mixing the organic sorbent with the PUREX waste resulted in bulking or fluffing of the waste form. This is illustrated in Figure 4-8 (a) and (b) for the Imbiber Beads waste form, (c) and (d) for the Nochar A610 waste form, and (e) and (f) for the Nochar A650 waste form. Volume increases are most apparent for the low density organic polymer sorbents such as the Nochar A650. The Petroset II waste forms did not display bulking or fluffing. However, the consistency of the

Petroset II waste forms resulted in final products that resembles moist clay. (The consistency of the Petroset II waste forms may be improved with the addition of cement and/or other reagents.)

Bulk densities and waste to waste form volume increases for the 1:1 and 1:2 waste forms were measured. Results are listed in Tables 4-5 and 4-6, respectively. In addition, the waste forms were manually compacted with a plunger and the compacted volume, initial rebound, and 24 hour later rebound volumes were measured. The applied compaction force was approximately 50 pounds.

The Petroset II/Petroset II Granular waste forms at the 1:1 and 1:2 waste loadings had the highest waste volume loadings of the materials tested, 1.6 and 1.3 times volume increase relative to the PUREX waste volume, respectively. The Petroset waste form material itself is not compressible. However, the waste forms are thick pastes and completely filling a disposal container may require special filling techniques.

The Imbiber Bead and Imbiber Bead NG 1:2 waste forms had the second lowest (best) volume increases of 2 times relative to the initial waste volume. The Imbiber Bead waste forms showed almost no benefit from compaction after accounting for the rebound that occurred within the first 24 hours. The volume increase for the 1:2 Imbiber Bead waste form is less than that for the 1:1 waste form, 2.0 versus 2.7 times the volume of the PUREX waste. This roughly corresponds to the additional volume of PUREX waste in the 1:2 versus the 1:1 waste forms.

The Imbiber Beads NG 1:1 waste form had a high volume increase relative to the volume of the PUREX waste but was easily compacted. However, after a 24 hour rebound period, most of the benefit from compaction was lost resulting in a 3.5 time volume increase relative to the PUREX waste volume. The 1:2 Imbiber Bead waste form had a volume increase relative to the waste of 2.3 and after the 24 hour rebound period showed a volume increase of 2.0 times relative to the initial PUREX waste. The difference in the rebounded 1:1 and 1:2 products is more than can be accounted for by the additional volume of waste. Consequently, compaction at the level of the test resulted in reducing the pore volume in the product to achieve an additional 10 percent decrease in waste form volume.

The volume increase for the Nochar A610 waste form at a 1:1 waste loading was almost 6 times the volume of the PUREX waste. After the 24 hour rebound period, the volume increase was 3.8 times. The 1:2 waste forms showed much lower volume increases before and after rebound, 3.3 and 2.1, respectively. After rebound the 1:2 Nochar A610 product has a similar waste form to waste volume ratio as the Imbiber Bead products. Again, compaction resulted in reducing the porosity of the waste form and the compaction appears to be more effective at higher waste loading for the Nochar A610 products. Higher waste loadings may result in even more reduction in the waste form to waste volume ratio.

Table 4-5. Bulk density and volume relations for 1:1 solidified PUREX waste forms.

Sorbent Waste loading	Sorbent Weight	Sorbent Volume	Sorbent Bulk Density	PUREX Weight	PUREX Volume	PUREX Density	Waste Form Weight	Waste Form Packing/Compaction	Waste Form Volume	Waste Form Bulk Density	Waste Form : PUREX Waste Vol. Increase	PUREX per 55 gal Drum (gal)
	(g)	(cm ³)	(g/cm ³)*	(g)	(cm ³)	(g/cm ³)	(g)		(cm ³)	(g/cm ³)		
Imbiber Beads 1:1	9.990	14	0.71	9.990	12.00	0.833	19.98	no compaction	37	0.54	3.1	17.8
								max. compaction	22	0.91	1.8	30.0
								initial rebound	30	0.67	2.5	22.0
								24 hr. rebound	32	0.62	2.7	20.6
Imbiber Beads NG 1:1	10.000	50	0.20	10.010	12.00	0.834	20.01	no compaction	50	0.40	4.2	13.2
								max. compaction	14	1.43	1.2	47.1
								initial rebound	36	0.56	3.0	18.3
								24 hr. rebound	42	0.48	3.5	15.7
Nochar A610 1:1	10.000	46	0.22	10.000	12.00	0.833	20.00	no compaction	70	0.29	5.8	9.4
								max. compaction	30	0.67	2.5	22.0
								initial rebound	36	0.56	3.0	18.3
								24 hr. rebound	46	0.43	3.8	15.7
Nochar A650 1:1	9.990	28	0.36	9.990	12.00	0.833	19.98	no compaction	34	0.59	2.8	19.4
								max. compaction	24	0.83	2.0	27.5
								initial rebound	24	0.83	2.0	27.5
								24 hr. rebound	24	0.83	2.0	27.5
Petroset II 1:1	10.000	20	0.50	10.000	12.00	0.833	20.00	no compaction**	20	1.00	1.7	33.0
								max. compaction	19	1.05	1.6	34.7
								initial rebound	21	0.95	1.8	31.4
								24 hr. rebound	22	0.91	1.8	30.0
Petroset II Granular 1:1	10.000	12	0.50	10.000	12.00	0.833	20.00	no compaction**	20	1.00	1.7	33.0
								max. compaction	19	1.05	1.6	34.7
								initial rebound	21	0.95	1.8	31.4
								24 hr. rebound	18	1.11	1.5	36.7

* The bulk densities reported in this table are values measured for the samples used in this particular experiment.

**These waste forms are pastes and an estimate of the pre-compaction volume is problematic since some material was attached to the sides of the measuring device.

Table 4-6. Bulk density and volume relations for 1:2 solidified PUREX waste forms.

Sorbent Waste loading	Sorbent Weight	Sorbent Volume	Sorbent Bulk Density	PUREX Weight	PUREX Volume	PUREX Density	Waste Form Weight	Waste Form Packing/Compaction	Waste Form Volume	Waste Form Bulk Density	Waste Form : PUREX Waste Vol. Increase	PUREX per 55 gal Drum (gal)
	(g)	(cm ³)	(g/cm ³)*	(g)	(cm ³)	(g/cm ³)	(g)		(cm ³)	(g/cm ³)		
Imbiber Beads 1:2	6.79	11	0.62	13.20	16	0.825	19.99	no compaction	35	0.57	2.2	25.14
								max. compaction	25	0.80	1.6	35.20
								initial rebound	32	0.62	2.0	27.50
								24 hr. rebound	32	0.62	2.0	27.50
Imbiber Beads NG 1:2	6.8	28	0.24	13.20	16	0.825	20	no compaction	36	0.56	2.3	24.44
								max. compaction	24	0.83	1.5	36.67
								initial rebound	28	0.71	1.8	31.43
								24 hr. rebound	32	0.63	2.0	27.50
Nochar A610 1:2	6.8	32	0.21	13.20	16	0.825	20	no compaction	52	0.38	3.3	16.92
								max. compaction	26	0.77	1.6	33.85
								initial rebound	32	0.63	2.0	27.50
								24 hr. rebound	34	0.59	2.1	25.88
Nochar A650 1:2	6.81	18	0.38	13.19	16	0.8244	20	no compaction	24	0.83	1.5	36.67
								max. compaction	22	0.91	1.4	40.00
								initial rebound	22	0.91	1.4	40.00
								24 hr. rebound	24	0.83	1.5	36.67
Petroset II 1:2	6.81	14	0.49	13.20	16	0.825	20.01	no compaction**	20	1.00	1.3	44.00
								max. compaction	20	1.00	1.3	44.00
								initial rebound	20	1.00	1.3	44.00
								24 hr. rebound	20	1.00	1.3	44.00
Petroset II Granular 1:2	6.8	10	0.68	13.20	16	0.825	20	no compaction**	20	1.00	1.3	44.00
								max. compaction	20	1.00	1.3	44.00
								initial rebound	20	1.00	1.3	44.00
								24 hr. rebound	18	1.11	1.1	48.89

* The bulk densities reported in this table are values measured for the samples used in this particular experiment.

**These waste forms are pastes and an estimate of the pre-compaction volume is problematic since some material was attached to the sides of the measuring device.

The Nochar A650 waste form volume to waste volume ratio at the 1:1 waste loading was 2.0, similar to that for the Imbiber Bead and A610 1:2 waste loading. However, at a waste loading of 1:2 the Nochar A650 waste form softened to a self-leveling gel. A low waste form volume to PUREX volume of 1.3 was measured.

The volume increases expected for waste forms prepared without mixing will be similar to those measured for the compacted samples. Rebound is not expected from samples prepared by pouring waste into a container with pre-placed sorbents. However, it is difficult to obtain a uniform waste distribution for this type of waste form processing.

4.2.2.2 Solid Property Determination (Paint Filter Test)

The paint filter test was used to determine whether the waste forms were solids or liquids as defined by EPA [7]. By this definition, solid waste does not have any drainable liquid. All of the solidified PUREX waste forms passed this test for a solid material and passed the solids waste criteria for landfill disposal. However the Nochar A650 waste form with 1:2 parts by weight sorbent to simulated PUREX waste form flows as a viscous fluid as illustrated in Figure 4-7. The Petroset II waste forms have the consistency of a thick paste and pass the paint filter test. Preliminary testing indicates that portland cement can be added to the Petroset II – PUREX material to produce a more rigid solid waste form.

4.2.2.3 Liquid Release at 50 psi

The Liquid Release Test (LRT) is used to evaluate whether the waste/waste form will release liquid when subjected to the disposal site overburden [8]. All of the waste forms tested in this study pass the liquid release test. None of the waste forms expressed any liquid as the result of 50 pounds of pressure being applied for 10 minutes. The actual pressure applied to the sample is 14 pounds per square inch using the standard EPA 9096 LRT device manufactured by Associated Design and Manufacturing Company.

4.2.3 Waste Form-PUREX Interactions

Chemical interactions between the simulated PUREX waste and the six sorbents tested are summarized in Table 4-7. FTIR spectra for the waste forms are provided in Figures 4-9 to 4-13. TGA/DTA patterns are provided in Appendix C.

Weight changes as a function of temperature are determined by TGA. Some thermal events, such as melting, plastic transition point, and phase changes take place at discrete temperatures. Other thermal events, such as volatilization of a compound from a sample as it diffuses to the surface, take place over a temperature range.

Differential thermal gravimetric analysis is a differentiation of the TGA data and is a useful tool for component identification. DTA provides a precise measurement of the rate of temperature change as heat is added to the material. This information is also used to identify the type and amount of components in a mixture.

FTIR spectroscopic analysis is used to identify the types and lengths of chemical bonds in a sample. Changes in the FTIR spectra can be correlated with the formation of new

bonds/compounds caused by some event, such as, chemical reaction, heating, irradiation or oxidation.

Table 4-7. Summary of the chemical interactions between the simulated PUREX waste and the sorbents.

Waste Form	Interactions between PUREX and sorbent*
Imbiber Beads™-Simulated PUREX Waste Forms 1:1 and 1:2 waste loadings by weight	No chemical interactions are indicated between simulated PUREX and Imbiber Beads. - DTA/TGA indicates volatilization of organic compounds is identical for pure simulated PUREX liquid and Imbiber Bead waste form. This indicates PUREX diffuses into and out of sorbent without chemical interaction - FTIR indicates no change in P=O bond.
Imbiber NG™-Simulated PUREX Waste Forms 1:1 and 1:2 waste loadings by weight	Bead fraction of the NG material shows no interaction with the simulated PUREX waste. The wicking component (polyethylene) seems to indicate some form of weak interaction with the simulated PUREX waste. - DTA/TGA indicates slower release (broader peak) of PUREX compared to Imbiber Bead waste forms. - FTIR indicates no chemical interactions between the TBP (phosphate groups) in the PUREX and the Imbiber NG.
Nochar A610™-Simulated PUREX Waste Forms 1:1 and 1:2 waste loadings by weight	Some chemical interactions between the Nochar A610 and the simulated PUREX are indicated. - Volatilization of the organic compounds in the simulated PUREX occurs at a slightly higher temperature in the A610 waste forms compared to the Imbiber Bead waste forms. - Degradation of the Nochar A610 resin occurs at a higher temperature for the Nochar A610 –PUREX waste forms compared to the Nochar A610 by itself. - FTIR indicates no appreciable chemical interaction between the TBP in the PUREX and the Nochar A610.
Nochar A650™-Simulated PUREX Waste Forms 1:1 and 1:2 waste loadings by weight	Some slight chemical interactions between the Nochar A650 and the simulated PUREX are indicated after short curing times (7 days). At longer curing times, additional interactions are observed. - Volatilization of the organic compounds in the simulated PUREX occurs at a slightly higher temperature in the A610 waste forms compared to the Imbiber Bead waste forms. - FTIR for samples cured 7 days show very little chemical interaction between the TBP and the Nochar A650.
Petroset II™ and Petroset II Granular™-Simulated PUREX Waste Forms 1:1 and 1:2 waste loadings by weight	Chemical interactions between the Petroset II and the Simulated PUREX are indicated by DTA/TGA and FTIR spectra. - Volatilization of organic components in the simulated PUREX is indicated by the broadening of the PUREX peak in the TGA pattern between 50 and 200°C. - A new peak is found in the TGA pattern of the waste form at 425°C that indicates formation of new chemical bonds. - FTIR spectra indicates a P=O bond shift from 1230 to 1205 cm-1 which suggests that the tributylphosphate in the simulated PUREX is chemically interacting with the intercalated quaternary amines in the montmorillonite.

* FTIR was used to detect interactions between polar molecules like Tributylphosphate (TBP) in the PUREX and the sorbents. TGA was used to detect changes in hydrocarbon-hydrocarbon interactions.

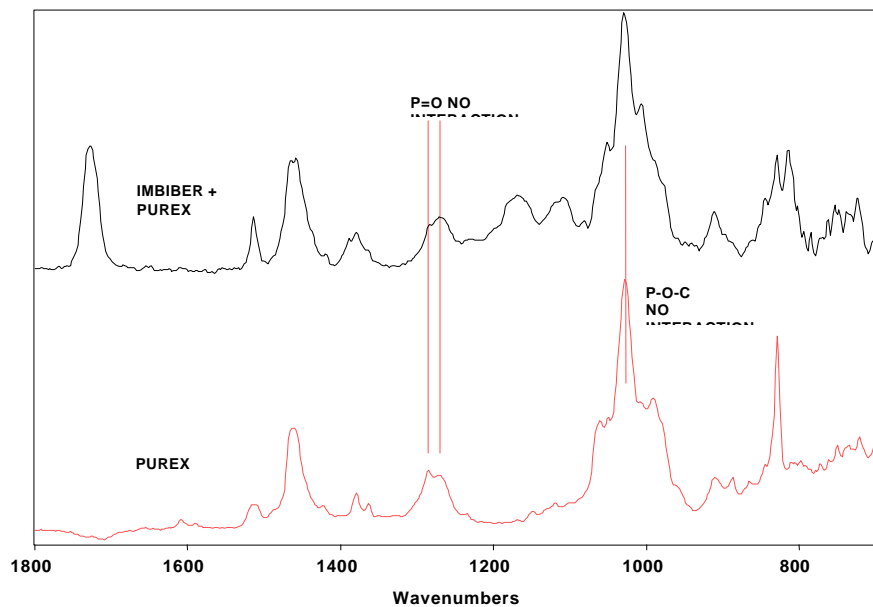


Figure 4-9. FTIR spectra of Imbiber Beads – Simulated PUREX waste form.

No shift of the P=O and P-O-C bonds indicates the absence of chemical reactions between TBP and the Imbiber Bead sorbent.

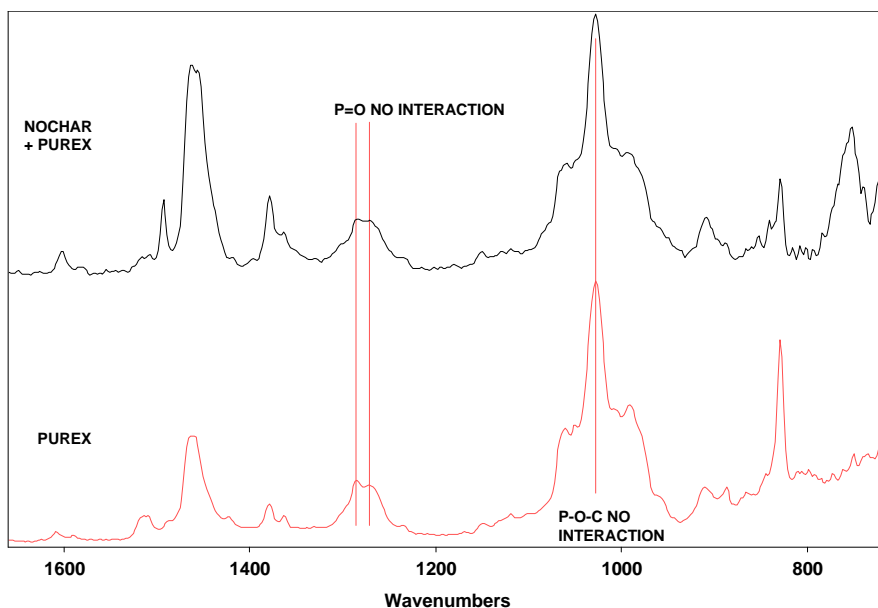


Figure 4-10. FTIR spectra of Nochar A610 – Simulated PUREX waste form. No interactions between the Nochar A610 and the simulated PUREX waste.

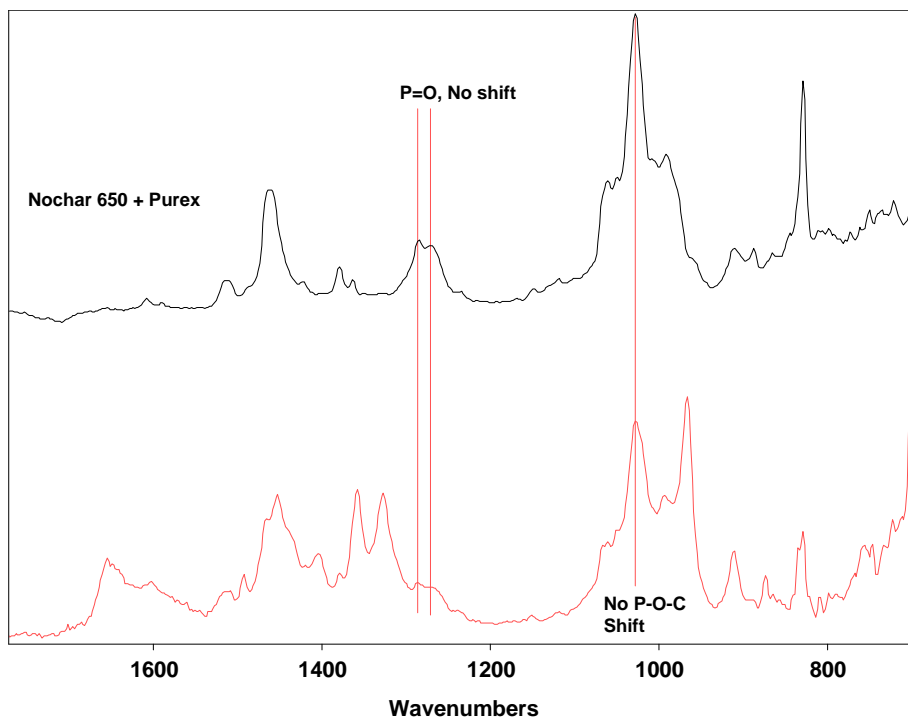


Figure 4-11. FTIR spectra of Nochar A650 – Simulated Purex waste form. No P=O or P-O-C shift is seen, and therefore no interaction between TBP and Nochar 650.

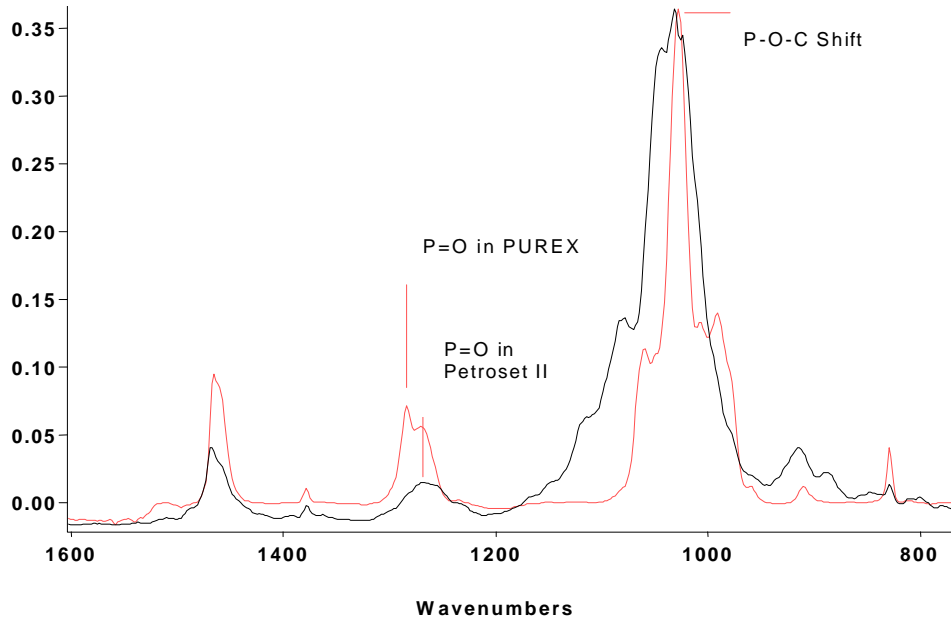


Figure 4-12. FTIR spectra of Petroset II– Simulated PUREX waste form.

Shifts in the P=O and P-O-C are clear indications of interaction between TBP and Petroset II.

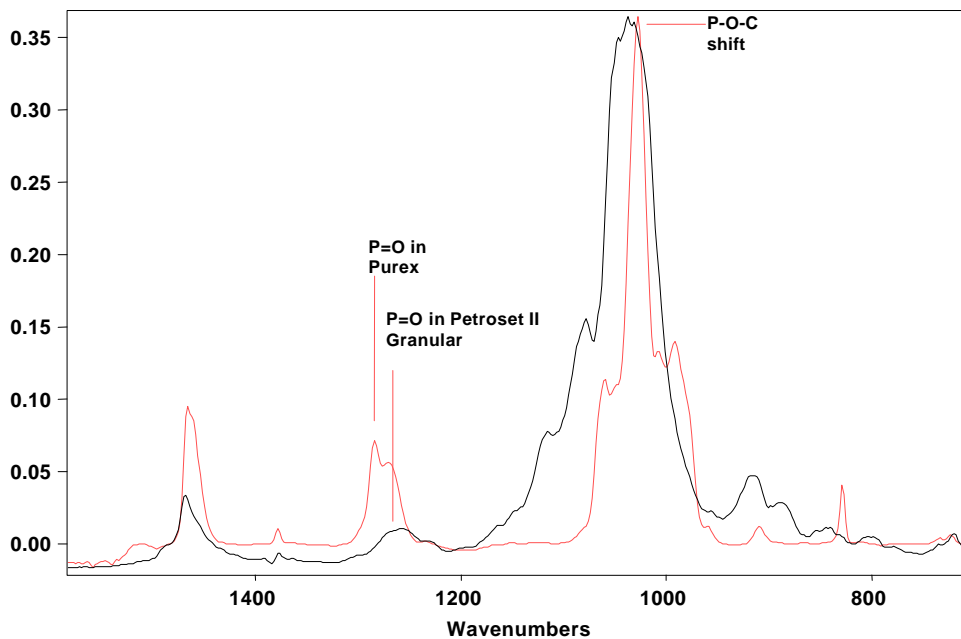


Figure 4-13. FTIR spectra of Petroset II Granular waste form and simulated PUREX waste.

The shift in P=O and P-O-C is due to interaction between TBP and Petroset II granular

4.2.4 Storage and Transportation Properties

4.2.4.1 *Vibration Testing*

All of the samples passed the vibration test. No free liquid was detected after 4 hours of vibration. Based on previous vibration test results involving resins [18], these waste forms are not expected to release any liquid during transportation from SRS to the Nevada Test Site (travel time of approximately 42 hours by truck). Longer laboratory vibration testing times are unnecessary based on the 4-hours responses.

4.2.4.2 *Storage Temperature Effects*

TGA/DTA results indicate that changes in the waste forms between ambient temperature and about 200°C is due to volatilization (release) of the organic compounds in the PUREX waste. The shapes of the TGA/DTA graphs in this temperature range indicate that the release is due to diffusion and volatilization of the PUREX ingredients. The rates of PUREX waste diffusion were not dependent on the waste loadings over the range studied (1:1 and 1:2 loadings, i.e., 50 to 66 wt. % waste).

At higher temperatures, above 250°C, the sorbents thermally degrade and carbonize. Data are presented in Appendix C and are summarized in Table 4-8. Since the Imbiber Beads and the Imbiber Beads Nuclear Grade sorbents do not chemically interact with the simulated PUREX, the thermal decomposition profiles of the sorbents and the waste forms were essentially identical. The Nochar A610 – PUREX waste forms begins to decompose at a higher temperature (about 300°C) than the Nochar A610 sorbent (about 250°C). This indicates that the components of the PUREX chemically interact in some way with the sorbent.

The Nochar A650 – PUREX waste form decomposes at about the same temperature as the Nochar sorbent without PUREX even though the A610 and A650 are very similar with respect to the organic polymers detected. This behavior of the A650 is difficult to explain and is tentatively attributed to the calcium carbonate in the A650 acting as a heat sink during this relatively short thermal treatment.

Some changes in the volatilization of the PUREX components were observed for the Petroset II and Petroset II Granular waste forms. A portion of the PUREX appears to be retained in/on the clay structure above 200°C. Consequently, some of the PUREX appears to be bound/stabilized by the Petroset. The Petroset sorbent substrates were not degraded at temperatures up to 500°C. However, there is evidence for breakdown in the amine compounds between 200 and 500°C. A more detailed analysis of the decomposition products at elevated temperatures is beyond the scope of this study.

Table 4-8. Thermal decomposition of the sorbents with and without absorbed simulated PUREX waste.

Waste Form (1:1 and 1:2 waste loadings by weight)	Sorbent Decomposition Temperature(s) with and without PUREX waste
Imbiber Beads-Simulated PUREX Waste Forms	<ul style="list-style-type: none"> - Imbiber beads w and w/o PUREX decompose between 200 and 350°C and 400°C and 550°C. - PUREX organic compounds volatilize between ambient temperature and 200°C.
Imbiber Beads NG-Simulated PUREX Waste Forms	<ul style="list-style-type: none"> - Same as Imbiber Beads
Nochar A610-Simulated PUREX Waste Forms	<ul style="list-style-type: none"> - A610 w and w/o PUREX begins to decompose from 275 to 400°C - PUREX organic compounds volatilize between 25 and 180°C.
Nochar A650-Simulated PUREX Waste Forms	<ul style="list-style-type: none"> - A650 w and w/o PUREX begins to decompose 350°C. - Calcium carbonate decomposed at 560 to CaO + CO₂ - Volatilization of the organic compounds between 25 and 180°C.
Petroset II and Petroset II Granular-Simulated PUREX Waste Forms	<ul style="list-style-type: none"> - The amine compounds in the Petroset II decompose between 400 and 600°C. - A compound that is detected only in the waste forms decomposes between 400 and 460°C. - Volatilization of the organic compounds between 25 and 200°C

4.2.5 Leaching Properties

4.2.5.1 TCLP Results

Results of the TCLP extractions are presented in Table 4-9. The concentrations of the eight D-code metals and of the UHC metals qualify the waste forms to exit RCRA. The total benzene and TCE concentrations in the waste forms were also low enough to exit RCRA. All of the other UHC organic constituents were determined not to be present in the analysis performed for the SRS Site Treatment Plan [21].

The Petroset II 1:2 waste form was sent to General Engineering Laboratory, Inc. (GEL), for a TCLP extraction and total benzene analysis in order to obtain independent confirmation of the results. GEL is licensed to receive samples that contain environmental concentrations of radionuclides. However, GEL can receive and analyze only one sample of solidified PUREX waste at a time due to radionuclide inventory limitations in their laboratory.

The GEL TCLP results for one waste form, the Petroset II Granular at a 66 wt. % PUREX loading are also shown in Table 4-9 and the GEL report is provided in Appendix D. The results are consistent with the ADS/SRTC results for all of the waste forms. Treatment was successful in removing the toxicity characteristic from the waste form for the TCLP metals and other inorganic underlying constituents.

Table 4-9. TCLP results and total volatile organic analyses for the organic PUREX waste forms.

Analyte	Imbiber -Tank 35 1:2	Imbiber NG- Tank 35 1:2	Nochar A610 Tank 35 1:2	Nochar A650 Tank 35 1:2	Petroset II- Tank 35 1:2	Petroset II Gran- Tank 35 1:2	TCLP Limit (mg/L)	UTS Limit (mg/L)
(mg/L unless indicated otherwise)								
Ag	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	5	0.14
As						<i>0.0142 (U)</i>	5	5
Ba	0.649	3.61		0.537	0.510	0.560	100	21
Cd	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	1	0.1
Cr	<0.012	<0.012	<0.012	<0.012	<0.012	<0.012	5	0.6
Hg (µg/g)						<i>0.000362 (U)</i>	0.2	0.025
Pb	<0.459	<0.459	<0.459	<0.459	<0.459	<0.459	5	0.75
Se (µg/g)						<i>0.0559</i>	<1	5.7
Benzene (mg/kg)	5.5* total	4.5* total	2.4* total	0.24* total	5.5* total	5.5* total	0.5	10*
Trichloroethene (mg/kg)	0.33* total	0.16* total	0.114* total	0.007* total	0.15* total	0.032* total	0.5	6*
Tetrachloroethene (mg/kg)	0.16* total	0.024* total	0.035* total	0.004* total	0.042* total	0.001	0.7	6*
Be	<0.060	<0.060	<0.060	<0.060	<0.060	<0.060	-	1.22
Ni	<0.090	<0.090	<0.090	<0.090	<0.090	<0.090	-	11
Sb	0.078	0.047	0.166	0.059	0.056	0.080	-	1.15
Tl							-	0.2
V	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	-	1.6
Zn	0.292	1.86	0.342	0.269	0.293	0.232	-	4.3

*Total waste form concentrations rather than leachate concentrations.

Results in italics are certified by GEL, Inc., a SCDHEC certified laboratory. J indicates estimated value. The result was greater than the detection limit but less than the reporting limit. And U indicates the compound was analyzed for but not detected above the detection limit.

4.2.5.2 I-129 Distribution Coefficients

Results of the I-129 leaching studies are presented in Table 4-11. The I-129 concentrations for the leachates were reported as less than values in most cases and are at the lowest detection limit that can be reasonably achieved by ADS/SRTC. Consequently, most of the K_d values reported are reported as greater than values. This limitation provides conservative estimates but prevents a precise estimate of the I-129 K_d for the various waste forms. In this study, equilibrium was not verified because of the ubiquitous less than values. However, for modeling purposes, the measured R_d values are reported as K_d values. See Section 3.5.4.

For the Imbiber Bead 1:1 waste form, the I-129 K_d 's ranged from 9480 to 44000 mL/g. For the Imbiber Bead 1:2 waste forms the values ranged from 6980 to >25300 mL/g. All of the values for the Imbiber NG 1:1 were greater than values ranging from 7240 to 47100 mL/g. The Imbiber Beads NG 1:2 waste forms had K_d values of 1220 to 53000. The K_d values for the Nochar A610 1:1 and 1:2 waste forms ranged from 7670 to >28300 mL/g and >5560 to 21800 mL/g, respectively. The K_d values calculated for the Nochar A650 1:1 and 1:2 waste forms were all greater than values ranging from >9540 to >33600 mL/g. The Petroset II waste forms were all calculated to be greater than values except for one value of 44500 mL/g.

No conclusions were attempted with respect to comparing the leaching properties of the various waste forms. However, the smallest I-129 K_d inferred from these data, 6980 mL/g, is four orders of magnitude higher than the value of 0.6 mL/g currently used in the E-Area Performance Assessment. An I-129 analytical method with a lower detection limit to eliminate the problem of summing less than values which are at the detection limit and further testing may be desired to obtain meaningful K_d values.

4.2.5.3 Organic and Radionuclide Leaching Results

Gamma scans, Tank 50 rad screen for total alpha, total beta, and tritium, and volatiles and semivolatiles analyses were determined for the ANSI 16.1 leachates. No activity above background was detected for the 38 radionuclides included in the gamma scans. All leachates had none detect values for the Tank 50 total alpha, total beta and tritium scans. Because of the non-detect/less than values these data could not be used to determine the fraction leached or the ANSI 16.1 Leach Indices for any of the radionuclides.

Leaching results for the volatile organics and semivolatile organics indicate that the solidified waste forms are successful at reducing the release of the waste components into the environment. The ANSI 16.1 leachates were analyzed for semivolatile compounds including tributyl phosphate and volatile organic compounds. Volatile organic compounds were not detected in any of the leachates. The TPB concentrations in the 24 hr. leachates are given in Table 4-10. The concentrations in the leachates are well below the solubility limit for TBP in water, (0.606 vol. % or 1 ml per 165 ml of water, Merck Index, 9th ed., Entry 1069).

The leaching information should be useful for determining waste loadings for the solidification process. For example, higher waste loadings may be achieved for the Nochar A610 material

without affecting leaching. The optimum waste loading for Petroset II is probably in the range of 50 to 66 wt.% since the leaching of the organics increases as loading increases. Semivolatile organic compounds were detected in the 24-hour leachate for only one waste form; Imbiber Beads NG with a 66 wt. % waste loading. (The Imbiber Bead NG sorbent contains hydrophilic material. The Imbiber Beads NG waste forms also gelled and dispersed throughout the leachate. Consequently, it was rejected from further consideration.)

Benzene was not detected in the ANSI 16.1 leachates. Stabilization of benzene was confirmed by the TCLP zero-head space extraction results shown in Table 4-9.

Table 4-10. Leachate results for organics for the 24 hour interval.

Waste Form Loading	TPB in ANSI 16.1 in Leachate for 24 hr. Interval (mg/L)	Semivolatiles in ANSI 16.1 Leachate for 24 hr. Interval (mg/L)
Imbiber Beads		
1:1	4.3	ND
1:2	9.3	ND
Imbiber Beads NG		
1:1	15	ND
1:2	55	*
Nochar A610		
1:1	12	ND
1:2	13	ND
Nochar A650		
1:1	7	ND
1:2	7	ND
Petroset II		
1:1	5.9	ND
1:2	10	ND
Petroset II Granular		
1:1	6.3	ND
1:2	18	ND

* The concentrations of the semivolatile organic compounds in the gelled leachate are listed below.

(IMB NG 24 Hours 1:2) 3-168725

Analyte	Concentration, mg/L
Tributyl phosphate	55
Benzene, 1,4-diethyl-	35
Benzene, 1,4-diethyl-	26
Tridecane	24
Tetradecane	22
Benzo[b]triphenylene, 10,11,12,	11
Dodecane	11
1-Octanamine, N,N-dioctyl-	6.7
Undecane	6.4
Undecane, 6-ethyl-	5.1
Undecane, 2,6-dimethyl-	3.2
Pentadecane	2.5
Nonane, 5-butyl-	2.4
1-Octanamine, N,N-dioctyl-	2.2
Benzene, diethyl-	1.9
Heptylcyclohexane	1.7
Benzene, 1-(1,1-dimethylethyl)-	1.7
1-Heptanamine, N,N-diheptyl-	1.6
Cyclohexane, pentyl-	1.6
Dodecane, 2-methyl-	1.5
Tridecane, 2-methyl-	1.5
Undecane, 2,4-dimethyl-	1.4
Decane	1.3
Undecane, 3-methyl-	1.2
trans-Decalin, 2-methyl-	1.2
Tetradecane	1.2
Heptacosane	1.2
Undecane, 2-methyl-	1.1
Cyclohexane, hexyl-	1.0
Undecane, 5-methyl-	1.0
Cyclododecane	0.94
Tridecane, 3-methyl-	0.94
Dodecane, 4-methyl-	0.91
1-Octanamine, N,N-dioctyl-	0.86
Cyclohexane, 1-methyl-3-pentyl-	0.78

Table 4-11. Leaching data and I-129 K_d values for actual Tank 35 PUREX.

Sample ID	Leach Time	Sample Wt (g)	PUREX in Sample (g)	[I-129] in Leachate (mCi/mL)	Vol Leachate (mL)	Total I-129 in Waste Form (mCi)	I-129 R_d (K_d) (mL/g)
Imbiber Beads 1:1	unleached	11.1	5.531	0	0	6.20E-04	NA
Imbiber Beads 1:1	30 sec	11.1	5.531	2.51E-09	8.50E+02	6.20E-04	22247
Imbiber Beads 1:1	2 hr	11.1	5.531	1.50E-09	8.50E+02	6.20E-04	37227
Imbiber Beads 1:1	7 hr	11.1	5.531	1.27E-09	8.50E+02	6.20E-04	43968
Imbiber Beads 1:1	24 hr	11.1	5.531	5.89E-09	8.50E+02	6.20E-04	9480
Imbiber Beads 1:2	30 sec	10.9	7.269	< 2.95E-09	8.50E+02	8.15E-04	> 25333
Imbiber Beads 1:2	2 hr	10.9	7.269	3.20E-09	8.50E+02	8.15E-04	23354
Imbiber Beads 1:2	7 hr	10.9	7.269	3.43E-09	8.50E+02	8.15E-04	21788
Imbiber Beads 1:2	24 hr	10.9	7.269	1.07E-08	8.50E+02	8.15E-04	6984
Imbiber Beads NG 1:1	30 sec	7.5	3.753	< 1.19E-09	8.50E+02	4.21E-04	> 47123
Imbiber Beads NG 1:1	2 hr	7.5	3.753	< 4.40E-09	8.50E+02	4.21E-04	> 12745
Imbiber Beads NG 1:1	7 hr	7.5	3.753	< 6.88E-09	8.50E+02	4.21E-04	> 8151
Imbiber Beads NG 1:1	24 hr	7.5	3.753	< 7.75E-09	8.50E+02	4.21E-04	> 7236
Imbiber Beads NG 1:2	30sec	10.1	6.741	< 1.41E-09	8.50E+02	7.55E-04	> 53045
Imbiber Beads NG 1:2	2 hr	10.1	6.741	3.78E-09	8.50E+02	7.55E-04	19787
Imbiber Beads NG 1:2	7 hr	10.1	6.741	6.14E-09	8.50E+02	7.55E-04	12181
Imbiber Beads NG 1:2	24 hr	10.1	6.741	2.73E-09	8.50E+02	7.55E-04	27397

Table 4-10. Leaching data and I-129 K_d values for simulated PUREX (continued).

Sample ID	Leach Time	Sample Wt (g)	PUREX in Sample (g)	[I-129] in Leachate (mCi/mL)	Vol Leachate (mL)	Total I-129 in Waste Form (mCi)	I-129 R_d (K_d) (mL/g)
Nochar A610 1:1	30 sec	5.1	2.528	< 2.08E-09	8.50E+02	2.83E-04	> 26706
Nochar A610 1:1	2 hr	5.1	2.528	< 2.02E-09	8.50E+02	2.83E-04	> 27499
Nochar A610 1:1	7 hr	5.1	2.528	< 1.96E-09	8.50E+02	2.83E-04	> 28341
Nochar A610 1:1	24 hr	5.1	2.528	7.24E-09	8.50E+02	2.83E-04	7672
Nochar A610 1:2	30 sec	5.7	3.815	< 3.44E-09	8.50E+02	4.28E-04	> 21803
Nochar A610 1:2	2 hr	5.7	3.815	< 3.45E-09	8.50E+02	4.28E-04	> 21740
Nochar A610 1:2	7 hr	5.7	3.815	< 3.45E-09	8.50E+02	4.28E-04	> 21740
Nochar A610 1:2	24 hr	5.7	3.815	1.35E-09	8.50E+02	4.28E-04	5556
Nochar A650 1:1	30 sec	5.9	2.955	< 1.67E-09	8.50E+02	3.31E-04	> 33609
Nochar A650 1:1	2 hr	5.9	2.955	< 3.73E-09	8.50E+02	3.31E-04	> 15047
Nochar A650 1:1	7 hr	5.9	2.955	< 5.80E-09	8.50E+02	3.31E-04	> 9677
Nochar A650 1:1	24 hr	5.9	2.955	< 3.12E-09	8.50E+02	3.31E-04	> 17989
Nochar A650 1:2	30 sec	11.4	7.611	< 5.29E-09	8.50E+02	8.53E-04	> 14143
Nochar A650 1:2	2 hr	11.4	7.611	< 4.62E-09	8.50E+02	8.53E-04	> 16194
Nochar A650 1:2	7 hr	11.4	7.611	< 3.95E-09	8.50E+02	8.53E-04	> 18941
Nochar A650 1:2	24 hr	11.4	7.611	< 7.84E-09	8.50E+02	8.53E-04	> 9543

Table 4-10. Leaching data and I-129 K_d values for simulated PUREX (continued).

Sample ID	Leach Time	Sample Wt (g)	PUREX in Sample (g)	[I-129] in Leachate (mCi/mL)	Vol Leachate (mL)	Total I-129 in Waste Form (mCi)	I-129 R_d (K_d) (mL/g)
Petroset II 1:1	30 sec	10.1	5.028	< 3.19E-09	8.50E+02	5.64E-04	> 17488
Petroset II 1:1	2 hr	10.1	5.028	< 6.32E-09	8.50E+02	5.64E-04	> 8827
Petroset II 1:1	7 hr	10.1	5.028	< 9.44E-09	8.50E+02	5.64E-04	> 5910
Petroset II 1:1	24 hr	10.1	5.028	< 3.31E-09	8.50E+02	5.64E-04	> 16854
Petroset II 1:2	30 sec	12.0	8.001	< 3.79E-09	8.50E+02	8.97E-04	> 19715
Petroset II 1:2	2 hr	12.0	8.001	< 3.46E-09	8.50E+02	8.97E-04	> 21595
Petroset II 1:2	7 hr	12.0	8.001	< 3.13E-09	8.50E+02	8.97E-04	> 23872
Petroset II 1:2	24 hr	12.0	8.001	< 6.17E-09	8.50E+02	8.97E-04	> 12110
Petro II Granular 1:1	30 sec	10.7	5.355	< 3.37E-09	8.50E+02	6.00E-04	> 16642
Petro II Granular 1:1	2 hr	10.0	5.355	< 3.75E-09	8.50E+02	6.00E-04	> 16003
Petro II Granular 1:1	7 hr	7.0	5.355	< 4.13E-09	8.50E+02	6.00E-04	> 20757
Petro II Granular 1:1	24 hr	10.7	5.355	< 3.31E-09	8.50E+02	6.00E-04	> 16944
Petro II Granular 1:2	30 sec	11.7	7.812		8.50E+02	8.76E-04	
Petro II Granular 1:2	2 hr	11.7	7.812		8.50E+02	8.76E-04	
Petro II Granular 1:2	7 hr	11.7	7.812	1.68E-09	8.50E+02	8.76E-04	44538
Petro II Granular 1:2	24 hr	11.7	7.812	< 4.74E-09	8.50E+02	8.76E-04	> 15786

4.2.6 Durability/Aging Properties

4.2.6.1 Short-Term Aging Effects

Changes in some of the waste forms after curing for two months were detected in the FTIR spectra. Only the waste forms with the 1:2 waste loadings were evaluated. The Nochar A650 showed the most noticeable change after 60 days curing. The butadiene (rubber) component in the A650 is degraded by one or more of the compounds in the simulated PUREX. The most likely reaction is between the tributylphosphate and the elastomer component.

Table 4-12. Short-term aging effects based on FTIR spectra.

Waste Form	Short Term Aging
Imbiber Beads™-Simulated PUREX Waste Forms	None
Imbiber NG™-Simulated PUREX Waste Forms	None
Nochar A610™-Simulated PUREX Waste Forms	Slight shift in the P=O bond stretch which indicates minor amount of plasticization of the sorbent.
Nochar A650™-Simulated PUREX Waste Forms	This sample showed some miscibility between the PUREX components and the sorbent substrate. The PUREX appears to be plasticizing the styrene and butadiene even for short exposure times.
Petroset II™ and Petroset II Granular™-Simulated PUREX Waste Forms	No short-term changes in the clay except for possible expansion of the basal spacing.

4.2.6.2 Degradation Effects from Co-60 Irradiation

Chemical changes in the solidified PUREX waste forms due to irradiation are summarized in Table 4-12 and were determined from interpretation of FTIR spectra of waste forms exposed to Co-60 gamma rays for up to 90 hours. The degradation rate and relative proportions of the degradation products obtained from Co-60 gamma irradiation cannot be determined from these data. However, the degradation products are expected to be the same as those obtain from the energy imparted by the isotopes in the PUREX waste. Scission of the chemical bonds in the organic polymer sorbents by the gamma rays results in degradation products that may combine to form new compounds and/or free radicals. Increased cross-linking of the polymer chains also occurs. These changes are manifested in color changes and in the waste forms becoming harder and somewhat brittle as they age (absorb more dose). The formation of C-O and C-O-H bonds renders the waste form more

hydrophilic. Visual changes in waste forms are summarized in Table 4-13 and documented in photographs in Figures 4-14 to 4-18.

Table 4-13. Chemical changes in simulated PUREX waste forms as the result of Co-60 irradiation.

Waste Form	Degradation Effects
Imbiber Beads™-Simulated PUREX Waste Forms	Formation of C=C double bonds and carbonyl bonds, C=O
Imbiber NG™-Simulated PUREX Waste Forms	Formation of C=C double bonds and carbonyl bonds, C=O plus ethers, C-OH
Nochar A610™-Simulated PUREX Waste Forms	Formation of carbonyl bonds C=O, Reduction in aliphatic compounds, and postulated formation of H ₂ from amines CH ₃ , CH ₂
Nochar A650™-Simulated PUREX Waste Forms	Formation of a small amount of carbonyl C=O (calcium carbonate filler probably provides shielding)
Petroset™ and Petroset Granular™-Simulated PUREX Waste Forms	Formation of a very small amount of carbonyl C=O (alumino silicate clay provides shielding)

Weight loss data as a function of exposure times (dose) for the 1:2 waste forms are listed in Table 4-13 and plotted in Figure 4-19. (The 1:1 waste forms showed similar trends.) Weight loss is attributed to breaking of chemical bonds and the liberation of gases produced by radiolysis of the sorbent/waste form. Further evidence of gas generation was the observation that new bubbles or voids were formed in some of the irradiated waste forms made with the organic polymer sorbents (Nochar A650 1:2). Weight gain was attributed to oxidation and/or hydration of the organic polymers. Identification of the evolved gases was beyond the scope of this study.

None of the waste forms showed significant weight change for doses up to 4.46E+06 rad, which corresponds to the dose received from the PUREX after about 500 years. The Imbiber Bead waste forms lost weight over the entire dose interval. (The Imbiber Beads starting material was the most uniform of the organic polymers.) The Imbiber Beads NG waste forms showed weight gains up to 8.91E+06 rad (1000 years of irradiation). At higher doses, the Imbiber waste forms showed weight losses (bond breaking) followed by a gain (oxidation or hydration) at even higher doses.

The Nochar A610 waste forms lost weight up to a dose of 4.46E+07 rad (5000 years of exposure) and then gained weight at 8.91E+07 rad (10,000 years). The Nochar A650 waste forms lost weight up to 8.91E+06 rad (gases liberated) and then gained weight at higher doses. The Petroset II waste forms showed the smallest weight changes. The Nochar A650 waste forms showed the greatest weight loss. Collection and analyses of the radiolytic gases were beyond the scope of this study.

Table 4-14. Description of solidified PUREX waste forms exposed to Co-60 irradiation.

Waste Form	Method/Parameter	Imbiber	Imbiber NG	Nochar A610	Nochar A650	Petroset II	Petroset Granular
1:1 Absorbent : Simulated PUREX Waste (by weight)	Color change Gel Express liquid	Yellowing at 3.5E+05 rad Changing from beads to gel up to 3.2E+06 rad	Yellowing at 3.5E+05 Changing from beads to gel up to 3.2E+06 rad	Yellowing at 1.7E+06 rad and particles are bonded together,	Yellowing at 3.7E+04 rad, hardening and gas (voids) generation at 1.7E+06 rad	No change except it feels drier at 1.7E+06 rad	No change except it feels drier at 1.7E+06 rad
1:2 Absorbent : Simulated PUREX Waste (by weight)	Color change Softening Gas generation	Yellowing at 3.5E+05 rad and begins change from beads to gel up to 3.2E+06 rad	Yellowing at 3.5E+05 rad and begins change from beads to gel up to 3.2E+06 rad	Rubbery clumps form after 1.9E+05 rad, Yellow at 1.7E+06 rad, gas generation (voids) at 3.2E+06 rad	Yellowing at 3.7E+04 rad, hardening and gas (voids) generation at 1.7E+06 rad, amber, hard, at 3.2E+06 rad	No change except it feels drier at 1.7E+06 rad	No change except it feels drier at 1.7E+06 rad



















Imbiber Beads						
Imbiber Beads + Simulated PUREX 1:1 by wt.						
Imbiber Beads + Simulated PUREX 1:2 by wt.						
Exposure Time Absorbed Dose Equivalent Years	0 hr. 0 rads 0 years	0.5 hr. 3.7 E+04 rads 50 years	4.5 hr. 1.9 E+05 rads 500 years	9 hr. 3.7E+05 rads 1000 years	45 hr. 1.7E+06 rads 5000 years	90 hr. 3.2 E+06 rads 10,000 years

Figure 4-14. Imbiber Beads and Imbiber Beads –PUREX waste forms exposed to Co-60 gamma radiation.

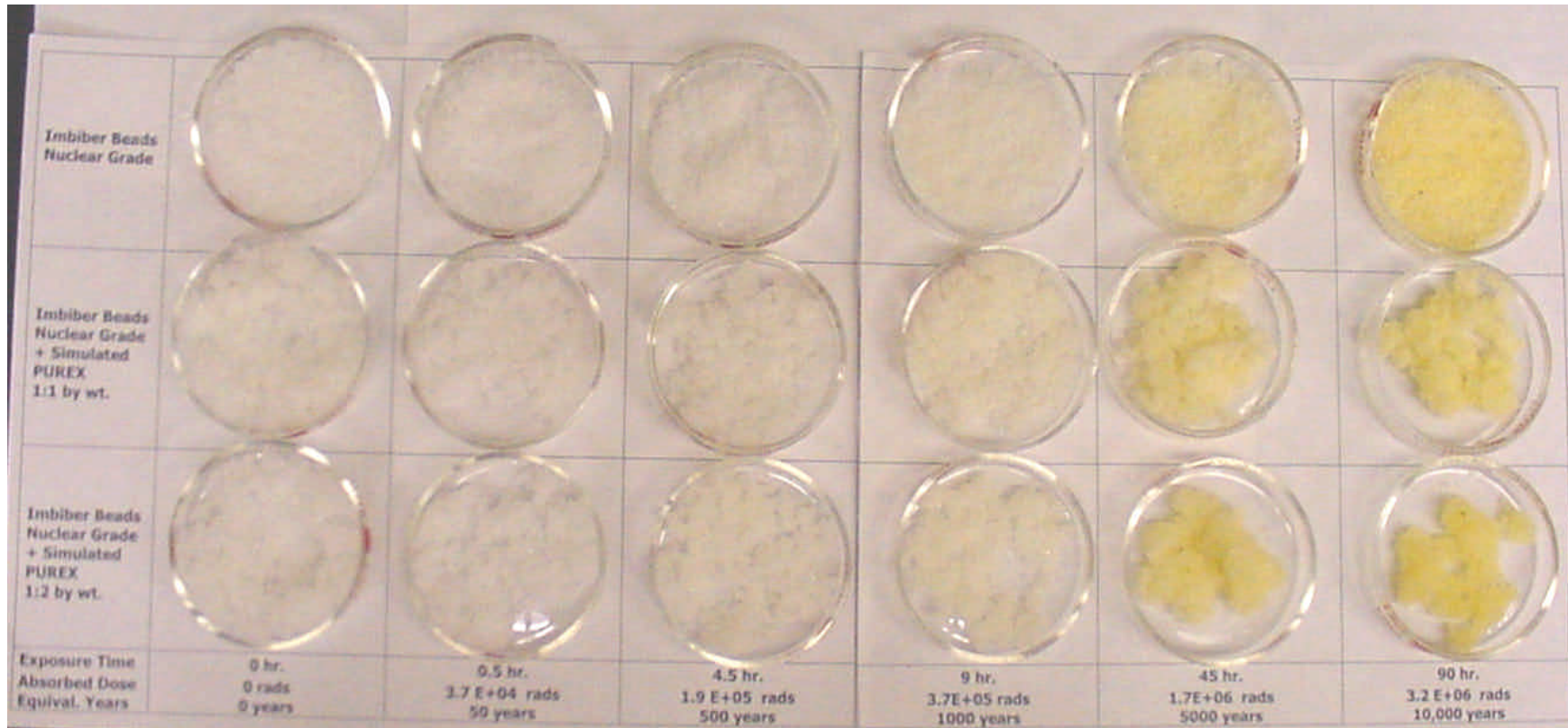


Figure 4-15. Imbiber Bead NG and Imbiber Bead NG – PUREX waste forms exposed to Co-60 gamma radiation.

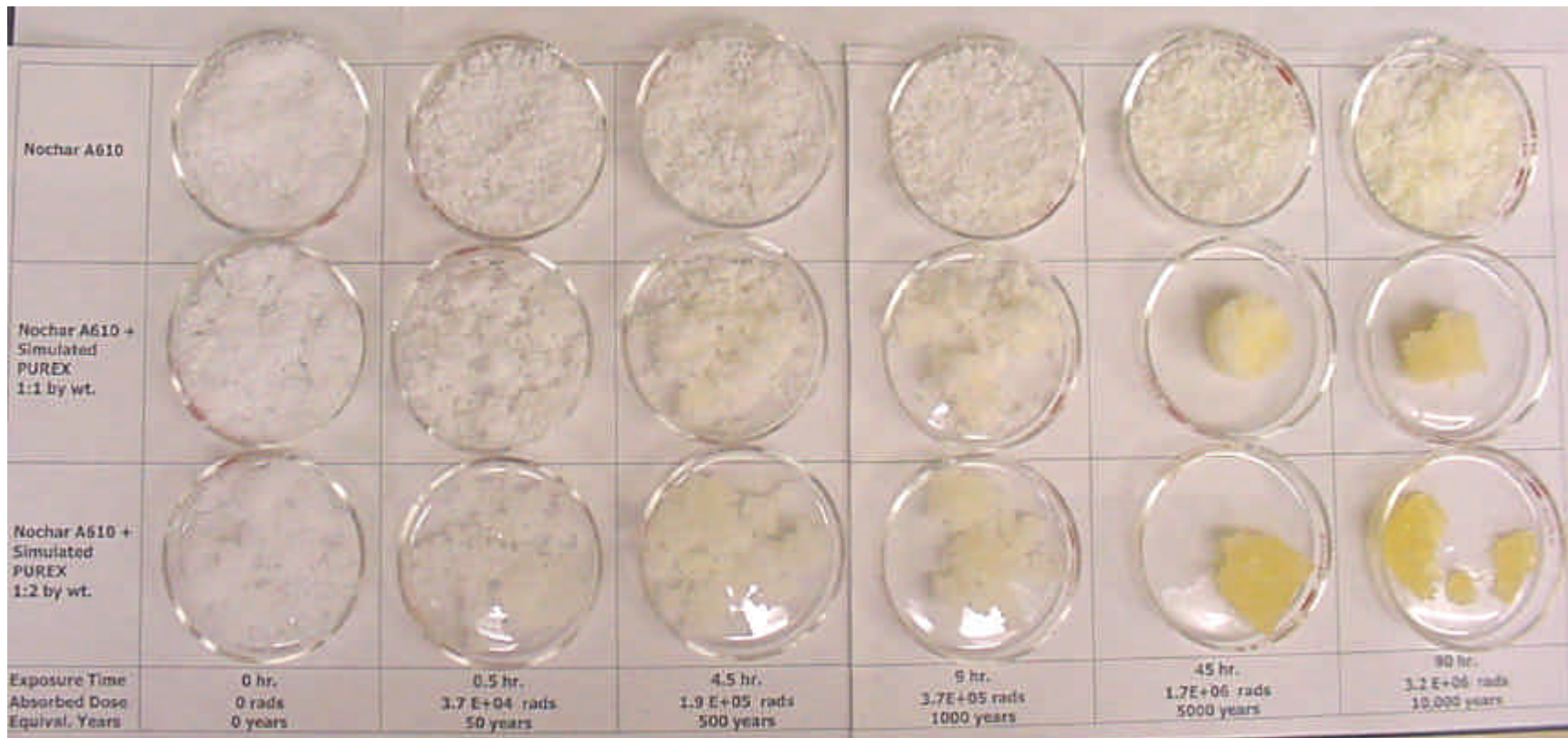


Figure 4-16. Nochar A610 and Nochar A610 –PUREX waste forms exposed to Co-60 gamma radiation.

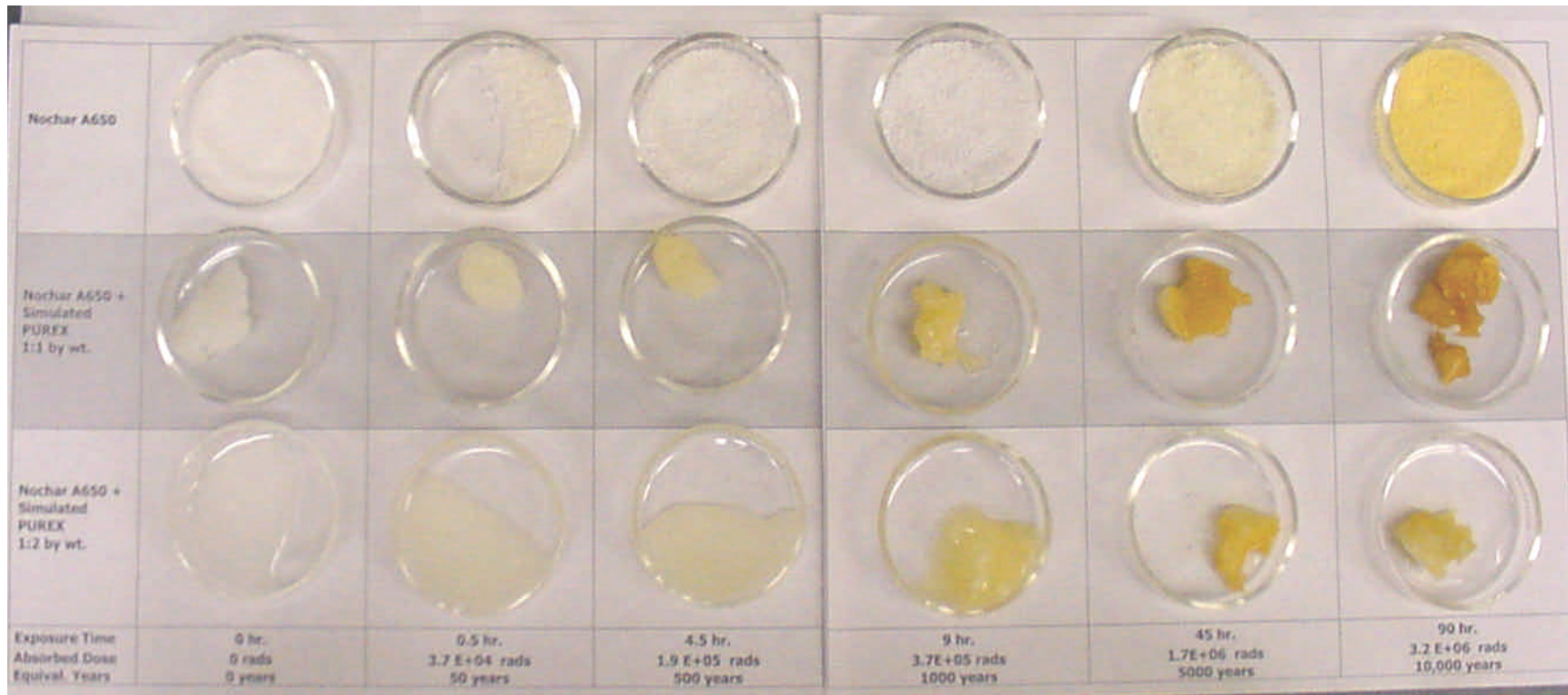


Figure 4-17. Nochar A650 and Nochar A650 –PUREX waste forms exposed to Co-60 gamma radiation.

Petroset II Granular						
Petroset II Granular + Simulated PUREX 1:1 by wt.						
Petroset II granular + Simulated PUREX 1:2 by wt.						
Exposure Time	0 hr.	0.5 hr.	4.5 hr.	9 hr.	45 hr.	90 hr.
Absorbed Dose	0 rads	3.7 E+04 rads	1.9 E+05 rads	3.7E+05 rads	1.7E+06 rads	3.2 E+06 rads
Equivalent, Years	0 years	50 years	500 years	1000 years	5000 years	10,000 years

Figure 4-18. Petroset II Granular and Petroset II Granular –PUREX waste forms exposed to Co-60 gamma radiation..

Table 4-15. Weight change as a function of exposure to Co-60.

Dose (rad) Exposure Time (yr.)	Weight Change after Exposure (%)				
	8.9E+05 100	4.46E+06 500	8.91E+06 1000	4.46E+07 5000	8.91E+07 10,000
Waste Form					
Imbiber Beads 1:2	-0.008	-0.050	-0.111	-0.266	-0.728
Imbiber NG 1:2	+0.029	+0.038	-0.020	-0.237	+0.15
Nochar A610	+0.003	-0.093	-0.280	-0.122	+0.162
Nochar A650	-0.029	-0.015	-0.034	+0.190	-0.134
Petroset II	+0.007	-0.010	-0.009	-0.017	-0.004
Petroset II Granular	-0.006	-0.018	-0.062	-0.14	-0.054

The error in the weight measurements is 0.005g.

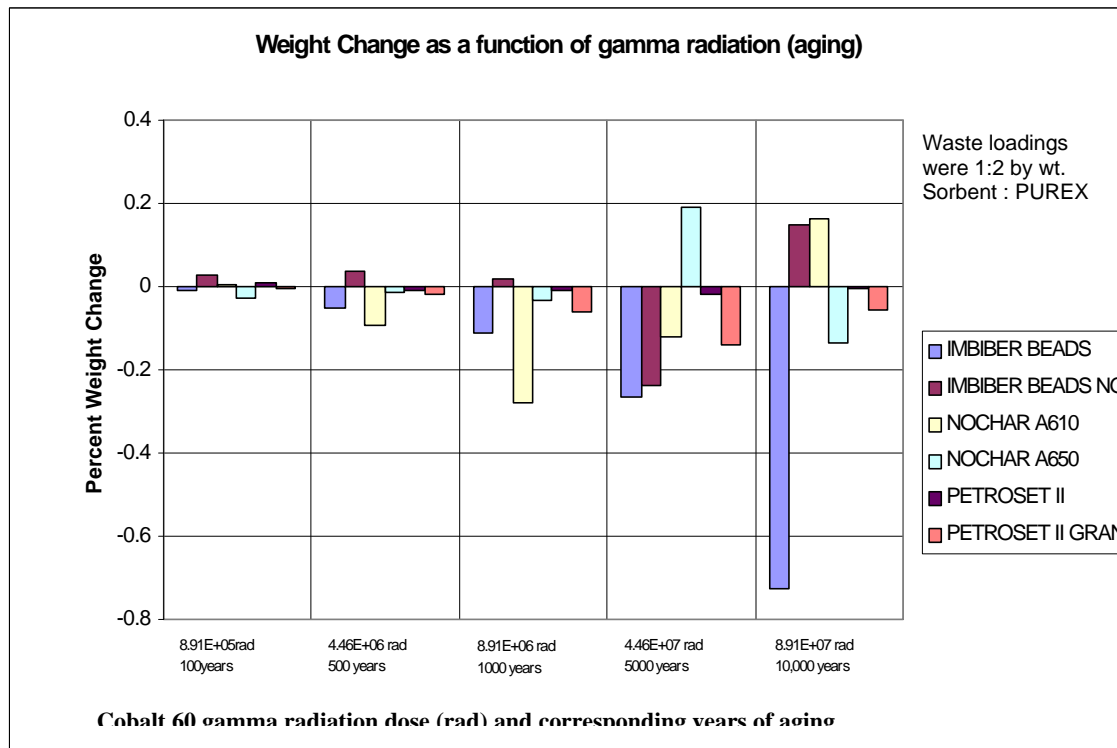


Figure 4-19. Weight change of the sorbent:PUREX waste forms as a function of exposure to gamma irradiation.

4.2.6.3 Degradation Effects from Ultraviolet Light Exposure

A pale yellow discoloration was evident for all of the waste form samples, except the brown-gray Petroset II samples, within a few hours of exposure to UV light. The color darkened progressively to a deeper yellow after 90 hours. The development of chromophores (color centers) indicates that the UV light degrades the materials. Physical changes in samples exposed to ultraviolet light are given in Table 4-15 and illustrated in Figure 4-20.

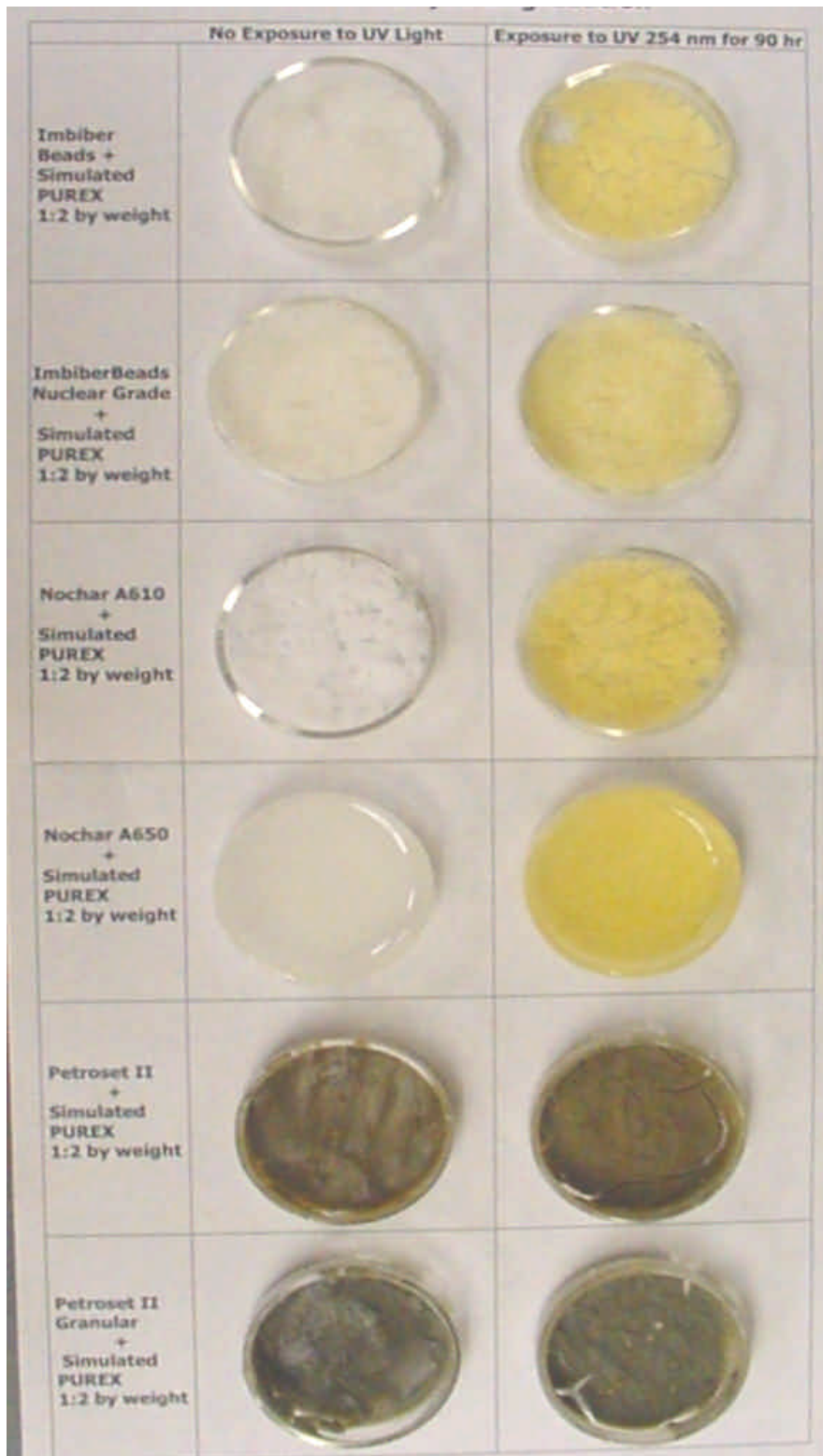


Figure 4-20. Degradation of the PUREX waste forms after exposure to 254 nm ultraviolet light for 90 hours.

PUREX simulant also showed color changes as the result of UV exposure. Therefore, all of the waste forms made with organic polymer sorbents are subject to UV degradation. Due to the dark gray color and fine-grained nature of the Petroset II waste forms it was not possible to discern color changes and degradation.

FTIR spectra also indicate chemical changes in the waste form compounds. These changes are listed in Table 4-16. Unlike gamma radiation, which penetrates the bulk of the material, the UV radiation, affects only the impinged surfaces.

Table 4-17. FTIR spectra for waste forms exposed to UV light.

Waste Form	FTIR spectra results
Imbiber Beads™-Simulated PUREX Waste Forms	Formation of C=O bonds Formation of C-O-C (ether)
Imbiber NG™-Simulated PUREX Waste Forms	Formation of C=O bonds
Nochar A610™-Simulated PUREX Waste Forms	No change
Nochar A650™-Simulated PUREX Waste Forms	Formation of C=C and C=O bonds
Petroset II™ and Petroset II Granular™-Simulated PUREX Waste Forms	No change

4.2.6.4 Hydration of Fresh and Aged Waste Forms

The 1:2 waste forms were soaked in water after receiving a gamma dose of 8.91E+07 rad. FTIR spectra of these hydrated waste forms were analyzed and the results are shown in Table 4-17. The formation of carboxyl compounds with O-C=O, C=O, and O=C-O-C bonds was correlated to the waste form becoming more hydrophilic.

Table 4-18. FTIR spectra for waste forms hydrated after exposure to Co-60 radiation.

Waste Form	FTIR spectra results
Imbiber Beads™-Simulated PUREX Waste Forms	Formation of carboxylate groups O-C=O
Imbiber NG™-Simulated PUREX Waste Forms	Same as above
Nochar A610™-Simulated PUREX Waste Forms	Formation of C=O and O=C-O-C groups
Nochar A650™-Simulated PUREX Waste Forms	Same as above
Petroset II™ and Petroset II Granular™-Simulated PUREX Waste Forms	Formation of C=O bonds

4.2.7 Microbial Degradation

Incubation of the six PUREX waste forms with a 1:2 waste loading was carried out according to ASTM G 21 (fungi) and ASTM G 22 (bacteria) test protocols [7 and 8, respectively]. The ASTM G 21 protocol was shortened from 28 to 21 days because only minimal fungal growth was observed during the first 21 days. The conclusion of this testing is that the solidified organic PUREX waste forms do not support microbial growth for the microbes specified in the ASTM test protocols. Alternative test protocols or modifications of ASTM G 22 (bacteria) are required to perform a more comprehensive evaluation of specialized microbes that may destroy the organic compounds in the waste in the shallow land disposal environment. A final report from Celsis Laboratory, Inc., containing details of the current testing is provided in Appendix E. Another report by Dr. R. D. Rogers summarizing the Celsis results providing recommendations for future testing is also included in Appendix E.

Results from the ASTM G 21 tests showed that there was minimal growth of all fungal species on the six waste forms tested. Fungal growth was noted around the margins of the waste forms but no direct growth was observed near or on the specimens. It appears that the waste forms could have actually prevented fungal growth. It is for this reason that the test period was shortened by six days. Overall the test results were given a rating of 1 per the test protocol, which indicates the lowest level of fungal growth on the inoculated surfaces.

Light or no growth on specimens inoculated with the SRP bacteria, #17-3, was reported for all of the waste forms tested. However, this observation may be an artifact of the ASTM G 22 test protocol, which specifies incubation temperatures of 35 to 37°C. In retrospect, these temperatures are not in the ideal range for productive growth of most microorganisms isolated from the environment. If future testing of microorganisms isolated from the SRS near surface environment is conducted the experiments should be performed in the range of 23 to 28°C, which is considered optimal. The ASTM G 22 protocol test results for the bacteria #17-3, which was isolated from the aqueous-organic interface of the actual waste are considered inconclusive. However, they provide guidance for further work. Dr. Rogers recommends batch testing with a more varied suite of bacteria.

In summary, this testing indicated that neither the sorbent materials nor the PUREX waste was significantly degraded by the microbes and protocol used in this study. Furthermore, the testing indicated that no changes took place that would result in leaching of the PUREX from the waste forms.

5.0 DISCUSSION

5.1 Regulatory Classification of the PUREX Waste and Solidified Waste Forms

The organic PUREX waste, designated SR-W045 in the SRS Site Treatment Plan, is classified as a mixed waste since it is radioactive and is also classified as a nonwastewater that displays hazardous characteristics per RCRA [22]. The RCRA D-codes listed in the Site Treatment Plan were assigned on the basis of analyses of waste samples collected from the old solvent tanks in E-Area. Analyses of samples recently collected from the material composited in Tanks 33 and 35 are listed in Table 5-1 columns 2 and 3 [21]. These results along with process knowledge needed for the determination of the regulatory classification of the waste form.

All of the chemical data for metals and organics obtained in this study indicate that all of the waste forms tested qualify to exit RCRA regulation and to be disposed of as low-level radioactive solid waste. In addition, leaching results for the volatile and semivolatile organic compounds in the original waste indicate that the organic compounds in the waste are retained in the waste form (stabilized) during the leaching process.

The metals and organics used to make the hazardous waste determination are listed in Group I, Table 5-1 as RCRA Hazardous constituents. A comparison of the TCLP Hazardous Limits in Column 4 of Table 5-1 with the analytical results for the waste in tanks 33 and 35 (Columns 2 and 3) indicates:

- Based on earlier analyses, the spent PUREX waste exceeded the TCLP limits for As, Ag, Ba, Cd, Cr, Hg, Pb, Se, benzene and trichloroethylene (TCE) [21]. Consequently the waste currently carries RCRA D-codes for these characteristically hazardous constituents.
- Re-analysis of the waste for metals and organics indicates that using a lower detection limit indicated that the waste is not hazardous for As, Ba, Se, and TCE since the concentrations in samples from both tanks are less than 5, 100, 1mg/L and 5 mg/L total, respectively. Removal of the RCRA D-code for TCE is recommended based on these results.
- Reanalysis of the waste for PCE using a lower detection limit was performed because PCE is often associated with TCE. The waste is not characteristically hazardous for PCE.

Given that the organic PUREX waste is classified as characteristically hazardous, in order to exit RCRA regulation the potential for additional leachable Underlying Hazardous Constituents (UHC) must also be evaluated. This evaluation was made by comparing the TCLP leachate results for the UHCs (Group II, Columns 2 and 3, Table 5-1) to the UTS limits (Column 6, Table 5-1). This comparison indicates that Ni, Sb, and Tl are UHCs and must be treated so that the TCLP leachate concentrations are below the limit identified in Column 6.

In summary, in order to exit RCRA the organic PUREX waste must be treated to:

1. Remove the hazardous characteristics for As, Ag, Ba, Cd, Cr, Hg, Pb, Se, benzene and TCE (original analysis) toxicity, and
2. Meet the Universal Treatment Standards (UTS) for Ni, Sb, Tl. See Group II, Underlying Hazardous Constituents in Table 5-1.)

Table 5-1. Summary of the analytical results related to RCRA classification.

Column 1	Column 2	Column 3	Column 4	Col.5	Column 6	Column 7
Analyte	Tank 33 Organic Highest Value(s) [21, 22] (mg/L)	Tank 35 Organic Highest Value(s) [21, 22] (mg/L)	TCLP Haz. Limit [13] (mg/L)	RCRA Codes	LDR Treatment Standard Limit [23] (mg/L in TCLP Leachate)	Worst Case Total Concentration in the PUREX Waste (mg/L)
Group I. RCRA Hazardous Constituents						
As	1.297 1.320	1.368 1.651	5	D004	5	
Ba	<2	<2	100	D005	21	
Cd	<3	<3	1	D006	0.11	
Cr	10	<7	5	D007	0.6	
Pb	<27	<27	5	D008	0.75	
Hg	0.9501 0.9802	0.4194 0.6280	0.2	D009	0.025	
Se	0.4505 0.6124	0.7850 0.6387	<1*	D010	5.7	
Ag	<6	<6	5	D011	0.14	
Benzene	<50	<50	0.5 mg/L total	D018	10 (mg/kg) total	5.6 mg/kg total in the organic liquid waste
Trichloro ethylene (TCE)	<50	<50	0.5 mg/L total	D040	6 (mg/kg) total	0.33 mg/kg total in the organic liquid waste
Tetrachloro ethylene (PCE)	--	--	0.7 mg/L total	D039	6 (mg/kg) total	0.16 mg/kg total in the organic liquid waste
Group II. Underlying Hazardous Constituents					UTS Limits [24] (mg/L in TCLP Leachate)	
Be	<1	<1	--		1.22	
Ni	25	15	--		11	
Sb	<64	<63	--		1.15	
Tl	<129	<129	--		0.2	

* If the waste contains >1 mg/kg Se, it is hazardous and carries a D-Code regardless of treatment and therefore must be disposed of in a RCRA Subtitle C landfill.

Bold type = Limits for the hazardous constituents that require treatment based on current analytical results and the treatment standards for these constituents. The limit for TCE is bold based on early results. Improved detection limits indicate that the waste is not hazardous for TCE.

Waste forms prepared by solidifying of the PUREX waste were tested to determine whether they met the above requirement. Waste forms with the highest waste loadings (1:2 by weight, i.e., 66 wt. %) were used for this comparison. The worst case (highest) leachate values for the metals and the highest total values for the organics were listed in Table 5-1, Column 7. A comparison of these results to the limits in Column 6 indicates that the treated waste is not hazardous. In conclusion, all six solidified PUREX waste forms (1:2 waste loadings) meet the requirements to exit RCRA and can be considered for disposal as low-level radioactive waste.

Finally, all analytical data must be certified to satisfy SC DHEC regulations. While SRTC analyses are acceptable for planning and engineering purposes, the final waste form must be analyzed by a SC DHEC certified laboratory in order to be land disposed. The complete list of UHCs (247) must be considered unless they are eliminated by process knowledge.

5.2 Disposal Options

All of the waste forms tested in this study meet the physical property and radionuclide requirements for disposal as low-level waste at the Nevada Test Site or in the SRS E-Area Facility. The waste forms also meet shipping requirements for the case of disposal at the NTS.

Additional characterization of the I-129 in the waste form leachates is necessary in order to select the appropriate SRS E-Area disposal option. Since the NTS does not have a ground water pathway for the release of radionuclides, additional testing/analyses are not necessary for NTS disposal.

The I-129 data obtained to date are less than values that are too high to enable reliable calculation of the I-129 partitioning coefficient between the waste form and leachate. The concentration of I-129 in the organic PUREX waste is also very low. Reported values are also at the detection limit. The less than values for the leachate typically indicated that the leachates contained more I-129 that was in the starting material.

Historically I-129 in solid waste is a common limiting factor in E-Area trench disposal because of the short ground water pathway and the low K_d currently applied to generic waste (0.6mL/g). Lower detection limits are expected to provide reproducible results that indicate stabilization of the I-129 in the waste forms since a mechanism for selective extraction of I-129 relative to the other constituents has not been identified.

5.3 Comparison of Sorbents Tested for Solidification of Organic PUREX Waste

The six sorbents used for solidify the organic PUREX from tanks 33 and 35 are compared in Table 5-2. Processing, transportation and storage properties, leaching and durability of the waste forms were used in the evaluation. Two of the sorbents, Imbiber beads NG and Nochar A650, resulted in waste forms that did not meet some of the requirements. Two of the four are basically the same inorganic material, Petroset II and Petroset II Granular. The other two, Imbiber Beads and Nochar A610 are organic polymers.

The Petroset II and Petroset II Granular waste forms had the lowest volume increase relative to the original waste volume (about 1.3 times increase) and were essentially unaffected by in all of the

Table 5-2. Comparison of sorbents for PUREX waste solidification.

Parameter	Imbiber-PUREX	Imbiber NG-PUREX	Nochar A610 PUREX	Nochar A650 PUREX	Petroset II-PUREX	Petroset II Gran.-PUREX
Processing						
Sorbent Handling	Light wt., “mm ball bearings”	Light wt., fluffy, not homogeneous	Light wt., Fluffy	Light wt., granular	Fine powder, dusty, nonflammable	Granular, nonflammable
Waste Form Mixing	Mixing required only for uniform distribution	Mixing required only for uniform distribution	Mixing required only for uniform distribution	Mixing required only for uniform distribution	Mixing required	Mixing required
Sorption Rate	Fast	Fast	v. Fast	Fast	Slow (24+ hr)	Slow (24+ hr)
Sorption Capacity	66 + wt % PUREX	66 wt % PUREX +/-	66 + wt % PUREX	50 wt. % max PUREX	66 + wt % PUREX	66 + wt % PUREX
Vol. waste:waste form	2	2	2.1	1.5	1.3	1.3
Waste form appearance	Sticky “ball bearings”	Sticky/fluffy particles	Soft clumps/particles	1:2 = flowable gel	Uncompress. Paste	Uncompress. Paste
Paint Filter/50 psi Liquid Release	Pass	Pass	Pass	Pass	Pass	Pass
Transportation/Storage						
Vibration Testing	Pass, no liquid release	Pass, no liquid release	Pass, no liquid release	Pass, no liquid release	Pass, no liquid release	Pass, no liquid release
Temperature to 150°C	No degradation	No degradation	No degradation	No degradation	No degradation	No degradation
Leaching						
TCLP/UTS	Exit RCRA	Exit RCRA	Exit RCRA	Exit RCRA	Exit RCRA	Exit RCRA
K _d I-129	E-Area or NTS	E-Area or NTS	E-Area or NTS	E-Area or NTS	E-Area or NTS	E-Area or NTS
Other radionuclides	E-Area or NTS	E-Area or NTS	E-Area or NTS	E-Area or NTS	E-Area or NTS	E-Area or NTS
Durability						
Radiation Stability	Good	Lowest	Good	Lowest	Best	Best
UV light	Good	Good	Good	Good	Good	Good
Microbial Attack	Limited to none	Limited to none	Limited to none	Limited to none	Limited to none	Limited to none
Exposure to Water	Hydrophobic	Swells, hydrophilic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic
Time (1-6 months)	--	--	--	Plasticizing	No change	No change
Ranking	Acceptable	Not Acceptable	Acceptable	Not Acceptable	Acceptable	Acceptable

Shading indicates lower than acceptable performance.

aging/degradation tests. The Imbiber Beads and the Nochar A610 have similar volume increases relative to the original waste volume (about 2 times) and became harder and less elastic (due to cross linking and new phase formation) as the result of the degradation testing. These changes did not result in an obvious release of the PUREX waste as was observed with the Nochar A650. Consequently the Nochar A610 and Imbiber Beads waste forms were considered to demonstrate long-term durability in the shallow land disposal environment.

5.4 Sorbents for Waste Treatment versus Spill Control

The specified properties of sorbent materials depend to some extent on the intended application. Very high sorption capacity and very rapid sorptivity are desirable for spill control and solidification of incidental liquids. Spill control materials must also be easily recovered. Therefore, fresh sorbents and used sorbents should be lightweight and granular (relatively dust free), and not leave a residue on contacted surfaces.

Very rapid sorption is not required and may be undesirable for solidifying waste oils and organic liquids especially when processing relatively large volumes of waste is required. It is relatively easy to combine a few gallons of organic waste with a fast acting sorbent designed for spill control. However, processing hundreds or thousands of gallons of waste presents challenges in achieving a uniform distribution of the waste in the waste form.

In addition, sorbents intended for spill control are designed to react with the organic liquid without mixing. Mixing “fluffs” the resulting product and significantly increases the volume of the final product. Bulking up of a sorbent is acceptable for solidification of small volumes of organic waste but it is undesirable for larger volumes of waste being treated for disposal in a solidification/stabilization process.

Slower acting sorbents may be more suitable for a process that requires mixing of the reagents and waste to achieve a uniform waste form. However, very slow sorption (days) is unsuitable because the processing time is effectively extended to include the storage/staging time. Consequently sorbents that are ideal for spill control may be unsuitable for waste form processing and vice versa.

Table 5-3. Properties of spill control sorbents versus waste treatment reagents.

Property	Spill Control	Small Volume Waste Treatment	Large Volume Waste Treatment
Rapid sorption	Required	Acceptable Provided a “crust” does not develop on the surface of the sorbent preventing penetration of the organic liquid	Problematic
High sorption capacity	Beneficial	Acceptable Same as above	Problematic
Granular particles	Beneficial	Acceptable	Acceptable
Spongy texture	Acceptable	Acceptable	May be Problematic in mixing
Non dusting	Beneficial	Beneficial	Beneficial

5.5 Review of Leaching Techniques for Hydrophobic Organic Waste Forms

The ANSI 16.1 accelerated leach test was used to evaluate the I-129 leaching from solidified PUREX waste forms. Modifications to this test are recommended for future work because:

The PUREX waste and the sorbents are hydrophobic (dislike water). Consequently, the wastefoms were not readily wetted by the leachate. However, in some cases the sorbents contained mixtures of organic and aqueous sorbents. The aqueous sorbents swelled in the leachate.

The waste forms had a density of less than water. Consequently, all of the waste forms floated in the deionized water leachate. The most hydrophobic waste forms floated on the surface of the leachate. (The hydrophobic behavior will also occur in the TCLP test.)

The low I-129 concentration necessitates a higher waste form to leachate ratio than specified in the ANSI 16.1 protocol. At least 50 to 100 gram samples will be leached in approximately 0.5 to 1 liter of leachate. Leaching will be performed at two time intervals, for example, 48 and 120 hours. Separate samples will be used for each leach interval. In the future, hydrophobic waste forms will be encased in an inert mesh basket that can be submerged in the leachate.

5.6 Accelerated Aging of Sorbents and Sorbent Waste Forms

Accelerated aging and degradation tests, including exposure to Co-60 gamma radiation, ultra violet light, elevated temperatures, and exposure to microbes, can be used to get an idea of the breakdown products as the result of exposure to certain conditions. The rate of breakdown and the proportion of these reaction products can not be obtained from the accelerated tests. In this study, the accelerated tests were used to compare sorbents and waste forms rather than to obtain life-time values.

Examples of the conclusions that can be drawn from this type of information include:

- The inorganic sorbents, Petroset II and Petroset II granular, are more resistant to aging damage (breaking of chemical bonds) from gamma and UV radiation than the organic sorbents, Nochar A610 and A650 and Imbiber Beads and Imbiber Beads NG.
- The inorganic filler in A650 (calcium carbonate) provides shielding and consequently, waste forms made with this sorbent show less deterioration than the Nochar products containing no inorganic filler.
- Polystyrene sorbents show less deterioration than butadiene or polyethylene for the waste forms prepared with simulated PUREX waste.

6.0 CONCLUSIONS

Solidification is a promising technology for treating the PUREX waste currently stored in H-Area, NSST for final disposal. Six sorbents were evaluated at two waste loadings, 50 and 66 wt % (1:1 and 1:2 formulations, respectively). All of the resulting waste forms prepared in this laboratory study met the general requirements for disposal as low-level waste in either E-Area/SRS or the Nevada Test Site. Environmental transport of I-129 may require further data and analysis for SRS E-Area disposal. However, actual disposal of any new waste stream in E-Area or the NTS requires that the generator obtain approval via the SRS Waste Certification process or the NTS Waste Profile acceptance process.

In addition to the regulatory criteria, long term properties including the potential for deleterious PUREX-sorbent interactions, were investigated and used to screen sorbents. Two organic sorbents, Imbiber Beads and Nochar A610, and two inorganic clay products, Petroset II and Petroset II Granular, warrant further testing.

The Imbiber Beads and the Nochar A610 have very rapid absorbencies and require rapid mixing to distribute the PUREX evenly throughout the waste form. The appearance, physical properties (except bulk density), leaching, and degradation properties/responses (heating, gamma radiation, and UV radiation) were the same for the 1:1 and 1:2 waste forms prepared with each sorbent. Therefore, 1:2 waste loadings are recommended for further testing.

Petroset II Granular sorbent reacts with the PUREX waste much more slowly than Petroset II and the organic polymer sorbents. After initial high-shear mixing, the Petroset II Granular waste forms required about 8 hours to completely absorb the PUREX. The Petroset II is a very fine powder and has a higher surface area. Therefore it absorbs the PUREX much faster than the Petroset II Granular.

Waste forms made with the inorganic Petroset sorbents underwent less degradation from heating, gamma radiation, and UV radiation than the waste forms made with the organic polymer sorbents. In addition, the Petroset waste forms appear to react with some components in the PUREX waste such that these components are chemically bound in the alumino silicate (clay) structure.

Imbiber Beads Nuclear Grade and Nochar A650 were not recommended for further testing. The Imbiber Beads Nuclear Grade contains both water and organic liquid sorbents, and swells on contact with water. The polymer sorbents in the Nochar A650 are plasticized (degraded) by components in the PUREX waste (probably the tributylphosphate).

Finally, it is worth emphasizing that the organic polymer sorbents were originally designed to control (rapidly absorb) organic liquid spills. Therefore it is difficult to achieve specific waste to sorbent ratios. This issue must be addressed by the mixing system used to combine the organic liquid stream with the polymer sorbent.

7.0 RECOMMENDATIONS

1. Four of the six sorbent reagents evaluated warrant further study to optimize:
 - waste loading,
 - physical properties, and
 - engineering and processing properties.For example, preliminary testing indicates that the consistency of the Petroset waste forms can be modified to a solid monolith by the addition of 10 to 30 weight percent portland cement.
2. Conduct pilot-scale-processing studies on the Imbiber Beads, Nochar A610, and Petroset II and Petroset II Granular, and include the results in the selection process for identifying a candidate reagent for treating spent PUREX waste.
3. Confirm the simulant used in the pilot-scale process testing by solidifying 1 to 10 liter batches of actual waste.
4. Review the I-129 analytical method and determine whether lower detection limits are possible. Re-calculate I-129 K_d values based on reassessment of I-129 leaching and detection limits. Reassess E-Area trench disposal based on this information.
5. Complete a Waste Profile for the Nevada Test Site and Initiate the Waste Certification process for a new waste form to establish that the solidified PUREX waste form is or is not accepted for disposal.

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C. L. Crawford, RPP/SRTC and D. Chris Beam, performed the dose calculations and managed the samples in the Co-60 source, respectively. G. D. Creech, MP&CT and M. P. Bussey and S. C. Smith, WPT/SRTC prepared samples for testing. Sample analyses were performed by A. R. Jurgensen, S. L. Crump, D. P. Diprete, J. E. Young, C. J. Coleman, ADS/SRTC. L. M. G. Looper, P&T/SW, coordinated sampling of Tanks 33 and 35. L. B. Collard, WPT, performed a Special Analysis for disposal of the solidified PUREX waste in various SRS E-Area disposal facilities. L. C. Martin, M. Hawkins, and B. M. Lawrence, evaluated the RCRA regulatory classification of the PUREX waste and solidified waste forms.

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**10.0 APPENDIX A. ANALYSES OF SPENT PUREX WASTE IN TANKS
33 AND 35**

Radioactive Analysis Results		Tank 33		Tank 35
Radioactive Constituents		Organic		Organic
		dpm/mL		dpm/mL
Pu-238		3.08E+04		6.45E+04
Pu-239		7.21E+02		3.42E+03
Pu-240		1.80E+02		8.56E+02
Pu-241		7.28E+03		1.91E+04
Pu-242		<9.69E+02		<9.69E+02
U-233		<2.37E+03		<2.37E+03
U-234		<1.53E+03		<1.53E+03
U-235		<5.33E-01		1.50E+00
U-236		<1.59E+01		<1.59E+01
U-238		2.64E-01		1.08E+02
Am-241		1.16E+03		1.41E+04
Am-243		1.83E+02		7.77E+02
Cm-244		2.12E+04		5.29E+04
Cm-245		<4.23E+04		<4.23E+04
Cm-246		<7.53E+04		<7.53E+04
Np-237		<1.74E+02		<1.74E+02
Np-239		1.37E+02		4.07E+02
Th-232		3.50E-02		5.76E-02
Ni-59	UL	<1.68E+02		<5.60E+01
Ni-63	UL	<8.85E+02		<1.49E+03
Tc-99	UL	<1.63E+02	UL	<3.51E+02
Sr-90		<4.47E+03		1.09E+04
Co-60		<1.40E+01		4.90E+01
Ru-106		<1.23E+02		<1.85E+02
Sb-125		<3.52E+01		1.13E+02
Cs-134		<1.22E+01		<1.98E+01
Cs-137		1.60E+01		3.16E+02
Eu-154		9.25E+02		2.45E+03
Eu-155		8.49E+01		5.15E+02
Ra-226	UL	<2.16E+02		<3.02E+02
Pa-234m/U238		<3.08E+01		<5.40E+01
Se-79		N/A		N/A
I-129		<1.49E+02		<2.04E+02
C-14		<1.77E+02		<1.17E+02
Tritium		2.66E+02		2.44E+02
Alpha		6.55E+04		1.87E+05
Beta		9.92E+03		3.55E+04
Gamma		2.49E+03		1.87E+04

UL - Denotes sample results as upper limits because of the evidence of other species or x-ray interference's that were close to the x-ray energy and biased the fitting of the x-ray region.
< - Indicates detection limit values.
N/A - Not Available (Organic not analyzed for Se-79)

RCRC Metal Analyses

Metals	Applicable D Codes For the Waste	Applicable UHC	UTS Limits (mg/L)	Haz Limit (mg/L)	Tank 33 Organic Waste (mg/L)	Tank 35 Organic Waste (mg/L)
As	X		5	5	1.297/1.320	1.368/1.651
Se	X		5.7	<1*	0.4505/0.6124	0.7850/0.6387
Hg	X		0.025	0.2	0.9501/0.9802	0.4194/0.6280
Ag	X		0.14	5	<6	<6
Ba	X		21	100	<2	<2
Be			1.22		<1	<1
Cd	X		0.1	1	<3	<3
Cr	X		0.6	5	10	<7
Ni		X	11		25	15
Pb	X		0.75	5	<27	<27
Sb		X	1.15		<64	<63
Tl		X	0.2		<129	<129
V					<3	<3
Zn					64	42
Zr					<4	<4

*Under Part 261, if waste is 1 ppm or greater, it is hazardous and carries a D code and must be disposed of in a RCRA Subtitle C landfill.

Chemical Analysis Results	Tank 33 Organic	Tank 35 Organic
Volume (gallons)	14,000	10,800
Specific Gravity	0.8254	0.8278
PH	N/A	N/A
Volatiles	% Conc.	% Conc.
Aliphatic Hydrocarbons	0.74	0.67
Aromatic Hydrocarbons	0.31	7.1
Butanol		
	mg/L	mg/L
Benzene	<50	<50
Trichloroethylene	<50	<50
Semivolatiles		
Aliphatic Hydrocarbons	22	34
Aromatic Hydrocarbons	48	23
Tributyl Phosphate	8.7	20
Aliphatic Amines	8.4	2.7
Anions	ug/mL	ug/mL
Chloride	ND	ND
Nitrate	ND	ND
Nitrite	ND	ND
Oxalate	ND	ND
Sulfate	ND	ND
Phosphate	ND	ND
Formate	ND	ND
Fluoride		
	ug/mL	ug/mL
Cations		
Ammonium ion	ND	ND
Sodium	9.24	1.91
Dibutyl Phosphate	ND	ND

ND = Not Detected.

**11.0 APPENDIX B. DOSE CALCULATIONS FOR COBALT-60
IRRADIATION**

Table 1 Tank 33 Aqueous Data

Tank 33 Aqueous			Radionuclide	% of Total	Half Life	Decay	Mev/dis	Initial Absorbed
				Activity	Years	Constant		Dose
	Dpm/mL	Ci/g				(years) ⁻¹		(R)
	1.95E+03	8.78E-10	Pu-239	0.01	2.41E+04	2.87E-05	5.10E+00	8.33E+01
	5.50E+02	2.48E-10	Pu-240	0.00	6.56E+03	1.06E-04	5.16E+00	2.38E+01
	1.11E+05	5.00E-08	Pu-238	0.42	8.77E+01	7.90E-03	5.50E+00	5.11E+03
	2.36E+04	1.06E-08	Pu-241	0.09	1.44E+01	4.81E-02	5.30E-03	1.05E+00
<	9.78E+01	4.41E-11	Pu-242	0.00	3.76E+05	1.84E-06	4.90E+00	4.02E+00
<	2.40E+02	1.08E-10	U-233	0.00	1.59E+05	4.35E-06	4.82E+00	9.69E+00
	1.93E+02	8.69E-11	U-234	0.00	2.45E+05	2.82E-06	4.77E+00	7.72E+00
	1.14E+00	5.14E-13	U-235	0.00	7.04E+08	9.85E-10	4.58E+00	4.37E-02
	1.92E+00	8.65E-13	U-236	0.00	2.34E+07	2.96E-08	4.49E+00	7.23E-02
	7.44E+01	3.35E-11	U-238	0.00	4.47E+09	1.55E-10	4.21E+00	2.62E+00
	8.60E+03	3.87E-09	Cm-244	0.03	1.81E+01	3.83E-02	5.80E+00	4.18E+02
<	4.27E+03	1.92E-09	Cm-245	0.02	8.50E+03	8.15E-05	5.62E+00	2.01E+02
<	7.60E+03	3.42E-09	Cm-246	0.03	4.73E+03	1.47E-04	5.39E+00	3.43E+02
	2.21E+02	9.95E-11	Co-60	0.00	5.27E+00	1.31E-01	2.60E+00	4.82E+00
<	7.08E+00	3.19E-12	Cs-134	0.00	2.06E+00	3.36E-01	1.72E+00	1.02E-01
	5.48E+04	2.47E-08	Cs-137	0.21	3.02E+01	2.30E-02	8.30E-01	3.81E+02
	3.57E+02	1.61E-10	Eu-154	0.00	8.80E+00	7.88E-02	1.53E+00	4.58E+00
<	5.64E+01	2.54E-11	Eu-155	0.00	4.96E+00	1.40E-01	1.28E-01	6.05E-02
<	6.46E+02	2.91E-10	Ra-226	0.00	1.60E+03	4.33E-04	4.78E+00	2.59E+01
	5.13E+02	2.31E-10	I-129	0.00	1.57E+07	4.41E-08	8.04E-02	3.46E-01
	2.05E+02	9.23E-11	C-14	0.00	5.73E+03	1.21E-04	4.95E-02	8.50E-02
	4.66E+04	2.10E-08	H-3	0.18	1.23E+00	5.62E-01	5.68E-03	2.22E+00
<	1.75E+01	7.88E-12	Np-237	0.00	2.14E+06	3.24E-07	4.86E+00	7.12E-01
<	4.77E+01	2.15E-11	Np-239	0.00	6.45E-03	1.07E+02	4.26E-01	1.70E-01
	6.16E-03	2.77E-15	Th-232	0.00	1.41E+10	4.93E-11	4.01E+00	2.07E-04
<	4.44E+01	2.00E-11	Ni-59	0.00	7.50E+04	9.24E-06	6.72E-03	2.50E-03
<	1.70E+02	7.66E-11	Ni-63	0.00	1.00E+02	6.92E-03	1.71E-02	2.44E-02
<	1.46E+03	6.58E-10	Tc-99	0.01	2.13E+05	3.25E-06	8.46E-02	1.03E+00
	1.16E+02	5.23E-11	Sr-90	0.00	2.85E+01	2.43E-02	1.13E+00	1.10E+00
<	3.53E+01	1.59E-11	Ru-106	0.00	1.02E+00	6.79E-01	3.20E+00	9.46E-01
<	2.26E+02	1.02E-10	Sb-125	0.00	2.73E+00	2.54E-01	5.69E-01	1.08E+00
	3.62E+02	1.63E-10	Am-241	0.00	4.33E+02	1.60E-03	5.54E+00	1.68E+01
<	3.37E+02	1.52E-10	Am-243	0.00	7.38E+03	9.39E-05	5.31E+00	1.50E+01
Sums:		1.19E-07		1.00				6.66E+03

Table 2 Tank 33 Organic Data

Tank 33			Radionuclide	% of Total	Half Life	Decay	Mev/dis	Initial Absorbed
Organic				Activity	Years	Constant		Dose
	Dpm/mL	Ci/g				(years) ⁻¹		(R)
	7.21E+02	4.11E-10	Pu-239	0.00	2.41E+04	2.87E-05	5.10	3.9E+01
	1.80E+02	1.03E-10	Pu-240	0.00	6.56E+03	1.06E-04	5.16	9.8E+00
	3.08E+04	1.76E-08	Pu-238	0.11	8.77E+01	7.90E-03	5.50	1.8E+03
	7.28E+03	4.15E-09	Pu-241	0.03	1.44E+01	4.81E-02	0.01	4.1E-01
<	9.69E+02	5.53E-10	Pu-242	0.00	3.76E+05	1.84E-06	4.90	5.0E+01
<	2.40E+02	1.37E-10	U-233	0.00	1.59E+05	4.35E-06	4.82	1.2E+01
<	1.53E+03	8.72E-10	U-234	0.01	2.45E+05	2.82E-06	4.77	7.7E+01
<	0.533	3.04E-13	U-235	0.00	7.04E+08	9.85E-10	4.58	2.6E-02
<	1.59E+01	9.07E-12	U-236	0.00	2.34E+07	2.96E-08	4.49	7.6E-01
	2.64E-01	1.51E-13	U-238	0.00	4.47E+09	1.55E-10	4.21	1.2E-02
	2.12E+04	1.21E-08	Cm-244	0.07	1.81E+01	3.83E-02	5.80	1.3E+03
<	4.23E+04	2.41E-08	Cm-245	0.15	8.50E+03	8.15E-05	5.62	2.5E+03
<	7.53E+04	4.29E-08	Cm-246	0.26	4.73E+03	1.47E-04	5.39	4.3E+03
<	1.40E+01	7.98E-12	Co-60	0.00	5.27E+00	1.31E-01	2.60	3.9E-01
<	7.08	4.04E-12	Cs-134	0.00	2.06E+00	3.36E-01	1.72	1.3E-01
	1.60E+01	9.12E-12	Cs-137	0.00	3.02E+01	2.30E-02	0.83	1.4E-01
	9.25E+02	5.27E-10	Eu-154	0.00	8.80E+00	7.88E-02	1.53	1.5E+01
	8.49E+01	4.84E-11	Eu-155	0.00	4.96E+00	1.40E-01	0.13	1.2E-01
<	6.46E+02	3.68E-10	Ra-226	0.00	1.60E+03	4.33E-04	4.78	3.3E+01
<	1.49E+02	8.50E-11	I-129	0.00	1.57E+07	4.41E-08	0.08	1.3E-01
	9.93E+04	5.66E-08	C-14	0.34	5.73E+03	1.21E-04	0.05	5.2E+01
	2.66E+02	1.52E-10	H-3	0.00	1.23E+00	5.62E-01	0.01	1.6E-02
<	1.75E+01	9.98E-12	Np-237	0.00	2.14E+06	3.24E-07	4.86	9.0E-01
	1.37E+02	7.81E-11	Np-239	0.00	6.45E-03	1.07E+02	0.43	6.2E-01
	3.50E-02	2.00E-14	Th-232	0.00	1.41E+10	4.93E-11	4.01	1.5E-03
<	1.68E+02	9.58E-11	Ni-59	0.00	7.50E+04	9.24E-06	0.01	1.2E-02
<	8.85E+02	5.05E-10	Ni-63	0.00	1.00E+02	6.92E-03	0.02	1.6E-01
<	1.63E+02	9.29E-11	Tc-99	0.00	2.13E+05	3.25E-06	0.08	1.5E-01
<	4.41E+03	2.51E-09	Sr-90	0.02	2.85E+01	2.43E-02	1.13	5.3E+01
<	3.53E+01	2.01E-11	Ru-106	0.00	1.02E+00	6.79E-01	3.20	1.2E+00
<	1.13E+02	6.44E-11	Sb-125	0.00	2.73E+00	2.54E-01	0.57	6.8E-01
	1.16E+03	6.61E-10	Am-241	0.00	4.33E+02	1.60E-03	5.54	6.8E+01
	1.83E+02	1.04E-10	Am-243	0.00	7.38E+03	9.39E-05	5.31	1.0E+01
Sums:		1.65E-07		1.00				1.03E+04

Table 3 Tank 35 Aqueous Data

Tank 35 Aqueous			Radionuclide	% of Total	Half Life	Decay	Mev/dis	Initial Absorbed
	dpm/mL	Ci/g		Activity	Years	Constant (years) ⁻¹		Dose (R)
	2.95E+02	1.33E-10	Pu-239	0.00	2.41E+04	2.87E-05	5.10E+00	1.26E+01
	7.38E+01	3.32E-11	Pu-240	0.00	6.56E+03	1.06E-04	5.16E+00	3.19E+00
	1.51E+04	6.80E-09	Pu-238	0.14	8.77E+01	7.90E-03	5.50E+00	6.96E+02
	2.93E+03	1.32E-09	Pu-241	0.03	1.44E+01	4.81E-02	5.30E-03	1.30E-01
<	9.78E+01	4.41E-11	Pu-242	0.00	3.76E+05	1.84E-06	4.90E+00	4.02E+00
<	2.37E+03	1.07E-09	U-233	0.02	1.59E+05	4.35E-06	4.82E+00	9.57E+01
<	1.55E+02	6.98E-11	U-234	0.00	2.45E+05	2.82E-06	4.77E+00	6.20E+00
	6.79E-01	3.06E-13	U-235	0.00	7.04E+08	9.85E-10	4.58E+00	2.60E-02
<	1.61E+00	7.25E-13	U-236	0.00	2.34E+07	2.96E-08	4.49E+00	6.06E-02
	4.45E+01	2.00E-11	U-238	0.00	4.47E+09	1.55E-10	4.21E+00	1.57E+00
	3.17E+02	1.43E-10	Cm-244	0.00	1.81E+01	3.83E-02	5.80E+00	1.54E+01
<	4.27E+03	1.92E-09	Cm-245	0.04	8.50E+03	8.15E-05	5.62E+00	2.01E+02
<	7.60E+03	3.42E-09	Cm-246	0.07	4.73E+03	1.47E-04	5.39E+00	3.43E+02
	7.37E+01	3.32E-11	Co-60	0.00	5.27E+00	1.31E-01	2.60E+00	1.61E+00
	7.08E+00	3.19E-12	Cs-134	0.00	2.06E+00	3.36E-01	1.72E+00	1.02E-01
	2.29E+04	1.03E-08	Cs-137	0.21	3.02E+01	2.30E-02	8.30E-01	1.59E+02
	2.51E+02	1.13E-10	Eu-154	0.00	8.80E+00	7.88E-02	1.53E+00	3.22E+00
	5.64E+01	2.54E-11	Eu-155	0.00	4.96E+00	1.40E-01	1.28E-01	6.05E-02
	6.46E+02	2.91E-10	Ra-226	0.01	1.60E+03	4.33E-04	4.78E+00	2.59E+01
	3.39E+01	1.53E-11	I-129	0.00	1.57E+07	4.41E-08	8.04E-02	2.28E-02
<	1.31E+02	5.90E-11	C-14	0.00	5.73E+03	1.21E-04	4.95E-02	5.43E-02
	4.44E+04	2.00E-08	H-3	0.41	1.23E+00	5.62E-01	5.68E-03	2.11E+00
<	1.75E+01	7.88E-12	Np-237	0.00	2.14E+06	3.24E-07	4.86E+00	7.12E-01
	4.77E+01	2.15E-11	Np-239	0.00	6.45E-03	1.07E+02	4.26E-01	1.70E-01
	3.08E-03	1.39E-15	Th-232	0.00	1.41E+10	4.93E-11	4.01E+00	1.03E-04
<	4.73E+02	2.13E-10	Ni-59	0.00	7.50E+04	9.24E-06	6.72E-03	2.66E-02
<	1.08E+03	4.86E-10	Ni-63	0.01	1.00E+02	6.92E-03	1.71E-02	1.55E-01
<	3.84E+02	1.73E-10	Tc-99	0.00	2.13E+05	3.25E-06	8.46E-02	2.72E-01
	1.81E+03	8.15E-10	Sr-90	0.02	2.85E+01	2.43E-02	1.13E+00	1.71E+01
	3.53E+01	1.59E-11	Ru-106	0.00	1.02E+00	6.79E-01	3.20E+00	9.46E-01
	2.26E+02	1.02E-10	Sb-125	0.00	2.73E+00	2.54E-01	5.69E-01	1.08E+00
	1.55E+03	6.98E-10	Am-241	0.01	4.33E+02	1.60E-03	5.54E+00	7.19E+01
	9.12E+01	4.11E-11	Am-243	0.00	7.38E+03	9.39E-05	5.31E+00	4.06E+00
Sums:		4.84E-08		1.00				1.67E+03

Table 4 Tank 35 Organic Data

Tank 35 Organic			Radionuclide	% of Total	Half Life	Decay	Mev/dis	Initial Absorbed
	Dpm/mL	Ci/g		Activity	Years	Constant		Dose
						(years) ⁻¹		(R)
	3.42E+03	1.95E-09	Pu-239	0.01	2.41E+04	2.87E-05	5.10E+00	1.85E+02
	8.56E+02	4.88E-10	Pu-240	0.00	6.56E+03	1.06E-04	5.16E+00	4.68E+01
	6.45E+04	3.68E-08	Pu-238	0.22	8.77E+01	7.90E-03	5.50E+00	3.76E+03
	1.91E+04	1.09E-08	Pu-241	0.06	1.44E+01	4.81E-02	5.30E-03	1.07E+00
<	9.69E+02	5.53E-10	Pu-242	0.00	3.76E+05	1.84E-06	4.90E+00	5.04E+01
<	2.37E+03	1.35E-09	U-233	0.01	1.59E+05	4.35E-06	4.82E+00	1.21E+02
<	1.53E+03	8.72E-10	U-234	0.01	2.45E+05	2.82E-06	4.77E+00	7.74E+01
	1.50E+00	8.55E-13	U-235	0.00	7.04E+08	9.85E-10	4.58E+00	7.28E-02
<	1.59E+01	9.07E-12	U-236	0.00	2.34E+07	2.96E-08	4.49E+00	7.57E-01
	1.08E+02	6.16E-11	U-238	0.00	4.47E+09	1.55E-10	4.21E+00	4.82E+00
	5.29E+04	3.02E-08	Cm-244	0.18	1.81E+01	3.83E-02	5.80E+00	3.25E+03
<	4.23E+04	2.41E-08	Cm-245	0.14	8.50E+03	8.15E-05	5.62E+00	2.52E+03
<	7.53E+04	4.29E-08	Cm-246	0.25	4.73E+03	1.47E-04	5.39E+00	4.30E+03
	4.90E+01	2.79E-11	Co-60	0.00	5.27E+00	1.31E-01	2.60E+00	1.35E+00
	3.16E+02	1.80E-10	Cs-137	0.00	3.02E+01	2.30E-02	8.30E-01	2.78E+00
	2.45E+03	1.40E-09	Eu-154	0.01	8.80E+00	7.88E-02	1.53E+00	3.98E+01
	5.15E+02	2.94E-10	Eu-155	0.00	4.96E+00	1.40E-01	1.28E-01	6.99E-01
<	6.46E+02	3.68E-10	Ra-226	0.00	1.60E+03	4.33E-04	4.78E+00	3.28E+01
<	2.04E+02	1.16E-10	I-129	0.00	1.57E+07	4.41E-08	8.04E-02	1.74E-01
<	1.17E+02	6.67E-11	C-14	0.00	5.73E+03	1.21E-04	4.95E-02	6.14E-02
	2.44E+02	1.39E-10	H-3	0.00	1.23E+00	5.62E-01	5.68E-03	1.47E-02
<	1.75E+01	9.98E-12	Np-237	0.00	2.14E+06	3.24E-07	4.86E+00	9.01E-01
	4.07E+02	2.32E-10	Np-239	0.00	6.45E-03	1.07E+02	4.26E-01	1.84E+00
	5.76E-02	3.28E-14	Th-232	0.00	1.41E+10	4.93E-11	4.01E+00	2.45E-03
<	5.60E+01	3.19E-11	Ni-59	0.00	7.50E+04	9.24E-06	6.72E-03	3.99E-03
<	1.49E+03	8.50E-10	Ni-63	0.01	1.00E+02	6.92E-03	1.71E-02	2.70E-01
<	3.51E+02	2.00E-10	Tc-99	0.00	2.13E+05	3.25E-06	8.46E-02	3.15E-01
	1.09E+04	6.22E-09	Sr-90	0.04	2.85E+01	2.43E-02	1.13E+00	1.31E+02
<	3.53E+01	2.01E-11	Ru-106	0.00	1.02E+00	6.79E-01	3.20E+00	1.20E+00
	1.13E+02	6.44E-11	Sb-125	0.00	2.73E+00	2.54E-01	5.69E-01	6.82E-01
	1.41E+04	8.04E-09	Am-241	0.05	4.33E+02	1.60E-03	5.54E+00	8.28E+02
	7.77E+02	4.43E-10	Am-243	0.00	7.38E+03	9.39E-05	5.31E+00	4.38E+01
Sums:		1.69E-07		1.00				1.54E+04

Table 5 Data for Co-60 Irradiations

Time (h)	0.9	4.5	9	45	90
Dose (Rad)	8.91E+05	4.46E+06	8.91E+06	4.46E+07	8.91E+07
Years	100	500	1000	5000	10000

12.0 APPENDIX C. TGA/DTA FOR SIMULATED SPENT PUREX-SORBENT WASTE FORMS

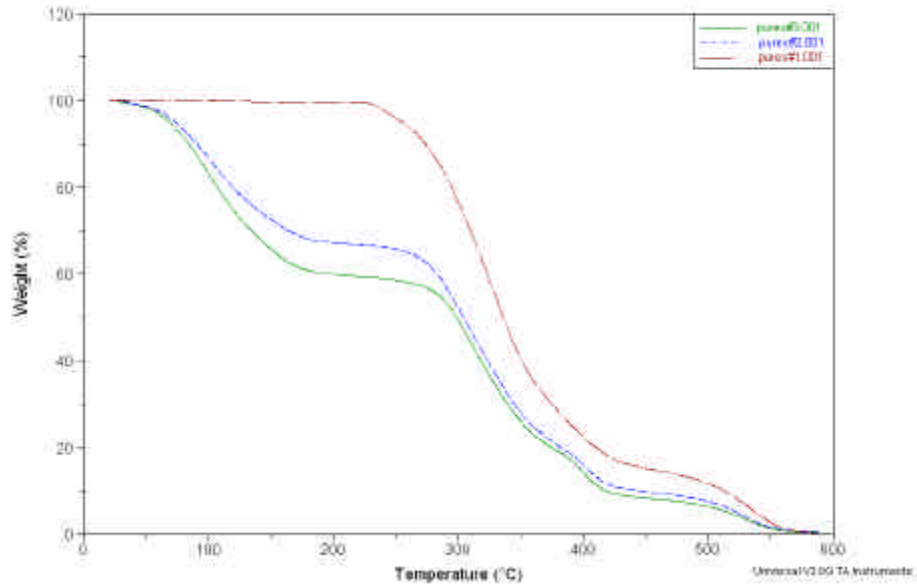


Figure C-1. TGA: Imbiber –Simulated Purex 1:1 and 1:2 Waste Forms and Simulated PUREX Waste.

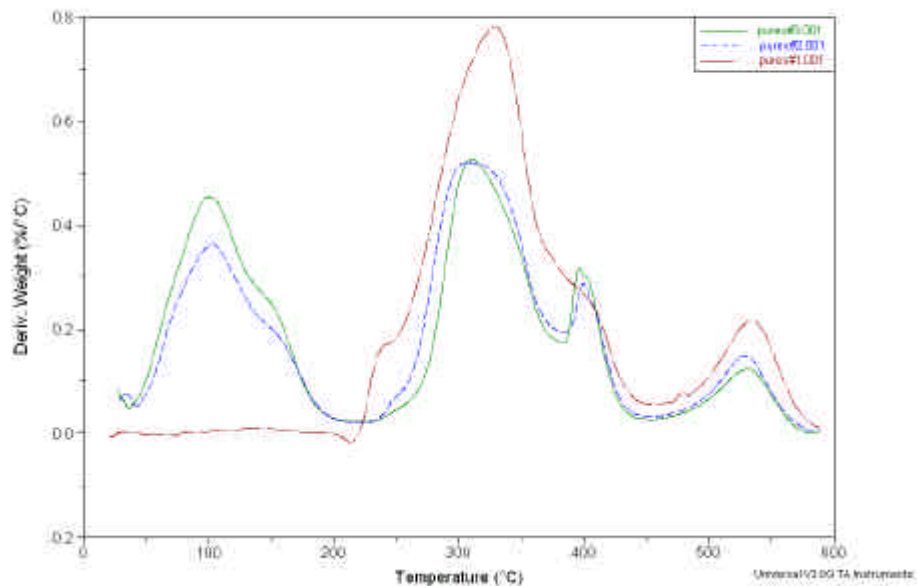


Figure C-2. DTA: Imbiber –Simulated Purex 1:1 and 1:2 Waste Forms and Simulated PUREX Waste.

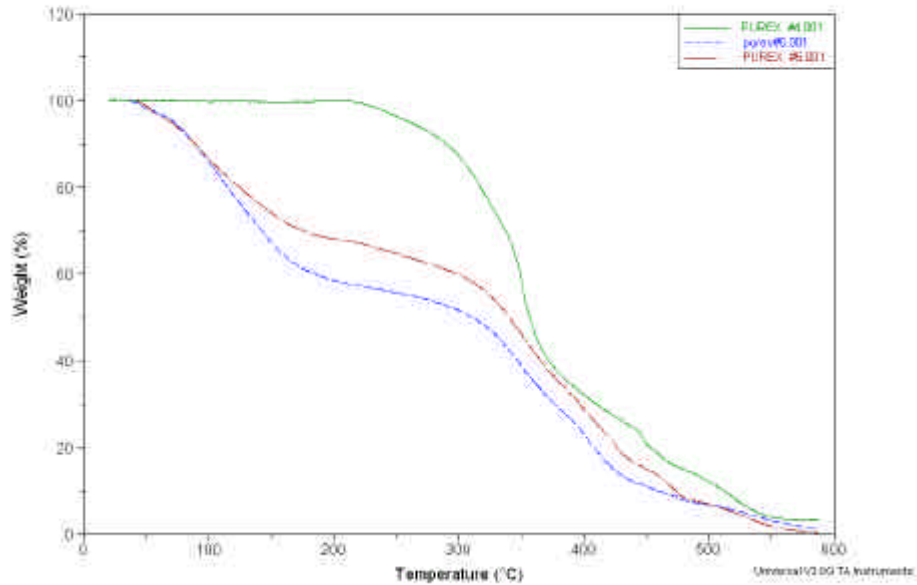


Figure C-3. TGA: Imbiber Nuclear Grade–Simulated Purex 1:1 and 1:2 Waste Forms and Simulated PUREX Waste.

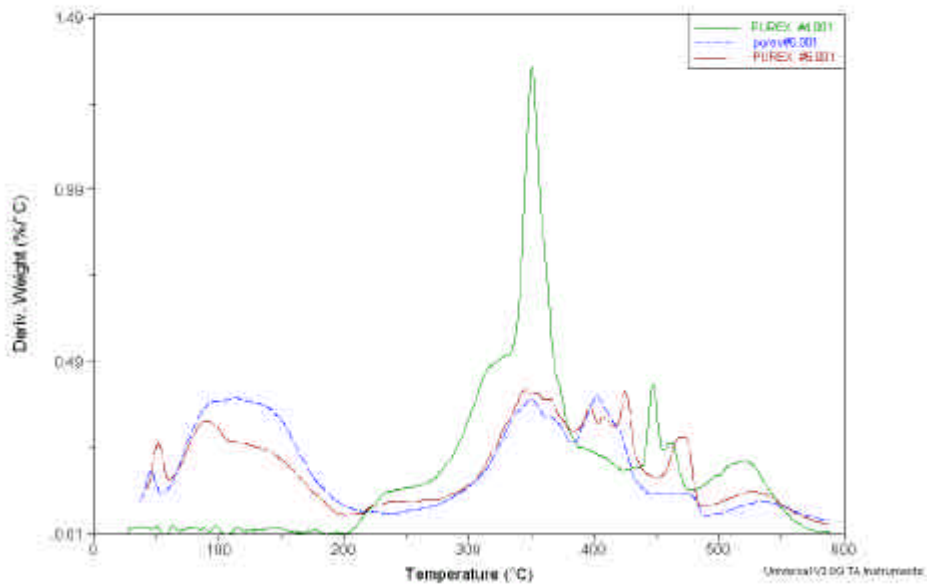


Figure C-4. DTA: Imbiber Nuclear Grade –Simulated Purex 1:1 and 1:2 Waste Forms and Simulated PUREX Waste.

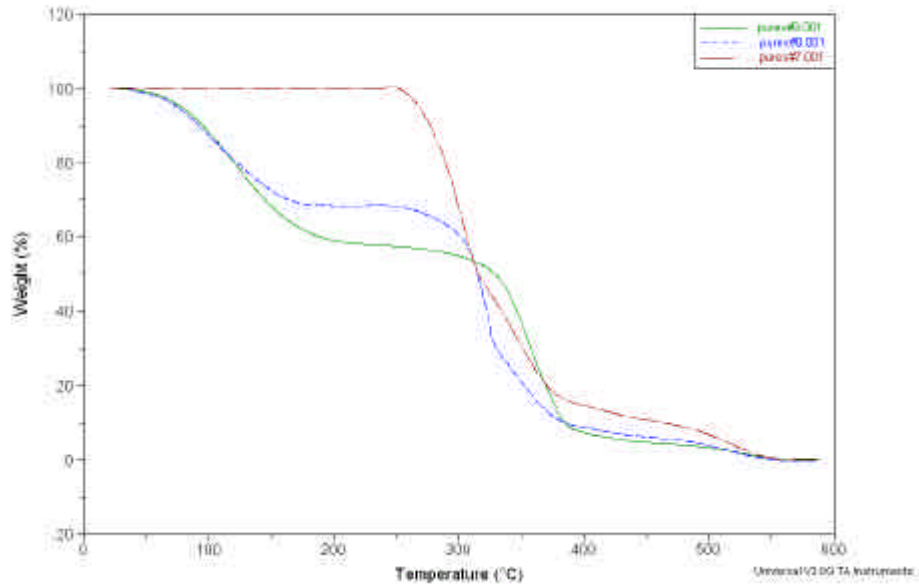


Figure C-5. TGA: NocharA610–Simulated Purex 1:1 and 1:2 Waste Forms and Simulated PUREX Waste.

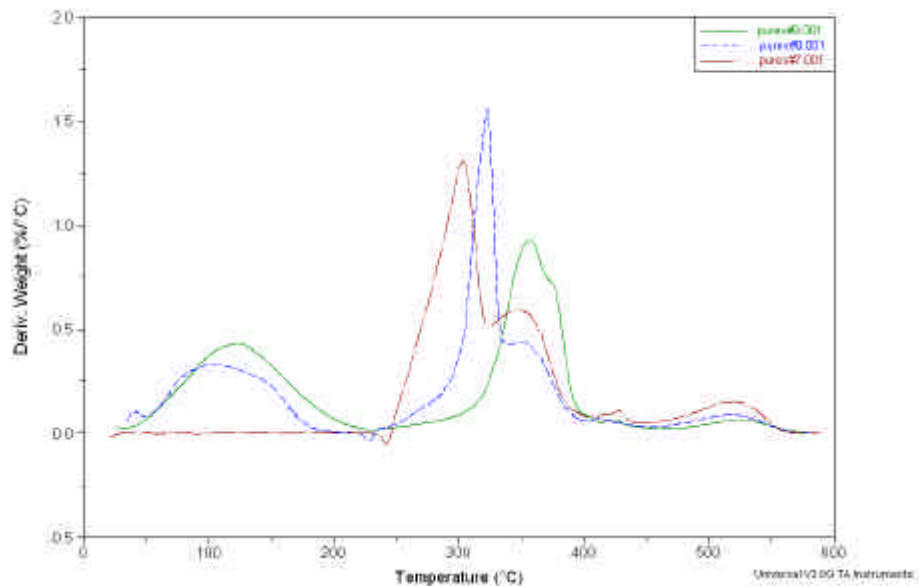
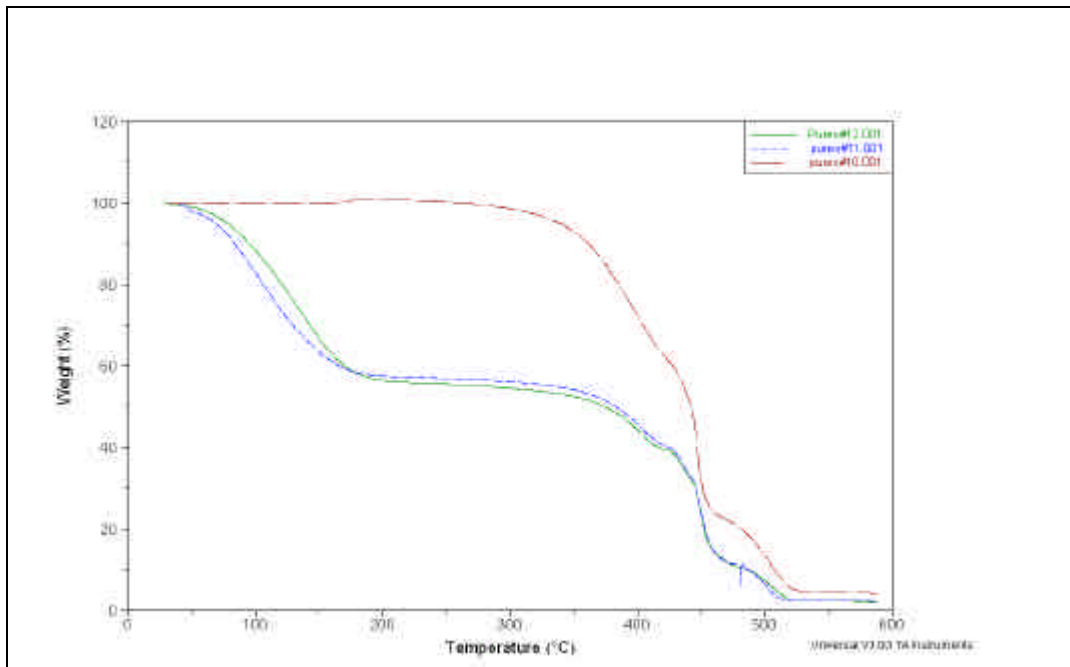
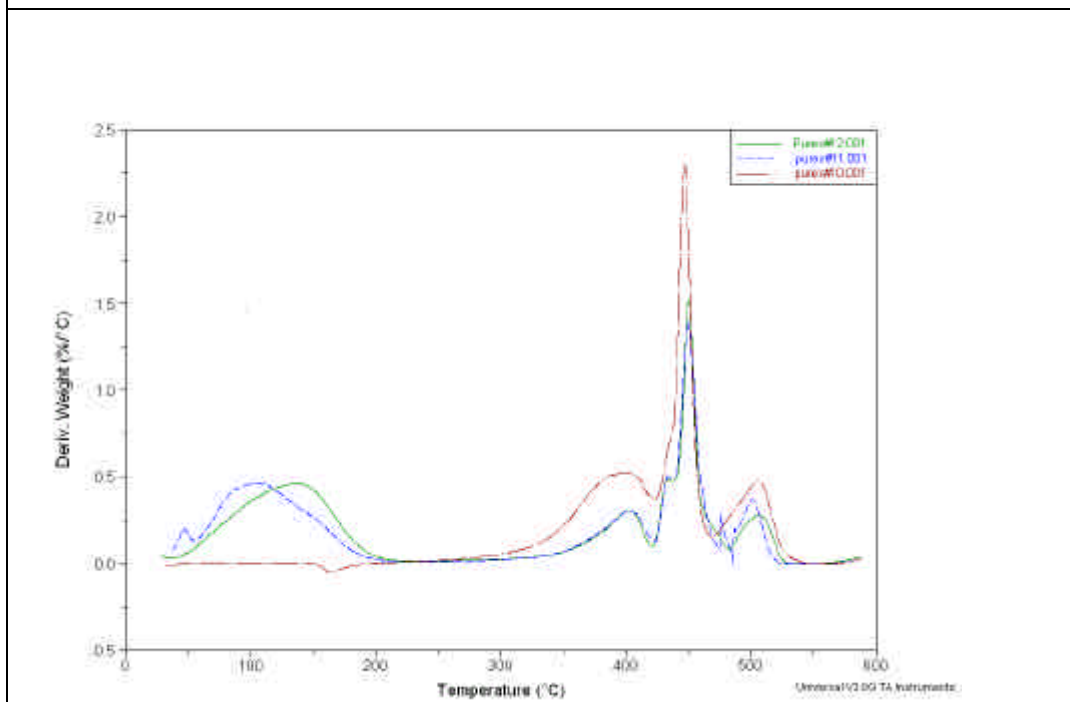


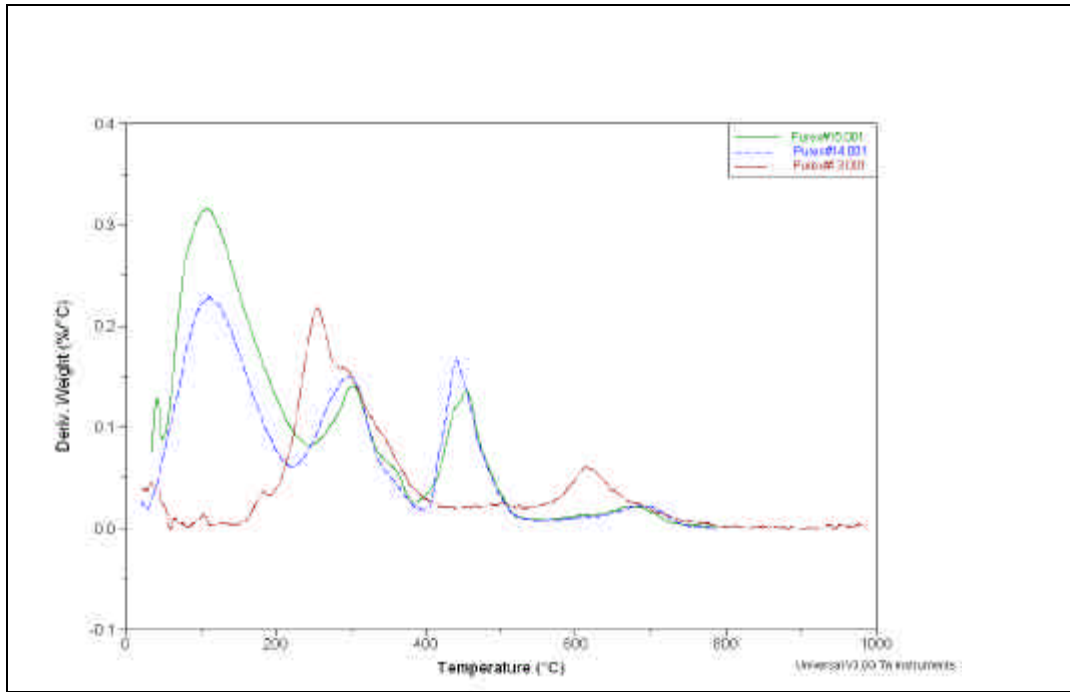
Figure C-6. DTA: Nochar A610–Simulated Purex 1:1 and 1:2 Waste Forms and Simulated PUREX Waste.



Nochar A650

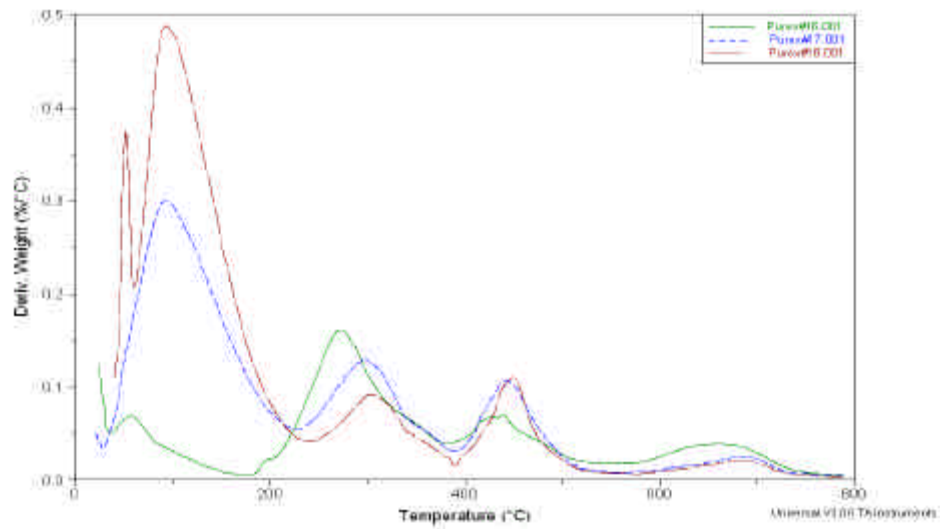


Nochar A650



Petroset II

Petroset II Granular



Petroset II Granular

13.0 APPENDIX D GEL, INC. RESULTS

14.0 APPENDIX E MICROBIAL DEGRADATION REPORTS



Biodegradation
Systems Inc.

BSI – 0101 REV 1

REPORT

MICROBIAL DEGRADATION OF ABSORBENTS SATURATED WITH PUREX

December 7, 2001

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Prepared for
Westinghouse Savannah River Company
Contract Number 3E5492

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Microbial Degradation Of Absorbents Saturated With PUREX

Introduction

The Westinghouse Savannah River Company (WSRC) has been task to determine if absorbents, those under consideration for immobilization of PUREX solvent, are susceptible to biodegradation. WSRC selected the ASTM standard biodegradation tests G21 (Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi) and G22 (Standard Practice for Determining Resistance of Plastics to Bacteria) for the initial microbial degradation testing of various mixtures of sorbents and PUREX solvent. Biodegradation Systems Inc. (BSI) developed the protocol for the tests while Celsis Laboratory Group (CLG) conducting the ASTM tests with BSI evaluating the results. This report provides details of the test plan, a discussion of the significances of test results, and a recommendation for additional evaluation of immobilized PUREX solvent.

Testing Procedures

Test Specimens

Absorbent material evaluated for susceptibility to biodegradation included two variations of each of the following three products:

- Imbiber Beads (organic polymer beads)
 - Imbiber Beads – as received
 - Imbiber Beads – nuclear grade
- Nochar (organic polymer)
 - Nochar A610
 - Nochar A650
- Petroset (inorganic graduals)
 - Petroset II – as received
 - Petroset II granular

Test specimens were prepared by WSRC and sent to CLG. The specimens were composed of each type of the six absorbents that have been treated with simulated Purex at a ratio of one part absorbent to two parts Purex (1:2) on a weight basis. A total of 100 g of each of the treated absorbents was prepared and sent to CLG for testing. In addition to the test specimens the testing matrix had controls consisting of each of the untreated absorbents as well as the simulated Purex solution.

Physical Appearance of Test Specimens

The ASTM G21 and G22 test protocols were developed to determine if material(s) can be biodegraded, i.e. used by microorganisms as a source of carbon and energy. Therefore, the test procedures were designed to provide the essential nutrients and conditions, except a source of carbon and energy, necessary to promote growth of microorganisms. Testing was conducted with solid agar media in closed containers, in this case petri dishes. The testing setup was adapted to accommodate the physical rigidity of the specimen. In this study, the specimens consisted of small particles with sorbed liquid and, therefore, did not have a preformed shape. Rather the loaded specimens had the consistency of a very viscose liquid

or paste. The control specimens consisted of powder like material or in the case of the Purex, a liquid.

Incorporation Of Test Specimens Into Testing Procedure

CLG used the ASTM procedures with BSI modifications for exposing specimens to the test environment. In all testing two (2) g of specimen material was used and the tests were conducted in triplicate. Two different approaches were used to expose the specimen material to specified microorganisms.

1. One set of triplicated tests was conducted with the specimen material being incorporated into the agar medium. The specimen was added to the prescribed molten agar contained in a petri dish after the agar had cooled to approximately 50 C. Contents were then gently swirled to facilitate mixing and then allowed to cool. Inoculation with the microbial component was as specified by each ASTM procedure. Incubation conditions and microbial growth evaluations were carried out as specified by each ASTM procedure.
2. One set of triplicated tests was conducted with the specimen material being spread on the surface of the prescribed, solidified agar. An effort was made to maintain at least a 10 mm margin between the specimen material and edge of the petri dish. Inoculation with the microbial component was as specified by each ASTM procedure. Incubation conditions and microbial growth evaluations were as specified by each ASTM procedure.

Microbial Component

Both ASTM G 21 (Standard Practice for Determining Resistance of Plastics to Fungi) and ASTM G 22 (Standard Practice for Determining Resistance of Plastics to Bacteria) specify the species of microorganisms that will be used to challenge the test specimens. The fungal species stipulated in G 21 were used for that test. However, a single bacterial species that had been isolated from stored PUREX waste was used for the G 22 test rather than the specified bacterium.

Testing Matrix

An outline of the test matrix is provided in Table 1.

Table 1. Matrix of tests conducted in triplicate using both methods for incorporating specimens for both the ASTM G 21 and ASTM G22 protocols.

Absorbent	Purex loading 1:2	Non Purex ^a control	Purex control ^b
Imbiber Beads – as received			
Imbiber Beads – nuclear grade			
Nochar A610			
Nochar A650			
Petroset II – as received			
Petroset II granular			

a. Absorbent only without addition of Purex.

b. No absorbents will be used. This is a control using the Purex liquid only and was only conducted once in triplicate.

Results

Incubation of specimens for both the ASTM G 21 and G 22 tests was terminated after 22 days. The G 22 procedure specifies a minimum of 21 days of incubation while the G 21 requires a period of 28 days. This period of testing provided the required time for the G 22 bacteria test and shortened the G21 fungi test by six days. Early termination of the G 21 procedure was considered appropriate for reasons that will be discussed.

CLG reported light or absent growth for specimens inoculated on the SRP bacterial isolate. However, it was suggested that these results might not be an accurate reflection of the degradative potential of this species of bacteria. This is because the G 22 testing protocol requires that inoculated specimens be incubated at a temperature of 35 to 37 C (this is the optimal temperature range for *Pseudomonas aeruginosa* the bacteria suggested for the test). These elevated temperature are not considered an ideal range for productive growth of most microorganisms isolated from the environment (a range of 23 to 28 C is considered optimal). Therefore, results from the G 22 tests can be considered inconclusive.

Results from the G 21 tests showed that there was minimal growth of all fungal species used. Fungal growth was noted around the margins of the WSRC specimens but no direct growth was noticed near or on the specimens. It appears that the specimens could have prevented fungal growth. It was for this reason that it was decided to terminate the test. In CLG’s estimation, overall the test results could be given a rating of 1 which indicates light growth over 10 to 30% of inoculated surface.

CLG also reported that mixing the WSRC specimens into the agar medium (as outlined in approach 1) caused the solidified agar to liquefy after 14 days of incubation. The cause was not determined but it is suspected that the hydrophobic nature of the specimens could have been a factor.

Discussion

Background

There are three general types of tests that are used for assessing the potential for microbial degradation of materials: (a) tests to determine whether or not the material will support microbial growth; (b) tests simulating natural environments; and (c) field studies. While environmental simulations and field studies provide definitive answers they are most often not the methods of first choice due to the length of time for testing and the resulting expense. The most widely used test procedures involve some method to determine the potential of a material to support microbial growth. Results of these tests then serve as input in the process of evaluating biodegradation potential.

Biodegradation potential tests can be subdivided into two classes: those that determine ready biodegradability and ones that measure inherent biodegradability. Ready biodegradability tests are characterized by:

- The use of a non-specific analytical method to indicate the extent to which a particular substance is degraded;
- Exposure of a candidate material to a small number of microbial species in the absence of other carbon sources, and;
- The short duration of the test (normally three to four weeks).

Applicability Of Testing Methodology

The ASTM G 21 and G 22 procedures fit the protocol of those tests that determine ready biodegradability. There are recognized limitations inherent in these two ASTM procedures and in light of the present results the most apparent ones are: (a) they do not provide for natural selection of those microorganisms with the potential for degradation; (b) there are no procedures which favor microbial adaptation; and (c) no growth may not be sufficient proof of resistance to biodegradation.

However, results from the ASTM testing should be considered a worthwhile data point the interpretation of which shows that the material being evaluated is not suitable for a particular testing regimen. These results do not discount the possibility that the WSRC specimens can be subject to biodegradation. It merely shows that the use of a first line, convenient, standardized test did not confirm the potential biodegradability of these specimens. Such results can be anticipated from initial tests whose testing methodologies i.e. procedures and microorganism, have been refined for testing of particular types of materials, in this case commercial plastics. In the case of the WSRC specimens a more robust, ready biodegradability test needs to be used i.e. one with a wider spectrum of environmental

microorganisms and testing conditions that are more relevant to those environmental conditions that will promote microbial growth. An evaluation involving a multiorganism approach is appropriate for waste materials.

Recommendations

1. Testing of the potential biodegradability of the WSRC should be repeated using a more robust testing methodology. This will allow for continued use of an economical, short duration testing regime.
2. The testing method used as the follow on should be one that uses liquid culture techniques (no carbon source other than the specimens) and a robust microbial inoculate i.e. from sewage treatment facility, rich soil, etc.
 - a. Use of flasks that are amenable for use with a shaker are advisable.
 - b. A temperature in the range of 23 to 28 C should be used.
 - c. An acceptable method for determination of microbial growth should be applied i.e. visibility, reculturing, etc.
3. Plans should be made for the use of a cascade of gradually increasing sophisticated methods i.e. simulation of natural environments (soils) and field studies (use of lysimeters). These methods will provide the conditions and time necessary to provide for natural selection and adaptation of those microorganisms with the potential for degradation.