Sorbent Testing for Solidification of Organic Plutonium/Uranium Extraction Waste – Phase IV

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ABSTRACT

The U.S. Department of Energy (DOE) is evaluating various sorbents to solidify and immobilize hazardous constituents of the organic fraction of plutonium/uranium extraction (PUREX) process waste at the Savannah River Site (SRS).[5] The purpose of the solidification is to provide a cost-effective alternative to incineration of the waste. Incineration at the Consolidated Incinerator Facility (CIF) at SRS is currently identified as the treatment technology for PUREX waste. However, the CIF is not in operation at this time, so SRS is interested in pursuing alternatives to incineration for treatment of this waste.

The DOE Western Environmental Technology Office in Butte, MT was designated as the facility for conducting the sorbent testing and evaluation for the organic PUREX waste surrogate. MSE Technology Applications, Inc. tested and evaluated two clay and two polymer sorbents with the capability of solidifying organic PUREX waste. A surrogate organic PUREX waste recipe was utilized, and sorbents were tested and evaluated at bench-scale, 22-liter (5-gallon) scale, and 242-liter (55-gallon) scale.

This paper presents experimental results evaluating four sorbent materials including: Imbiber Beads™ IMB230301-R, Nochar A610 Petrobond™, Petroset II™, and Petroset II Granular™. Previous work at SRS indicated that these products could solidify organic PUREX waste on a bench scale [1]. The sorbents were evaluated using operational criteria and final wasteform properties. Operational criteria included: sorbent capacity; sorption rate; sorbent handling; and mixing requirements. Final wasteform evaluation properties included: ignitability; thermal stability; offgas generation, leachability tests and volumetric expansion. Bench-scale tests, 22-liter (5-gallon) tests, and initial 242-liter (55-gallon) tests are complete. This paper summarizes the results of the bench-scale, 22-liter (5-gallon) scale, and 242-liter (55-gallon) scale tests performed during FY05 with an aqueous/PUREX surrogate.

INTRODUCTION

Background

The U.S. Department of Energy (DOE) is evaluating various sorbents to solidify plutonium/uranium extraction (PUREX) process waste at the Savannah River Site (SRS). The PUREX waste, which is derived from an organic-aqueous isotope separation process at SRS, is stored in H-Area at the New Solvent Storage Facility at SRS. The total volume of legacy PUREX waste is 167,382 liters (38,000 gallons), consisting of 110,120 liters (25,000 gallons) of spent PUREX organic solvent and 57,262 liters (13,000 gallons) of aqueous waste. Organic PUREX waste, which is the focus of this study, contains n-paraffins and tributyl phosphate in addition to aromatic hydrocarbons and amine compounds [1]. The purpose of solidification is to provide a cost-effective alternative to incineration of the waste. Previously, incineration at the Consolidated Incinerator Facility (CIF) at SRS was identified as the treatment technology for PUREX waste. However, the CIF has been indefinitely shut down; therefore, SRS is interested in pursuing alternatives to incineration for treatment of this waste [1, 2].

During 2001, Westinghouse Savannah River Company (WSRC) performed a PUREX Waste Solidification Feasibility Study that evaluated solidification as an alternative treatment for organic waste. Six sorbents were tested for solidification of surrogate PUREX waste and four were chosen for further scale-up testing. The sorbent materials and the PUREX wasteforms 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 [1]. A surrogate of organic PUREX waste that was developed by WSRC was used for the subsequent scale-up testing at MSE Technology Applications, Inc. (MSE) in Butte, Montana.

Solidification of the organic fraction of the PUREX waste using sorbents was evaluated in four phases by MSE under the direction of DOE's Western Environmental Technology Office and SRS. Those phases were:

- Phase I—Bench-Scale Testing;
- Phase II—22-Liter-Scale, 242-Liter Scale, and Thermal Stability Testing;
- Phase III—Continued Monitoring of Existing FY03 Samples, and Optimized 22-liter and 242-Liter Testing; and
- Phase IV—Continued Monitoring of Existing FY04 Samples, and Aqueous Phase PUREX Surrogate Testing at Bench-Scale, 22-Liter-Scale and 242-LiterScale.

All four phases of testing are complete. Four sorbents capable of solidifying PUREX waste [Imbiber Beads® IMB230301 (Imbiber Beads), Nochar A610 Petrobond™ (Nochar Petrobond), Petroset II™ (Petroset II), and Petroset II Granular™ (Petroset II-G)] were tested during Phase I. A tradeoff study of available mixing technologies was also performed during Phase I of the project [3].

Recommendations resulting from the Phase I testing included further testing (Phase II) for three of the sorbents [4]. The three sorbent materials that were evaluated during Phase II included:

- Imbiber Beads;
- Nochar Petrobond; and

- Petroset II-G.

Petroset II was eliminated after Phase I due to concerns with dust production potential and the high viscosity of the sorbent/surrogate combinations that require mixing [3]. Based on the noncohesive nature of the final wasteform associated with Imbiber Beads, this material was eliminated after 22-liter-scale testing during Phase II [4]. Preliminary 242-liter drum tests were also performed using Nochar Petrobond and Petroset II-G with the simple PUREX surrogate during Phase II testing. Optimized 22-liter and 242-liter drum tests using Nochar Petrobond and Petroset II-G were performed during Phase III testing. Continued monitoring of FY 03 samples to determine long-term stability, offgas characterization/generation, and leachability tests was also performed during Phase III Testing.

This paper focuses on Phase IV testing, which addresses the addition of an aqueous component to the organic PUREX surrogate. Bench-scale, 22-liter bucket testing, and 242-liter drum testing were performed using the full PUREX organic surrogate with an aqueous phase. One task remained from Phase III testing, which was the generation of 242-liter-drum samples using the full PUREX surrogate at the optimum waste-loading ratios determined during FY04 testing. The generation of these 242-liter-drum samples was postponed during FY04 so that the SRS client could watch the sample generation during a visit in FY05.

TEST OBJECTIVES

In summary, the objective of the Phase IV experimental work was to identify a combination of sorbents capable of solidifying the PUREX organic surrogate waste with an aqueous component. The sorbent combinations must be cost effective and compatible with constituents in the PUREX waste and solidification processing equipment. The sorbent/surrogate combinations must remain stable under conditions that may be encountered during solidification, storage and shipment of the waste. In addition, the long-term stability of the waste forms was evaluated using samples from the previous year's testing (i.e., Phase III). Finally, Phase III full-scale sorbent testing (in which there was not an aqueous component) would be compared to Phase IV full-scale samples with both an aqueous and organic component.

MATERIAL DESCRIPTIONS

The surrogate organic PUREX recipe was developed at SRS during the PUREX Solidification Feasibility Study [1]. The SRS surrogate PUREX should provide a representative comparison with the actual PUREX waste requiring solidification. Sorbents tested at the MSE Test Facility were identified with input from SRS personnel and were recommended for further evaluation based on the results of the MSE Phases I, II, and III studies.

PUREX Surrogate Formulation

The recipe for the full PUREX surrogate (see Table I) was developed during the SRS feasibility study [1]. The recipe for the simple PUREX surrogate (see Table II) was developed for initial large-scale testing, since the cost of the full surrogate is very expensive.

Table I. Full PUREX Surrogate Recipe

Chemical Name	Weight Percent
Tributyl Phosphate	17.60
Aliphatic Hydrocarbons	
Undecane	8.45
Dodecane	8.45
Tridecane	8.45
Tetradecane	8.45
Aromatic Hydrocarbons	
Diethylbenzene	21.00
Di-isopropylbenzene	21.00
Aliphatic Amine	
Di-n-octylamine	6.60
Total	100

Table II. Simple PUREX Surrogate Recipe

Chemical Name	Weight Percent
Tributyl phosphate	17.6
Kerosene	82.4
Total	100

Sorbent Descriptions

Sorbents identified for testing include:

- Nochar Petrobond, a sorbent composed of proprietary polymer crystals, which is manufactured by Nochar, Inc.;
- Nochar 660 Acid Bond™ (Nochar Acid Bond), a granular polymer that stabilizes aqueous and acid spills by bonding them into a semi-solid waste manufactured by Nochar, Inc.;
- Petroset II-G, a modified clay, granular stabilizing agent, which is manufactured by Fluid Tech, Inc., that does not require mixing during the organic waste solidification process; and
- Aquaset™ (Aquaset), a water-activated, granular clay solidification agent used for the treatment of aqueous liquids manufactured by Fluid Tech, Inc., which does not require mixing.

EXPERIMENTAL ACTIVITIES

In summary, the objective of the Phase IV experimental work was to generate the two 242-liter drum samples with the full PUREX surrogate that were postponed during Phase III testing and to identify a combination of sorbents capable of solidifying the PUREX organic surrogate waste with an aqueous component. The sorbent combinations must be cost effective and compatible with constituents in the PUREX waste and solidification processing equipment. The sorbent/surrogate combinations must remain stable under conditions that may be encountered during solidification, storage and shipment of the waste.

PHASE III TESTING

242-Liter Drum Tests Remaining from FY04

The two sorbents, Nochar Petro Bond and Petroset II-G were scheduled for testing at 242-liter scale using the full organic PUREX surrogate without a water phase during Phase III testing. The purpose of the scale-up tests was to verify the sorbent-to-waste loadings determined in the 242-liter scale-up simple PUREX surrogate study during FY04. Sample preparation was delayed during Phase III testing at the customer's request. These samples were generated during April 2005 when the customer was present to observe the mixing process.

Each of the 242-liter tests solidified 20 gallons of full PUREX surrogate waste without an aqueous phase. The optimum weight-based waste loading ratios, determined during Phase III testing, were used to generate the 242-liter samples. The optimum waste-loading ratio for Petroset II-G was 1.7:1 and for Nochar Petro Bond it was 1:3 (sorbent to surrogate).

The Petroset II-G sample was generated by pouring the sorbent into the full PUREX surrogate and allowing the sorbent to sorb the organic liquid. At the 1.7:1 ratio, additional liquid was present after the addition of the sorbent material to the 242-liter drum. The liquid was sorbed in approximately six hours; however, the top edge of the sample was much softer than the rest of the sample since the additional PUREX surrogate waste sorbed into the top section of the sorbent material in the drum. The LRT value for a sample taken from the middle of the drum 14 days after sample generation was 0.032% release by volume showing that the Petroset II-G sample scales up to the 242-liter size without any problems.

The Nochar Petro Bond sample was generated by adding the full PUREX surrogate waste without a water phase into the Petro Bond sorbent material. The mixer was started and the sorbent material was mixed until the sorbent no longer had any clumps in the material and then the liquid surrogate waste was added and the sample was mixed vigorously until the 5-horse-powered drum mixer tripped. The sample was consistently mixed even through the mixer had tripped because the sample consistency was very thick and rubbery. The LRT value for a sample taken 14 days after sample generation was 0.169% release by volume showing that the Nochar Petro Bond sample scales up to the 242-liter size without liquid release problems at this ratio. However, the samples are extremely difficult to mix and turn into a rubbery consistency within one to two minutes. In order to achieve acceptable release liquid release values the sample must be mixed thoroughly, which can be problematic.

The two 242-liter samples were cut open six months after sample generation to verify the sample consistency and to check for void spaces in the samples. Neither sample showed any voids when cut open as shown in Figures 1 and 2. An LRT was performed on both of the 242-liter drum samples after they were cut open for inspection. The LRT for the Petroset II-G sample was 0.050% release by volume and for the Nochar sample was 0.195% release by volume, which is consistent with the initial LRT values of 0.032% for the Petroset II-G sample and 0.169% for the Nochar sample.

It was observed that the top of the Petroset II-G sample where the excess full surrogate sorbed into the Petroset II-G material was still much softer than the rest of the sample. The 1.7:1 waste-loading ratio of the Petroset II-G sample results in excess liquid surrogate on top of the sorbent

when the sample is generated, however a 2:1 ratio results in extra sorbent on top of the PUREX surrogate, which creates a much harder wasteform. Based on this information, the optimum waste-loading ratio for the Petroset II-G was changed from 1.7:1 to 2:1 to eliminate the softer top section in future samples, therefore, creating a much better wasteform with this product.

Fig. 1. Petroset II-G sample

Fig. 2. NocharPetro bond sample

PHASE IV TESTING

Bench–Scale Aqueous/PUREX Full Surrogate Testing

Bench-scale samples were generated using a combination of sorbents to tie up both the organic and aqueous phase of the PUREX surrogate. The Nochar products, Acid Bond and Petro Bond, were combined and mixed thoroughly and then the aqueous/PUREX full surrogate was added to the sorbent combination and mixed vigorously. The Fluid Tech products were used by adding the Aquaset first, and allowing it to drop through the liquid organic surrogate to sorb the aqueous phase in the bottom of the container and then adding the Petroset II-G and allowing it to sorb the PUREX organic phase without mixing.

The weight-based, waste-loading ratios for the organic phase of the full PUREX surrogate were selected based on Phase III testing. A 1:3 ratio was used for the Nochar Petro Bond to organic PUREX surrogate and a ratio of 1.7:1 was used for the Petroset II-G to organic PUREX surrogate. (NOTE: These samples were generated before the optimum waste-loading ratio was changed from 1.7:1 to 2:1 for the Petroset II-G sorbent.) Various ratios for the aqueous phase were tested during the bench-scale tests based on vendor recommendations and F-Canyon PUREX testing. The weight-based, water-loading ratios for the Aquaset sorbent ranged from 1.1 to 1.5 in increments of tenths, and the weight-based, water-loading ratios for the Nochar Acid Bond sorbent ranged from 1:1 to 1:6 (sorbent to water). The sample data for the preferred waste-loading ratios that were further tested is presented in Table III.

A Paint Filter Test (PFT) was performed on the bench-scale samples to determine the absence or presence of free liquid in the samples. If the samples passed the PFT, a Liquid Release Test (LRT) was performed to gather the liquid release numbers for the sorbent-to-surrogate ratios tested. Table III presents the test matrix and LRT test results for the bench-scale tests. Since all of the samples passed the PFT, that information is not presented in this table.

Table III. Bench-Scale Test Matrix and LRT Results for Nochar and Fluid Tech Sorbents

Sorbent Name	Weight-Based Waste-Loading Ratio (wt sorbent: wt surrogate)	Percent Water	Sorbent Surrogate Addition Method	Mixing/ No Mixing	Liquid Release Test Percent Release by Volume
					NTS WAC 0.5%
Petroset II-G Aquaset	1.7:1 1.5:1	10%	Sorbents added to surrogate	No mixing	0.146
Petroset II-G Aquaset	1.7:1 1.5:1	5%	Sorbents added to surrogate	No mixing	0.047
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	10%	Surrogate added to sorbent	Mixing	0.256
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	5%	Surrogate added to sorbent	Mixing	0.692

The LRT values show the combination of the Fluid Tech sorbents tie up the aqueous/PUREX surrogate better that the combination of the Nochar products during the bench-scale testing without the need for mixing. All of the samples generated with the Fluid Tech sorbents passed the PFT and LRT with LRT values ranging from 0.047% to 0.330% with an average value of 0.172% release by volume. All of the Nochar samples passed PFT and all but one passed LRT with LRT values ranging from 0.135% to 0.692% with an average value of 0.354% release by volume.

22-Liter Bucket Aqueous/PUREX Full Surrogate Testing

Based on the bench-scale testing and conversations with the vendors, ratios for the water phase were chosen for the 22-liter bucket tests. After discussions with the Nochar vendor, MSE decided that additional mixing was necessary for the Petro Bond and Acid Bond combinations of sorbent material before the introduction of the full aqueous/PUREX surrogate to the sorbent combination. Based on this additional information, a ratio of 1:2 for the Acid Bond sorbent to the aqueous phase was selected and a ratio of 1.5:1 for the Aquaset sorbent to aqueous phase was selected. The optimum weight-based waste loading of 1.7:1 for Petroset II-G and 1:3 for Petro Bond was used to sorb the organic phase of the full PUREX surrogate. (NOTE: These tests were performed before the optimum waste-loading ratio for large scale samples was changed from 1.7:1 to 2:1 for the Petroset II-G sorbent material during the large scale tests from Phase III testing.)

Smaller samples were collected for the different types of liquid release tests from the 22-liter bucket samples generated during this phase of testing. This provided the opportunity to assess behavior at selected waste-loading ratios for the full PUREX surrogate with an aqueous phase, including volumetric expansion, mixing requirements, sorption rate, final wasteform physical characteristics, curing behavior, and thermal stability. These samples were then subjected to the following tests.

The SW-846 Method 9095A—*Paint Filter Free Liquids Tests* and the SW-846 Method 9096—*Liquid Release Tests* were used to determine if free liquids existed in the final wasteforms after seven days of storage [7]. In addition to these tests, shaker tests and freeze-thaw tests were performed to provide a more complete picture of how tightly bound the aqueous/PUREX surrogate and sorbent combinations were at the ratios tested. Shaker tests and freeze-thaw tests were performed according to the procedures suggested by NTS [6].

The surrogate liquid/sorbent samples for Phase IV testing at the 22-liter scale were prepared using 8.8 liters (2 gallons) of full PUREX surrogate with a 10% or a 5% aqueous phase and the appropriate amount of sorbents to achieve the desired waste-loading ratios.

Table IV provides a matrix of the preferred sorbent-to-PUREX ratios and sorbent-to-water ratios tested, and the sorption rate, sample consistency, and volumetric expansion for each sample generated.

Observations made during the sorbent aqueous/PUREX 22-liter sample preparation included:

- time for the sorbent combinations to soak up the liquid;
- behavior of the surrogate/sorbent combinations over time;
- any loss of stability of the combinations over time (i.e., separation of surrogate from the sorbent);
- mixing behavior of the sorbent/surrogate combinations;
- consistency of the final products; and
- volumetric expansion of the sorbent/surrogate combinations.

Observations made during and after the 22-liter sample generation are presented in Table IV.

Table IV. Observations Made During and After the22-Liter Sample Generation

Sorbent Name	Weight-Based Waste-Loading Ratio (wt sorbent: wt PUREX)	Water Per Cent	Sorption Rate, Liters of PUREX/min	Consistency of the Mixture After Sample Sorption Time or Mixing and Mixing Behavior	Volumetric Expansion per Gal of PUREX
Petroset II-G Aquaset	1.7:1 1.5:1	5	0.13	Hard paste – no mix Soft to medium paste – no mix	1.81
Petroset II-G Aquaset	1.7:1 1.5:1	10	0.13	Hard paste – no mix Soft to medium paste – no mix	1.87
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	5	11.76–equals a 45-s mixing time	Medium Paste after mixing and somewhat flowable after 2 hours	0.71
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	10	11.76–equals a 45-s mixing time	Medium Paste after mixing and somewhat flowable after 2 hours	0.75

Mixing Requirements

Petroset II-G and Aquaset 22-liter bucket samples were not mixed and Aquaset was added to the aqueous/organic surrogate first and after one minute, the Petroset II-G was added and allowed to sorb the organic phase of the PUREX surrogate. This addition method was recommended by the vendor. All of the Nochar sorbent combinations were mixed thoroughly before the aqueous/PUREX surrogate was added to the sorbent combination. The Nochar samples were

then mixed vigorously for 45 seconds. Mixing was initiated as soon as the full PUREX surrogate with a water phase was added to the Nochar since solidification occurs very quickly with this sorbent/surrogate mixture. The Nochar samples were mixed for 45 seconds and were not as viscous as the Nochar Petro Bond samples without a water phase at the end of the mixing cycle.

Sorption Rate

Petroset II-G samples had a relatively slow sorption rate when compared to the Nochar samples. However, at the 1.7:1 ratio there is additional PUREX surrogate on top of the sorbent after the sorbent is added to the PUREX surrogate and it does take some time to sorb the additional free liquid in the samples. (NOTE: These samples were generated before the optimum waste-loading ratio was changed from 1.7:1 to 2:1 for larger scale testing.) The Nochar samples had a sorption rate of 11.76 liters per minute, which corresponds to the 45-second mixing cycle. It is hard to compare the sorption rate values for two sorbent combinations since one of the combinations requires mixing and the other does not.

Consistency of Sample Mixtures

The consistency of the samples was checked two hours after sample generation and daily for seven days. All of the Petroset II-G and Aquaset samples, regardless of the waste-loading ratio, had the consistency of a hard paste after sorption of the PUREX surrogate for the Petroset II-G section of the sample. The Aquaset portion of the sample had the consistency of a medium soft paste. All of the Nochar sorbent combination samples, regardless of the waste-loading ratio, had a thick syrupy consistency and the samples were flowable after two hours. The Nochar aqueous/PUREX sample consistency was similar to the 1:5 ratios generated for Nochar Petro Bond full PUREX surrogate samples during FY03 testing. None of the samples had any free liquid after being stored inside following sample generation earlier in FY05.

Volumetric Expansion

The volumetric expansion was calculated by dividing the final wasteform volume by the volume of PUREX surrogate that was solidified. Petroset II-G and Aquaset samples had expansion rates of 1.81 to 1.87, and the Nochar Petro Bond and Acid Bond samples had expansion rates of 0.71 and 0.75 depending on the percent of water in the samples. Extra volume is necessary in the Nochar sample containers if the samples are mixed and stored in the same container because of the vigorous mixing needed to obtain a well mixed wasteform. Table V presents the data resulting from the PFT, shaker tests, and LRT for the 22-liter samples.

Table V. Data Gathered During FY04 22-liter Sample Testing

Sorbent Name	Weight-Based Waste-Loading Ratio (wt sorbent: wt PUREX)	Sampling Date	Percent Water	LRT (liquid released during testing) % by Volume NTS WAC 0.5%	Shaker Tests (liquid released during testing) % by Volume NTS WAC 0.5%
Petroset II-G Aquaset	1.7:1 1.5:1	4-11-05	5	0.027	0.078
Petroset II-G Aquaset	1.7:1 1.5:1	4-11-05	10	0.021	0.076
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	4-11-05	5	0.155	0.225
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	4-11-05	10	0.172	0.230

Liquid Release Testing

All of the 22-liter samples were subjected to PFT, LRT, and shaker testing. None of the samples showed any evidence of free liquids after the seven-day storage period. All of the Petroset II-G and Aquaset sorbent combinations and the Nochar Petro Bond and Acid Bond combinations passed the PFT after seven days of storage; consequently, the samples were then subjected to an LRT. The volume of liquid released was calculated for the LRT, and shaker tests by weighing filter paper before and after each of these tests to determine the liquid released during the tests. All of the 22-liter samples tested passed the PFT, LRT and shaker tests as shown in Table V.

The aqueous/PUREX Petroset II-G and Aquaset samples released comparable amounts of liquid during the LRT for both the 5% and 10 % aqueous phase samples, which were 0.021% and 0.027% by volume. The aqueous/PUREX Nochar sorbent combination samples had a wider range for the LRT numbers, which were 0.155% to 0.172% by volume. All aqueous/PUREX LRT numbers were well below the NTS WAC for solidified wastes of 0.5% by volume. All of the aqueous/PUREX sorbent combinations passed the shaker tests with the Fluid Tech samples releasing liquid ranging from 0.076% to 0.078% and Nochar samples releasing liquid ranging from 0.225% to 0.230% by volume. The LRT values for the Petroset II-G sample ranged from 0.021% to 0.027% while the values for the Nochar samples ranged from 0.155% to 0.172% by volume. The liquid released by the Nochar wasteforms is an order of magnitude greater than the liquid released by the Fluid Tech wasteforms at the 22-liter scale.

242-Liter Aqueous/PUREX Full Surrogate Drum Tests

Two 242-liter drum samples were generated during this portion of the testing regime. A Petroset II-G and Aquaset sample combined with the aqueous/PUREX full surrogate with a 10% water component and a Petro Bond and Acid Bond sample combined with the aqueous/PUREX full surrogate with a 10% water component. The waste-loading ratios for the Petroset II-G sorbent to the organic phase of the aqueous/PUREX full surrogate was 2.3:1 and the ratio for the Aquaset sorbent to the water phase was 1.5:1. The waste-loading ratios for the Petro Bond sorbent to the organic phase of the aqueous/PUREX full surrogate was 1:3 and the ratio for the Acid Bond sorbent to the water phase was 1:2. (The optimum waste-loading ratio for the Petroset II-G sorbent material was increased to 2.3:1 because of inconsistencies between batch 17 and batch 18 of the sorbent. There were several differences in the batches of Petroset II-G, one of which required the waste-loading ratio to be bumped up to 2.3:1 from the 2:1 ratio previously identified

as the optimum waste-loading ratio from Phase III testing. The differences between Petroset II-G batches will be discussed later in this paper.)

The samples were prepared using the same methods as for the 22-liter bucket sample generation. Petroset II-G and Aquaset 242-liter drum samples were not mixed and the Aquaset was added to the aqueous/organic PUREX surrogate first and after 15 minutes, the Petroset II-G was added and allowed to sorb the organic phase of the PUREX surrogate. This addition method was recommended by the vendor and was successful at the 22-liter scale. All of the Nochar sorbent combinations were mixed thoroughly before the aqueous/PUREX surrogate was added to the sorbent combination and mixed vigorously.

Both of the 242-liter drum samples were collected by coring down the middle of the 242-liter drum to collect smaller samples from different horizons of the core for PFT and LRT. The sample consistency of the Fluid Tech sample was very hard with the bottom layer of the Aquaset sorbent having a consistency of a soft to medium paste. The cored section of the sample remained open after the core was pulled from the drum. The Nochar sample was more difficult to sample than the Fluid Tech sample since the sample's consistency was flowable like cool honey. The sample consistency can be seen in Figure 3 during the physical destruction of the sample in October 2005. After the core sample was collected form the Nochar 242-liter drum, the sample flowed into the area left by the coring devise to heal itself.

Fig. 3. Aqueous/PUREX Nochar sample.

Fig. 4. Aqueous/PUREX fluid tech sample

The Nochar sample was LRT tested one more time when both of the samples were physically destroyed at the end of October 2005 to check for void spaces and sample consistency in the scaled-up, 242-liter drum samples. The Fluid Tech sample had dried out around the cored area of the sample that was taken during the July 2005 sampling event and would not give a representative LRT value so it was not LRT tested at that time. A picture of the Petroset II-G and Aquaset aqueous/PUREX full surrogate sample is shown in Figure 4.

The LRT values for the smaller cored samples taken from the 242-liter drum samples are presented in Table VI. Four samples were taken from the core of the Petroset II-G and Aquaset aqueous/PUREX full surrogate sample after its curing period in July. Three samples were taken from the Petroset II-G and organic PUREX full surrogate section of the core and one sample was collected from the bottom layer of Aquaset and the aqueous component of the sample. As seen in Table VI, the samples collected from the organic phase of the sample produced good LRT values, but the sample taken from the aqueous phase of the sample failed the LRT. It is suspected that the Aquaset sorbent was coated with the organic phase of the PUREX surrogate while it traveled through that phase to the water phase in the bottom of the drum. This coating of the organic phase has interfered with the sorption capacity of the Aquaset sorbent so it did not sorb sufficiently when it encountered the water phase. A methodology will be developed during FY06 testing to solve for this phenomenon.

Two samples were collected from the Nochar aqueous/PUREX full surrogate sample in July 2005 since it was about half the volume of the Petroset II-G sample. The LRT values are not good for this sample; the bottom core sample failed the LRT and the top sample came very close to failing the LRT. The Nochar combination of sorbents does not tie up the aqueous/PUREX full surrogate as well as expected and does not compare to the Nochar sample generated with the full PUREX surrogate without a water phase. That sample is pictured in Figure 2 and one can really see the difference when compared to the sample in Figure 3 when a water phase was added to the surrogate waste stream. A water phase seems to have a negative effect on the Nochar sorbent materials at this scale. The LRT value of 0.453% from the sample taken in October 2005 during the sample destruction is not a very good value either since it approaches the NTS WAC of 0.5% by volume. Additional Acid Bond will have to be added to any other samples made at this scale in an attempt to tie up the water phase of the PUREX surrogate.

Table VI. Data Gathered after the 242-Liter Sample Testing

Sorbent Name	Weight-Based Waste-Loading Ratio (wt sorbent: wt PUREX)	Sampling Date	Percent Water	Sample Area in the 242-liter Drum or Sample Layer	LRT (liquid released during testing) % by Volume NTS WAC 0.5%
Petroset II-G	2.3:1	7-20-05 7-20-05 7-20-05	10	Top Middle Bottom Section for Petroset Layer	0.008 0.007 0.041
Aquaset	1.5:1	7-20-05		Aquaset Layer	0.536
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	7-20-05 7-20-05	10	Top Bottom	0.523 0.470
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	10-27-05	10	Destroyed Sample	0.453

Petroset II-G Sorbent Inconsistencies

For Phases I, II, III and part of Phase IV of the PUREX testing, batch 17 Petroset II-G sorbent material was used during sample generation. At the conclusion of the aqueous PUREX full surrogate 22-liter testing during Phase IV, MSE received Petroset II-G sorbent material from

batch 18 to generate the 242-liter drum samples. When the sorbent material was weighed out prior to sample generation, the testing personnel noticed a difference in color between the batches of sorbent material. Tests were then undertaken to determine what the differences between the sorbent materials were. Particle size analysis, density comparisons and x-ray diffraction tests were performed on the two different sorbent batches that showed differences in the material. Figure 5 shows an equal weight of batch 17 and batch 18 sorbent materials. The Petroset II-G batch 17 sorbent is gray and batch 18 sorbent is brown. The weight per volume is greater for batch 17 compared to batch 18. This factor required the weight-based, waste-loading ratio for the Petroset batch 18 to be increased to 2.3:1 instead of the optimum waste-loading ratio of 2:1 used for batch 17. This is an increase of 15% by weight, which translates to additional sorbent and therefore additional cost to treat the same volume of waste. Two 242-liter samples were generated with the simple PUREX surrogate using the different Petroset II-G batches.

Fig 5. Batch 17 and batch 18 Petroset II-G

Fig 6. 242-liter Petroset II-G samples

Figure 6 shows two samples generated with the different sorbent materials at the 242-liter scale. The products generate similar wasteforms with batch 18 sorbent generating a somewhat harder wasteform than the batch 17 sorbent. Table VII compares LRT values for the samples generated with the aqueous PUREX full surrogate and the different batches of Petroset II-G sorbent.

Table VII. Petroset II-G Batch Comparisons

Sorbent Name	Weight-Based Waste-Loading Ratio (wt sorbent: wt PUREX)	Sampling Date	Percent Water	Petroset II-G Batch Number	LRT (liquid released during testing) % by Volume NTS WAC 0.5%
Bench Scale Samples					
Petroset II-G Aquaset	1.7:1 1.5:1	4-11-05	5 10	Batch 17	0.047 0.147
22-liter Scale Samples					
Petroset II-G Aquaset	1.7:1 1.5:1	4-11-05	5 10	Batch 17	0.078 0.076
242-liter Scale Samples					
Petroset II-G Aquaset	2.3:1 1.5:1	4-11-05	10	Batch 18	0.008 0.007 0.041

The LRT values obtained from the Petroset II-G samples regardless of scale or batch number are all well below the NTS WAC of 0.5%. The sorbent material easily scales up to the 242-liter size and it does not seem to matter which batch of the sorbent material was used since they both produce solid wasteforms with very good LRT values.

Long-Term Stability Studies for FY04 Samples

Samples from the Phase III study in FY04 are stored outdoors in ultraviolet (UV) protected overpack drums to give an indication of the long-term stability of the combinations. Duplicate samples were generated for some of the sample ratios and these samples were not stored in UV-protected overpack drums to determine if UV exposure over time would degrade the samples. Daily high and low temperatures were recorded, and samples were exposed to the natural temperature variation (day to night) over a variety of seasons in Butte, Montana, for over a year of storage.

To date, instability of the Nochar samples when subjected to high temperatures and/or sunlight and the increased apparent offgas generation for all samples at higher temperatures were the only long-term stability issues noted.

PFT and LRT were performed on the samples 14 days after sample generation in FY04 and again at the end of FY05. Since all of the samples passed the PFT, they were subjected to the LRT. The results for the two sampling events are listed in Table VIII.

Table VIII. LRT Results for FY04 Samples

Sorbent Name	Weight-Based Waste-Loading Ratio (wt sorbent: wt PUREX)	Initial Sample Date	LRT % Release by Volume NTS WAC 0.05%	End of FY05 Sampling Date	LRT %Release by Volume NTS WAC 0.5%
Petroset II-G	2:1	5-18-04	0.006	9-6-05	0.005
Petroset II-G Duplicate *	2:1	5-18-04	0.010 *	9-6-05	0.006 *
Petroset II-G	1.9:1	5-18-04	0.023	9-6-05	0.005
Petroset II-G	1.8:1	5-18-04	0.020	9-6-05	0.006
Petroset II-G	1.7:1	5-18-04	0.026	9-6-05	0.006
Petroset II-G	1.6:1	5-18-04	0.017	9-6-05	0.015
Petroset II-G	1.5:1	5-18-04	0.059	9-6-05	0.022
Nochar	1:4	5-19-04	0.416	9-6-05	0.380
Nochar Duplicate *	1:4	5-19-04	0.403 *	9-6-05	0.568 *
Nochar	1:3	5-19-04	0.139	9-6-05	0.113
Nochar Duplicate *	1:3	5-19-04	0.140 *	9-6-05	0.153 *
Nochar	1:2.9	5-20-04	0.131	9-6-05	0.124
Nochar	1:2.8	5-20-04	0.091	9-6-05	0.135
Nochar	1:2.7	5-20-04	0.084	9-6-05	0.085
Nochar	1:2.6	5-20-04	0.066	9-6-05	0.069
Nochar	1:2.5	5-20-04	0.043	9-6-05	0.065
Nochar Duplicate *	1:2.5	5-20-04	0.063 *	9-6-05	0.075 *
Nochar	1:2.4	5-20-04	0.029	9-6-05	0.040
Nochar	1:2.3	5-20-04	0.031	9-7-05	0.055
Nochar	1:2.2	5-24-04	0.023	9-7-05	0.022
Nochar	1:2.1	5-24-04	0.006	9-7-05	0.018
Nochar	1:2	5-24-04	0.009	9-7-05	0.023
Nochar Duplicate *	1:2	5-24-04	0.009 *	9-7-05	0.026 *
* Duplicate samples were not stored in UV protected overpack drums					

The LRT values for the Petroset II-G samples did not significantly change during the storage period. In fact, less liquid was released from the Petroset II-G samples during the second sampling event in September 2005. Some of the LRT values for the Nochar samples did significantly change during the storage period as reflected by the LRT numbers in Table VII. The larger the waste-loading ratio of the sample, the bigger change from the initial sampling event to the September 2005 sampling event for the duplicate samples that were not UV protected. All of the duplicate samples released more liquid for the sampling event in September 2005. This indicates that UV has an affect on sample stability over time for the samples generated with Nochar Petro Bond and the full PUREX surrogate. Information from the WSRC solidification treatability study also indicates that UV light degrades polymer sorbents when combined with PUREX [2].

Cost Analysis Results

The results from the tests for FY05 were evaluated and a cost evaluation was performed to project the cost of solidifying PUREX using each sorbent (cost/4404 liters (1,000 gallons) of PUREX solidified). The cost evaluation data is summarized in Table VIII.

Table VIII. Cost Evaluation Data

Sorbent Name	Optimum Weight-Based Waste-Loading Ratio Based on FY04 Testing (wt sorbent:wt PUREX)	Unit Sorbent Cost ($/lb)	Sorbent Cost ($/4404 Liters of PUREX) using the Optimum Waste-Loading Ratio
Nochar	1:3	$8.25	$19,151
Petroset II-G	2.3:1	$2.60	$41,645

Petroset II-G is the most expensive option when sorbent cost alone is considered. However, mixing costs were not included in the cost evaluation, and Nochar would have a considerable associated mixing cost to solidify the PUREX waste.

CONCLUSIONS AND RECOMMENDATIONS

A comparison of the LRT values for the aqueous PUREX full surrogate samples at the different sample size is shown below in Table IX.

All of the samples created with the Fluid Tech sorbent products (Petroset II-G and Aquaset) and full PUREX surrogate or the aqueous PUREX full surrogate easily passed the NTS criteria for LRT with the exception of the Aquaset Layer in the 242-liter sample. However, a method will be developed to isolate the Aquaset from the organic PUREX phase while delivering it to the bottom of the samples during FY06 testing.

Petroset II-G is formulated to remove the need for mixing. Petroset II-G should be added to the liquid waste in one application. Any deployment with Petroset II-G would not require mixing or the associated mixing costs. The products are easy to use and solidification using these products is much less labor intensive and produces a solid freestanding wasteform.

The samples created with the Nochar sorbent products and the aqueous PUREX full surrogate do not scale up to the 242-liter scale. When the aqueous component was added to the surrogate PUREX waste stream, the Nochar combination of sorbent products had trouble tying up the liquid at the larger scale. Two LRT tests were performed on the aqueous/PUREX full surrogate 242-liter drum sample and each had high liquid release values when compared with the NTS WAC value of 0.5% release by volume. MSE does not recommend using a combination of Petro Bond and Acid Bond for a PUREX waste stream that has an aqueous component.

Table IX. Comparison of LRT Values at Different Scales

Sorbent Name	Weight-Based Waste-Loading Ratio (wt sorbent: wt PUREX)	Percent Water	Sample Container Sample Area or Sample layer	LRT (liquid released during testing) % by Volume NTS WAC 0.5%
Aqueous PUREX Full Surrogate Samples				
Bench-Scale Samples				
Petroset II-G Aquaset	1.7:1 1.5:1	10%	Jar	0.146
Petroset II-G Aquaset	1.7:1 1.5:1	5%	Jar	0.047
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	10%	Jar	0.256
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	5%	Jar	0.692
22-liter Scale Samples				
Petroset II-G Aquaset	1.7:1 1.5:1	5	Middle of Bucket	0.027
Petroset II-G Aquaset	1.7:1 1.5:1	10	Middle of Bucket	0.021
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	5	Middle of Bucket	0.155
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	10	Middle of Bucket	0.172
242-liter Scale Samples				
Petroset II-G Aquaset	2.3:1 1.5:1	10	Top Middle Bottom Section for Petroset Layer Aquaset Layer	0.008 0.007 0.041 0.536
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	10	Top Bottom	0.523 0.470
Nochar Petro Bond Nochar Acid Bond	1:3 1:2	10	Destroyed Sample	0.453
Full Surrogate PUREX Samples without an Aqueous Phase				
242-liter Scale Samples				
Petroset II-G	1.7:1	0	Middle	0.032
Nochar Petro Bond	1:3		Middle	0.169

Testing at the 242-liter drum scale shows that the full PUREX surrogate and the Nochar Petro Bond sorbent are difficult to mix at the 1:3 waste-loading ratio (without a water phase) because the mixture thickens very quickly during the curing process. Any deployment scenario using Nochar would have to address this mixing issue. MSE does not recommend mixing the Nochar and PUREX combinations in a 242-liter drum because it requires so much extra volume since very vigorous mixing is required for the combination. A mixer capable of fast continuous batch mixing should be identified for mixing the Nochar with the PUREX waste stream at the larger scale.

If B-12 and/or B-25 boxes will be used for deployment, simple PUREX surrogate tests using these containers are recommended due to the differing geometry of a box versus a 242-liter drum.

MSE recommends the separation of the aqueous and organic phases of the PUREX waste prior to treatment of the wastestream with sorbent materials to help avoid any complications or interferences with the different sorbent combinations.

MSE recommends further testing with actual waste at SRS once plausible deployment strategies are devised to ensure the waste-loading ratios will generate a product that meets Resource Conservation and Recovery Act disposal requirements and waste acceptance criteria for disposal at SRS or NTS.

The evaluation of sorbents for solidification of organic PUREX waste from SRS indicates that solidification could provide a cost-effective alternative to incineration of this waste.

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