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**PCB Extraction from ORNL Tank
WC-14 Using a Unique Solvent**

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CHEMICAL TECHNOLOGY DIVISION

PCB EXTRACTION FROM ORNL TANK WC-14 USING A UNIQUE SOLVENT

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EXECUTIVE SUMMARY

This report summarizes the development work of the Engineering Development Section of the Chemical Technology Division at Oak Ridge National Laboratory (ORNL) for an organic extraction method for removing polychlorinated biphenyls (PCBs) from tank WC-14. Tank WC-14 is part of the ORNL liquid low-level radioactive tank waste system and does not meet new secondary containment and leak detection regulations. These regulations require the tank to be taken out of service, and remediated before tank removal. To remediate the tank, the PCBs must be removed; the tank contents can then be transferred to the Melton Valley Storage Tanks before final disposal.

The solvent being used for the PCB extraction experiments is triethylamine, an aliphatic amine that is soluble in water below 60°F but insoluble in water above 90°F. This property will allow the extraction to be carried out under fully miscible conditions within the tank; then, after tank conditions have been changed, the solvent will not be miscible with water and phase separation will occur. Phase separation between sludge, water, and solvent will allow solvent (loaded with PCBs) to be removed from the tank for disposal. After removing the PCBs from the sludge and removing the sludge from the tank, administrative control of the tank can be transferred to ORNL's Environmental Restoration Program, where priorities will be set for tank removal.

Experiments with WC-14 sludge show that greater than 90% extraction efficiencies can be achieved with one extraction stage and that PCB concentration in the sludge can be reduced to below 2 ppm in three extractions. It is anticipated that three extractions will be necessary to reduce the PCB concentration to below 2 ppm during field applications. The experiments conducted with tank WC-14 sludge transferred less than 0.03% of the original alpha contamination and less than 0.002% of the original beta contamination.

1. INTRODUCTION

The Federal Facilities Agreement imposes design and operating requirements on the Oak Ridge National Laboratory (ORNL) liquid low-level radioactive waste tank system, which includes tank WC-14. Tank WC-14 does not meet new secondary containment and leak detection requirements and contains a sludge with polychlorinated biphenyls (PCBs) and radioactive contaminants. The ORNL Waste Management and Remedial Action Division is working to transfer administrative control of the tank to the Environmental Restoration Program, where priorities for tank removal will be set. The PCB contamination will be removed before remediation of the radioactive materials and tank removal.

Tank WC-14 is a below-grade 1000-gal stainless steel tank that was installed at ORNL in 1951. It was one of the liquid waste tanks used in the collection and transfer of aqueous radioactive waste solutions from research and development laboratories in Building 4501 (Fig. 1). Tank WC-14 still contains residual waste from past operations and nonprogrammatic inflows. Tank liquids are removed periodically when the liquid level reaches about 60 vol % of its capacity. The liquids are then transferred to the central waste collection header.

Tank WC-14 has both liquid and sludge phases. The liquid comes from nonprogrammatic inflows from the collection header that occur when liquids are removed from the tank farm and backflows from the valve box drain into tank WC-14. The inflow into tank WC-14 has ranged from 0 to 110 gal/month during a previous 12-month period. Only 2 months out of the 12 had inflows greater than 45 gal, with normal inflows of ~5 gal. The sludge volume is estimated at approximately 110 gal if the dish bottom of the tank is full to a depth of 11.5 in. from the bottom. The liquid was sampled in November 1992, two sludge cores were taken in March 1993, and the liquid was sampled again in August 1993 for PCBs. The liquid and sludge samples were analyzed for inorganic, radiochemical, and organic constituents and for some physical properties.

The liquid sample contained high levels of radioactive materials, with ^{137}Cs being the principal contributor. The concentrations of metals listed as hazardous under the Resource Conservation Recovery Act (RCRA) were below the level of regulatory concern. The principal inorganic constituents were sodium, chloride, nitrate, and sulfate. The liquid was neutral pH when the tank was sampled in November 1992 but alkaline when the sludge samples were collected in March 1993. The pesticide/PCB analysis indicated 278 $\mu\text{g/L}$ of Arochlor 1248 in the aqueous liquid.

The sludge in tank WC-14 contains high levels of alpha emitters. It is contaminated with PCBs in excess of 50 ppm, the regulatory limit for PCB discharge, and contains metals listed as hazardous under RCRA. The principal metals in the sludge are uranium, thorium, iron, and sodium. The sludge is a transuranic (TRU) waste containing $\sim 1,000$ nCi/g (wet basis) of TRU components with half-lives greater than 20 years.

An investigation of PCB-removal technologies was completed through literature reviews of potential treatment technologies. The technologies reviewed had to operate inside the tank, which contained a mixture of high-level radiation, TRU isotopes, RCRA metals, and PCBs. The review suggested that solvent extraction using triethylamine (TEA) may have a high probability of success for removing PCBs from radioactive tank sludge.

TEA is an aliphatic amine with a unique inverse-miscibility characteristic with water that gives TEA potential advantages over other solvents. TEA is soluble in water below 60°F but insoluble in water above 90°F. This property allows the water/solvent/oil extraction to be carried out efficiently under fully miscible conditions ($<60^\circ\text{F}$), followed by phase separation between the water and solvent/organic phases at a higher temperature. Under fully miscible conditions, the extraction system becomes two phases (solvent-water and sludge) rather than three phases (solvent, water, and sludge). These characteristics make this solvent the best candidate for in-tank extraction of PCBs. Prior work, completed by the Technical Division at the Oak Ridge K-25 Site, showed potentially

W-17° W-18

Fig 1. Map of site, Building 4501, WC-14 tank farm.

high extraction efficiencies with TEA.¹ The K-25 Site Technical Division investigated several solvent extraction methods for removing organics from sludge containing both hazardous organic materials and radioactive materials. Extraction results from this work revealed that TEA had the highest single-stage extraction efficiency of combined phenol, oil, and grease extractions. Some transfer of uranium was observed in the tests; however, experiments were conducted at 70°F, and did not take advantage of the inverse-miscibility property. At higher temperatures and higher pH, the phase separation is not expected to allow transfer of radioactive materials to the TEA phase. This report describes the results of experimental extractions to remove PCBs from tank WC-14 sludge by solvent extraction with TEA.

1.1 SCOPE

The Engineering Development Section of the ORNL Chemical Technology Division is developing an extraction method to remove PCBs from tank WC-14 sludge while leaving radionuclides in the sludge. The tasks necessary to remove the PCBs and transfer tank WC-14 to the Environmental Restoration Program include a technology investigation, extraction experiments, remedial design, and sludge treatment. The technology investigation was completed prior to the extraction experiments that are the subject of this report.

1.2 TECHNOLOGY INVESTIGATION

A technology investigation was completed before selecting a method for removing PCBs from tank WC-14. Technologies selected had to show a potential for application to the sludge in the tank, demonstrated removal efficiencies, and a high potential for use in a radioactive environment. After a technology was selected, the process modifications for application to the sludge inside the tank had to be completed.

The objective of the technology investigation was to identify a technology demonstrated on similar types of materials for removal and/or destruction of PCBs. The technology must be applied to the WC-14 sludge in the tank. The criterion for in-tank application is necessary due to the high levels of radiation associated with the sludge material. Thermal and nonthermal technologies were researched through previous work and literature reviews. A sample of technologies investigated² and associated problems with using the technology for the WC-14 waste stream are listed below.

Thermal Treatment

- *Incineration*—The Toxic Substances Control Act (TSCA) Incinerator at the Oak Ridge K-25 Site cannot accept the high levels of alpha contamination.
- *Thermal desorption*—Thermal desorption is not practical in situ because the high temperatures necessary for desorption would require too much energy input to an underground tank and the mixing requirements cannot easily be ensured.

Nonthermal Treatment

- *Wet-catalyzed oxidation*—The reduced temperature and pressures as compared with those of the conventional oxidation process are not feasible in an underground storage tank.
- *Solvated electrons*—Solvated electrons have been successfully generated in liquid ammonia, which is not feasible in an underground storage tank. (Unsuccessful attempts were made to generate solvated electrons in solvent TEA.)
- *Polyethylene glycol (PEG)-potassium hydroxide (KOH)*—This technology operates at temperatures above 300°C and is not applicable to an in-tank approach.

- *Base-catalyzed decomposition*—This is a two-stage process using enhanced thermal desorption at 350°C to vaporize the PCBs. The PCBs are then processed in a separate reactor at 350°C. This technology is thus not applicable to an in-tank approach.
- *Microbial destruction*—Most PCB-degrading aerobic bacteria can easily biodegrade only the lower-chlorinated PCB congeners, which may not successfully reduce the PCB concentration to the required limits of <2 ppm.

Solvent extraction was selected because of its ability to solubilize PCBs, modest operating conditions, capability for in-tank application, ability to be recycled, and effectiveness in reducing PCB levels to acceptable concentrations. The solvent extraction process has been proven on organics and PCB matrices and is currently being used at industrial sites;³ furthermore, the process produces wastes that can be disposed of at the TSCA Incinerator. The TEA solvent exhibits several very beneficial characteristics:⁴

- *High vapor pressure*—The solvent can be easily recovered from the extract of oil, water, and solvent through simple steam stripping.
- *Alkalinity*—The solvent works best in an alkaline solution of pH 10 or higher; therefore, metal hydroxides are not solubilized and will remain in the tank sludge.
- *Low heat of vaporization*—The solvent can be recovered from the treated sludge by simple heat with a low energy input.
- *Inversely miscible with water*—This property allows the water/solvent/oil extraction to be carried out under fully miscible conditions with water, followed by phase separation between the water and solvent/organic phases at slightly elevated temperatures (90°F).

The solvent extraction process extracts PCBs from the sludge by transferring the PCBs into the solvent phase. This process may be applied in several configurations, with two approaches being most applicable to the WC-14 PCB removal task. In both of these approaches, extraction of PCBs from the radioactive sludge takes place inside the tank; however, the location for the separation of solvent and water differs. The first approach uses in-tank separation, and the second employs

out-of-tank separation. The first approach is preferred to eliminate handling of high-activity sludge and/or material out of the tank. The second approach was not tested, because of the success of the first approach. The following paragraphs further describe differences between the two approaches.

In Situ Extraction with In Situ Separation of Water and Solvent—Solvent extraction and phase separation of the solvent and water will be conducted in tank WC-14. The primary advantage of this approach is that radioactive materials will not be processed out of the tank. A potential disadvantage is that extraction efficiencies could be affected by the concentration of water in the sludge.

In Situ Extraction with Ex Situ Separation of Water and Solvent—The extraction of PCBs into the solvent will be conducted in the tank; however, the phase separation of the solvent and water will be conducted outside the tank. The primary advantage of this approach is that each extraction stage reduces the water content in the tank, which also should increase the efficiency of each successive extraction stage.

2. EXPERIMENTAL DESIGN

Experiments were conducted on both a nonradioactive surrogate and the radioactive WC-14 sludge to determine the feasibility of using TEA to extract PCBs from tank WC-14 sludge. The nonradioactive surrogate sludge was developed for conducting preliminary experiments in a nonradiological laboratory prior to the confirmatory experiments on the actual WC-14 sludge in a radiological facility.

Experiments on the surrogate sludge were conducted in three sets. The first set of experiments was designed to determine approximate operating conditions and to determine the approximate

number of extraction stages required to reduce the PCB concentration to below 2 ppm. The second set of experiments was conducted to define the optimum operating parameters including solvent loading, contact time, and mixing requirements. The final set of experiments was conducted based on the most promising results from previous experiments to estimate the potential for radioactive material transfer.

Experiments on the WC-14 sludge were based on the results of the surrogate analysis and performed on three aliquots of actual WC-14 sludge. Preliminary results indicated excellent PCB extractions and transfer of a small amount of activity to the solvent. Based on this analysis, a second series of experiments was conducted, with the resulting solvent being filtered. Gross alpha, beta, and gamma scans were conducted on either side of the filter to determine the transfer mode of the radioisotopes.

2.1 SURROGATE WASTE PREPARATION

Analytical results of the two sampling campaigns conducted in March and August 1993 were the basis for selecting a surrogate sludge. During each sampling campaign, two sludge cores were collected and then sonicated to form composite samples, which were analyzed for PCBs, organics, and inorganics. A summary of the analytical results from the March 1993 sampling is shown in Tables 1 and 2.

The surrogate sludge formulation was based on the chloride, sulfate, and nitrate surrogate sludge described in DOE/MWIP-16⁵ and was modified to resemble the WC-14 sludge. The carbon content was decreased from 5% to about 2%, and PCBs were added to the mixture as a solution in methanol. Cerium nitrate was used as a surrogate for radioactive metals in the sludge. The modified surrogate sludge formulation is shown in Table 3.

Table 1. Analytical data for tank WC-14 sludge^a

Parameter	Value	Parameter	Value
Physical properties and miscellaneous data			
Density (g/mL)	1.094	IC (mg/kg)	4500
TC (mg/kg)	15,300	TDS (mg/g)	20
TOC (mg/kg)	10,800	TS (mg/g)	147
RCRA metals (mg/kg)			
Ag	<0.0009	As	<0.006
Ba	64	Cd	140
Cr	360	Hg	8.5
Ni	1330	Pb	580
Se	<0.006	Tl	b
Process metals (mg/kg)			
Al	650	Ca	2600
Co	58	Cu	68
Fe	6200	K	180
Mg	780	Mn	74
Na	13,000	Th	12,000
U	50,000	Zn	140
Anions (mg/kg)			
Br ⁻	*	Cl ⁻	*
CN ⁻	0.26	F ⁻	*
NO ₃ ⁻	*	PO ₄ ³⁻	*
SO ₄ ²⁻	*		
Alkalinity			
pH (units)	c	OH ⁻ (M)	NA
CO ₃ ²⁻ (M)	NA	HCO ₃ ⁻ (M)	NA
Radiochemical screening (pCi/g)			
Gross alpha	9.7E+05	Gross beta	1.4E+07
Beta/gamma emitters (pCi/g)			
¹⁴ C	<8.1E+02	⁶⁰ Co	3.43E+05
¹³⁴ Cs	7.35E+04	¹³⁷ Cs	4.27E+06
¹⁵² Eu	7.14E+06	¹⁵⁴ Eu	2.29E+06
¹⁵⁵ Eu	5.70E+05	³ H	*
⁹⁰ Sr	6.05E+05		
Alpha emitters (pCi/g)			
²⁴¹ Am	3.8E+05	²⁴⁴ Cm	3.5E+04
²³⁷ Np		²³⁸ Pu	6.2E+04
²³⁹ Pu/ ²⁴⁰ Pu	5.9E+05	²²⁸ Th	
²³³ U/ ²³⁴ U		²³³ U/ ²²⁹ Th/ ²³⁷ Np	7.03+03
²³⁸ U	1.0E+04		

IC = inorganic carbon;

TC = total carbon;

TDS = total dissolved solid;

TOC = total organic carbon;

TS = total solids.

^aSample WC-14-S1 was a composite of the sludge phases in samples WC-14-S1 and WC-14-S2 collected March 24, 1993. The samples were combined and sonicated before taking aliquot.

^bAnalysis not run due to spectral interference from uranium.

^cThe pH of the supernatant liquid over the sludge at the time the sludge was sampled was 12.6. The pH of the sludge interstitial liquid was ~13-14 by qualitative analysis with pH stick.

Note: 1 pCi = 0.037 Bq.

Table 2. Organic analytical data hits and values for total inorganic carbons (TICs) for tank WC-14

Parameter	Sludge
Water-soluble organic compound analysis ^a	
methyl alcohol	<i>b</i>
Semivolatile organic compound analysis ($\mu\text{g/kg}$)	
Bis(2-ethylhexyl)phthalate	14,000 J ^c
Naphthalene	3500 J
Pesticides/PCBs analysis ($\mu\text{g/kg}$)	
Arochlor 1248	119,000 ^d
Heptachlor	7370
Semivolatile organic compound analysis: TICs (no. of TICs) ($\mu\text{g/kg}$) ^e	
Unknown TICs	734,000 J (7)
Unknown hydrocarbons	674,200 J (7)
C ⁴ -benzene	95,200 J (2)
Tributyl phosphate	270,000 J
Trichlorobiphenyl	25,500 J (2)
Tetrachlorobiphenyl	15,600 J (2)
Pentachlorobiphenyl	8,000 J

^aWater-soluble organics analysis also suggested the presence of acetone in WC-14-L1, but purge/trap gas chromatography/mass spectroscopy would be required for confirmation.

^bAnalysis not run because sample was insufficient to collect interstitial liquid.

^cJ indicates that the quantitative value is estimated. This qualifier will appear after a value that is below the quantitation limit (i.e., the compound was detected at some level below the concentration that can be accurately measured). This qualifier also appears after tentatively identified compounds for which no specific calibration was available.

^dTank was resampled for PCB analysis.

^eResult is the sum of TICs. The number of TICs is shown in parenthesis.

Table 3. Recipe for surrogate

Constituent	Weight (%)
PCB (Arochlor 1248)	50 or 312 ppm (<1)
CH ₃ OH	7
NaOH	6
NaCl	2
Na ₂ SO ₄	1
Na ₂ CO ₃	1
CaCl ₂	<1
Fe(NO ₃) ₃	1
Ni(NO ₃) ₃	<1
Pb(NO ₃) ₂	<1
Cr(NO ₃) ₃	<1
Ce(NO ₃) ₃	18
H ₂ O	>60

2.2 SOLVENT EXTRACTIONS

The solvent extractions on both the surrogate sludge and the WC-14 sludge were conducted using the same extraction method. Based on the surrogate experiments, an optimized set of operating conditions was developed for radiological experiments. The analytical procedure for determining PCB concentrations in the solvent was similar to the analytical procedure used for the ORNL gunite and associated tank sludges and is described in this section.

2.2.1 Surrogate Experiments

To verify PCB concentration in the surrogate sludge, three samples were extracted with hexane for PCB analysis prior to extraction experiments. The samples were then extracted with TEA under various operating parameters. After each sample had been extracted with TEA, the sludge was reextracted with hexane to determine residual PCB concentration. The extraction procedures for both TEA and hexane are included in the following discussion.

A sample of surrogate sludge (approximately 20 g) was placed in a preweighed jar containing a magnetic stir bar. The jar was reweighed to verify the weight of the sludge before a known volume of TEA (or hexane) was added. Samples being extracted with hexane were placed on a rotator and allowed to extract for 24 h. Samples being extracted with TEA were placed in a cooling bath and stirred for a predetermined amount of time at 40°F. The samples with TEA were then placed in a second bath at 90°F to allow phase separation between TEA and water. After complete phase separation, a sample of TEA was withdrawn for analysis.

This procedure was used for three sets of experiments, with each set having a specific objective. The first set was a screening process to define approximate operating conditions including contact time and solvent-to-sludge ratios. This set of extractions was conducted using sludge with a PCB concentration of 50 ppm, ratios of TEA to sludge ranging from 1:2 to 3:1 (milliliters of TEA per gram of sludge), and contact times from 1 to 72 h, which included 1 h of mixing. Sequential extraction stages were conducted for a few of the experiments.

Using information gained from the first set of experiments, the second set allowed determination of optimum parameters for solvent loading, contact time, and mixing requirements. When a sludge with 312 ppm PCBs was used, solvent-to-sludge ratios varied from 1:1 to 1:3 and contact times ranged from 15 min to 1 h. The experiments were first conducted with mixing and then repeated without mixing.

The third set consisted of one experiment, conducted in triplicate, based on the best operating parameters found previously to estimate radioactive material transfer to the TEA. After the extractions, the TEA phase was submitted to the Analytical Services Organization (ASO) for metals analysis, which permits an understanding of the potential for transfer of radioactive material. Excessive transfer of radioactive materials could cause either operational safety problems or difficulties in disposing of spent solvent from the process. The extractions were conducted using a solvent loading of 1 mL of TEA per gram of sludge with a mixing time of 1 h.

2.2.2 Radiological Experiments

Unused samples from tank sampling campaigns in 1993 were combined by stirring the samples together to form one composite WC-14 tank sludge sample. Seven aliquots of the WC-14 tank sludge were measured into separate volatile organic analysis vials: three for initial PCB concentration, one for solvent partitioning behavior, and three for TEA extractions. The analytical procedure for the PCB concentration was the same as that used for the gunite and associated tank sludges. In general the aliquots were mixed with sodium sulfate (drying agent) and then extracted three times in an ultrasonic bath with methylene chloride/acetone [50:50 (vol:vol)]. The extracts were solvent exchanged into hexane and then extracted with concentrated sulfuric acid until the extracts were free of salts. The sulfuric acid extracts were back-extracted with hexane and washed with water. The hexane extracts were analyzed with a capillary-column gas chromatograph with an electron capture detector using external standards of Arochlor 1248.

The TEA extractions were conducted on the three 10-g sludge aliquots with equal volumes of TEA. The sludge and TEA mixture was stirred for 1 h for each extraction in an ice bath. The mixture was then placed in a 120°F water bath for approximately 5 min and then centrifuged. The

TEA phase was pipetted off and dried in the laboratory hood. The same procedure was used for each of the three sequential extractions, beginning with clean TEA before each extraction. Nitric acid was added to the dried TEA, with a 10-mL sample used for a gamma scan, two 5-mL samples used for gross alpha and beta analysis, and another sample used for metals analysis by inductively coupled plasma/atomic absorption.

3. RESULTS

Two types of experiments were conducted: (1) surrogate experiments and (2) radiological experiments with WC-14 sludge. The surrogate results provided the basis for continuing radiological experiments with WC-14 sludge.

3.1 SURROGATE SLUDGE EXTRACTIONS

Results of the first set of experiments with the surrogate sludge indicated little effect on extraction efficiencies of either solvent loading ratios of TEA to sludge or contact times above approximately 1 h (data not shown). PCB concentrations were reduced to less than 10 mg/kg in a single extraction stage for most experiments. Based on these results, the conditions for the second set of surrogate experiments were defined.

The second set of surrogate experiments tested three different parameters: (1) volume ratios of TEA to sludge, (2) contact time between sludge and TEA, and (3) mixing versus nonmixing. The results, shown in Fig. 2, illustrated that mixing during the extraction procedure greatly increased extraction efficiencies. These extraction efficiencies will reduce the PCB concentration to below 2 ppm in approximately three extractions. The data collected during surrogate experiments also

Fig. 2. Effect of contact time on extraction efficiencies.

indicated that contact times of more than 1 h and ratios of TEA to sludge above 1:1 did not appear to affect PCB removal significantly.

The third set of experiments was conducted to determine the potential for transfer of radioactive materials to the solvent. Analytical results indicated that, except for sodium, metal concentrations in TEA after extraction were not higher than in the method blank (extraction of water) or the TEA blank (no extraction). This finding was also true for cerium (a surrogate for uranium) since it was not detected in any samples (see Fig. 3). This observation supports the theory that radioactive elements are not expected to transfer to TEA during extraction. Transfer of other radioactive materials was determined by extracting PCBs with TEA from actual WC-14 sludge.

With successful results on surrogate materials, experiments with WC-14 sludge samples were initiated through ASO to confirm PCB removal efficiencies and the lack of radionuclide transfer into the solvent phase. ASO used the same experimental procedure described for the surrogate materials.

3.2 WC-14 SLUDGE EXTRACTIONS

To confirm the results of the surrogate sludge experiments, PCBs were extracted from WC-14 tank sludge. The WC-14 sludge was extracted three times with fresh TEA for each consecutive extraction. All extractions were conducted using the same procedure, which takes advantage of the inverse-miscibility property of the solvent. The first extraction had an average PCB extraction efficiency greater than 90%, and after three extractions, the PCB concentration in the sludge was reduced to less than 1 ppm (Table 4). In sample no. 5 the first extraction efficiency is 0 because the sample vial was not properly fixed in place prohibiting mixing of the sludge and TEA. This efficiency is based on the PCB concentration in the extract versus the total PCBs extracted by the

Fig. 3. Metals detected in TEA for third set of surrogate experiments.

Table 4. WC-14 sludge extraction with triethylamine

	Extraction efficiency	Concentration of PCBs after extraction (ppm) ^a
Sample 5		0.4
Extraction 1	0	
Extraction 2	97	
Extraction 3	3	
Sample 6		0.2
Extraction 1	83	
Extraction 2	15	
Extraction 3	2	
Sample 7		0.1
Extraction 1	91	
Extraction 2	8	
Extraction 3	1	

^aOriginal average PCB concentration in sludge was 163 ppm.

solvent. During the second extraction of sample number 5, the apparatus was properly set up and the extraction was effectively conducted. The extractions with WC-14 sludge indicate that the material must be mixed and that a temperature of 90°F or higher is necessary for a distinct phase separation between the TEA and water phases. The extractions of WC-14 sludge also confirmed that a 1:1 (vol:vol) ratio of sludge to solvent is sufficient for extracting PCBs.

Based on the surrogate results, radionuclides were not expected to transfer into the solvent phase. To determine if the radionuclides transferred into the solvent, gross alpha, beta, and gamma scans were conducted on the loaded solvent after the third extraction of each of the three WC-14 sludge aliquots. A metals analysis was also conducted on the solvent after the third extraction to determine the metals that had transferred into the solvent (Table 5). The gross alpha and beta analyses indicate that radioactive contamination transferred into the spent solvent. The transfer of

radioactive contamination into the TEA was a concern because of the acceptance criteria at the TSCA Incinerator (solvent destination).

To determine if the radionuclides transferred into the spent solvent as particulates, a series of extractions was conducted, followed by filtering the solvent through a 0.45- μ m filter after extraction of the PCBs. Gross alpha, beta, and gamma scans on both sides of the filter were determined to be essentially unchanged. It was concluded that the radioactive isotopes are transferring into the solvent as dissolved species.

The concentration of isotopes in the solvent does not cause a disposal problem as long as the TSCA Incinerator does not have to operate as a TRU facility. Because of the low concentrations of TRU isotopes in the waste solvent, the TSCA facility should not have to function as a TRU facility. The TSCA personnel have reviewed the radionuclide data from the WC-14 experiments. The review indicates that the solvent loaded with PCBs can be accepted and burned at the TSCA Incinerator. The following parameters have been reviewed, and based on the data submitted, the spent solvent will meet the TSCA waste acceptance criteria.

Environmental impact statement—The National Environmental Policy Act (NEPA) Environmental Impact Statement does not specify a limit for specific isotopes; therefore, the solvent can be accepted because the waste dose rate calculations for radioactive isotopes are within acceptable limits.

NESHAP—The TEA solvent generated from PCB extraction of WC-14 sludge to be submitted to the TSCA Incinerator was determined to be below the National Emission Standards for Hazardous Air Pollutants set for the TSCA Incinerator.

Table 5. WC-14 sludge experiments analyses^a

Analyte	Average concentration of 5, 6, 7	Units	Original concentration in sludge	Units	Transfer from sludge to solvent (%)
Gross beta	3.26E+02	Bq/g	1.10E+06	Bq/g	0.0296
Gross alpha	9.51E-01	Bq/g	5.90E+04	Bq/g	0.0016
Co-60	2.04E+01	Bq/g	1.90E+04	Bq/g	0.1077
Cs-134	5.42E+00	Bq/g	3.70E+03	Bq/g	0.1467
Cs-137	3.88E+02	Bq/g	1.40E+05	Bq/g	0.2780
Eu-152	3.32E+01	Bq/g	4.30E+05	Bq/g	0.0077
Eu-154	1.51E+01	Bq/g	1.60E+05	Bq/g	0.0094
Eu-155	6.35E+00	Bq/g	4.00E+04	Bq/g	0.0159
Ag	1.23E-01	ug/g	1.14E+01	ug/g	1.0917
Al	3.81E-01	μg/g	4.00E+02	μg/g	0.0953
Ba	7.06E-02	μg/g	8.78E+01	μg/g	0.0805
Be	1.51E-03	μg/g	6.77E+00	μg/g	0.0223
Ca	7.94E-01	μg/g	4.34E+03	μg/g	0.0183
Cd	1.11E-01	μg/g	2.36E+02	μg/g	0.0471
Co	8.24E-02	μg/g	4.49E+01	μg/g	0.1838
Cr	4.53E-02	μg/g	4.56E+02	μg/g	0.0099
Cu	2.29E-01	μg/g	7.83E+01	μg/g	0.2938
Fe	6.18E-01	μg/g	6.14E+03	μg/g	0.0101
K	8.02E-01	μg/g	1.72E+02	μg/g	0.4687
Mg	2.82E-01	μg/g	7.33E+02	μg/g	0.0385
Mn	1.75E-01	μg/g	3.09E+02	μg/g	0.0565
Na	4.48E+01	μg/g	1.06E+04	μg/g	0.4248
Ni	2.43E-01	μg/g	1.15E+03	μg/g	0.0211
Pb	1.21E+00	μg/g	1.19E+01	μg/g	11.3060
Sb	1.50E+00	μg/g	1.49E+01	μg/g	11.1760
Th	3.02E-01	μg/g	1.36E+04	μg/g	0.0022
Tl	1.06+01	μg/g	3.90E+01	μg/g	37.2589
U	6.96E-01	μg/g	5.11E+04	μg/g	0.0014
V	6.52E-02	μg/g	5.66E+00	μg/g	1.1661
Zn	1.94E-01	μg/g	1.77E+02	μg/g	0.1096

^aComparison of the average concentration of isotopes and metals in the three TEA experiment extracts with the original concentration of isotopes and metals in the sludge.

Radiological inventory—The radiological inventory in the less than 200 gal of solvent proposed to be stored by TSCA is acceptable.

Radiological free—Provided the solvent is blended with another waste stream of at least 50 times the TRU contribution of uranium activity (325 dpm/ml uranium, in this example) prior to burning. It is understood that this waste must not require TSCA to operate as a TRU facility.

Transportation—Because of Department of Transportation regulations, the waste must be shipped in 55-gal-drum quantities from ORNL to the TSCA Incinerator at the Oak Ridge K-25 Site. Preliminary dose calculations indicate the exposure rate next to four drums of spent solvent to be approximately 3 mR/h. This calculation is based on one 55-gal drum filled with spent-PCB-loaded TEA with a concentration of isotopes equal to the average of the gamma scans for the three loaded TEA samples taken during extraction of WC-14 sludge.

3.3 CONCLUSION

The solvent extraction results for the WC-14 sludge confirmed the surrogate results that 90% extraction efficiencies can be achieved during the first extraction and that PCB concentrations in the sludge are <2 ppm after the third extraction. It is anticipated that three extractions, each beginning with fresh TEA (TEA may be recycled to obtain a fresh solvent), will be necessary in the field remediation to reduce the PCBs in the sludge to below 2 ppm. Based on dose calculations of experimental spent solvent, it is anticipated that the TEA removed from the tank will have an activity low enough to be contact handled outside of the tank. The transfer of radioactive isotopes is not a significant issue, because of the low concentrations in the spent solvent. The concentration

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in the spent solvent is significantly lower than the TRU waste definition of 100 nCi/g of isotopes with half-lives >20 years and an atomic number >92. This concentration should not cause problems for the TSCA Incinerator operations or downstream components such as the Central Neutralization Facility and incinerator bottom ash.

5. RECOMMENDATIONS

The draft TSCA Compliance Agreement⁶ states that historic PCB spills shall be remediated through the Environmental Restoration Program. It also states that radioactive PCBs and PCB items may be stored for more than 1 year but that they shall be scheduled for disposal as soon as possible. With these compliance agreements, it is recommended that the tank be isolated so that no further inflow into the tank occurs. If the inflow cannot be stopped completely, PCBs should be removed from the tank and the remaining tank contents considered non-TSCA, according to the U.S. Environmental Protection Agency and TSCA PCB spill cleanup policy outlined in 40 CFR 761.120. This will then allow all future nonprogrammatic inflows to be transferred to the Melton Valley Storage Tanks as non-PCB liquids. If the inflow can be completely stopped and no further liquid transfers from the tank are necessary, then this process should be used to remove the PCBs during decommissioning of the tank. It is also recommended that the unique TEA solvent be utilized in the removal of PCBs. This solvent has successfully removed PCBs from radioactive waste in both proof-of-principle and treatability studies. The solvent is most effective in the high pH media without dissolving or transferring significant quantities of radioactive materials and metals.

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