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ORGANIC COMPOUNDS IN SAVANNAH RIVER SITE HIGH-LEVEL WASTE

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ORGANIC COMPOUNDS IN SAVANNAH RIVER SITE HIGH-LEVEL RADIOACTIVE WASTE

D. D. Walker

SUMMARY

The Savannah River Site (SRS) tank farms contain the accumulated high-level radioactive waste from almost 50 years of site operations. This document summarizes information from waste analyses and chemical usage records related to organic compounds that have been sent to the tank farms. Information on potential decomposition products from the original organic compounds is also included. This information is pertinent to the caustic side solvent extraction (CSSX) process planned for decontaminating the liquid waste before disposal in Saltstone. Certain classes of organic compounds can interfere with the extraction process. The following conclusions result from the review.

- Organic compounds that can interfere with the solvent extraction process are present, have been sent, or are currently used in the tank farm.
- Examples of interfering compounds identified in this study include the following.
 - Tributylphosphate (extractant used in F and H Canyons) and its hydrolysis product, dibutylphosphate.
 - Siloxanes and siloxanols (breakdown products from defoaming agents)
 - Ion exchange resin fragments
 - Alkyl-aryl sulfonates (found in soaps, detergents, surfactants and certain process chemicals)
- With present information, it is not possible to determine the concentration (and therefore, the potential threat to the CSSX process) of the interfering compounds. A parallel study at Pacific Northwest National Laboratory (PNNL) involves analysis of samples from selected tanks to determine the concentration of organic compounds in waste samples.

Recommendations for additional work include a more thorough effort in searching available records related to chemical use and disposal, deployment of analytical methods for determining concentrations of compounds of interest, and a program of sampling and analysis.

INTRODUCTION

The SRS high-level waste tank farms store and process high-level liquid waste from a number of sources, including F- and H-Canyons, Receiving Basin for Off site Fuels (RBOF), the 299-H Decontamination Facility, Savannah River Technology Center, site analytical laboratories, and the Defense Waste Processing Facility (DWPF). The waste has been extensively analyzed for inorganic components and a data base containing the composition of the waste in each tank exists.¹ However, few analyses of organic compounds in waste have been obtained, largely because very little organic waste is sent to the tank farm and because, historically, SRS capabilities in this area have been limited.

The present study identifies organic compounds or classes of compounds that may occur in SRS high-level waste (HLW) based on a review of previous sample analyses and records of disposals of organic compounds to the HLW tank farms. Although in some cases the amounts of compounds sent to the tank farms are known and are included here, in general this report only seeks to identify compounds that may be present. Where possible, the chemical or radiolytic decomposition products from the initial compounds are identified.

This study was undertaken because certain categories of organic compounds can interfere with the caustic-side solvent extraction (CSSX) process proposed for decontamination of soluble high-level waste at the SRS. In 2001, the Department of Energy selected the CSSX process for removal of cesium from alkaline waste solutions prior to disposal in Saltstone.² Knowledge of the presence and concentrations of interfering compounds in SRS soluble waste is needed to ensure good process performance.

Recently, researchers at Pacific Northwest National Laboratory (PNNL) began development of analytical methods for several classes of organic compounds. The methods are suitable for high-level radioactive waste and the program includes analysis of several waste samples from the SRS.³ Early results from the study documented in this report identified the classes of compounds for which the PNNL researchers developed methods.

Categories of Organic Compounds that may Interfere with Solvent Extraction

Compounds that are known or expected to interfere with the CSSX process are characterized by the presence of a polar (ionic or neutral) end and a non-polar (aliphatic or aromatic) end. Usually, these compounds interfere by accumulating in the solvent, thereby affecting extraction or stripping of cesium. Small, polar or ionic organic molecules with appreciable water solubility tend not to interfere because they are purged in the aqueous process streams (e.g., they remain in the alkaline waste, or are removed from the solvent by the acidic strip or alkaline wash solutions). Lipophilic molecules containing large paraffinic or aromatic portions exhibit low solubility in water and high solubility in the CSSX solvent. The division between "small molecules" and "large molecules" occurs at 8 to 12 paraffinic or aromatic carbon atoms.⁴

The following sections describe examples of known or suspected compounds that interfere with the CSSX process.

Soaps and detergents

These compounds contain anionic head groups (typically sulfonates or carboxylates) with large, non-polar tails (either paraffinic, aromatic, or a combination). Examples include dodecylsulfonate⁵ and dimethylnaphthalenesulfonate⁶ which are known to interfere in CSSX stripping. Cleaning and decontaminating agents based on polyethylene glycols or chelating agents such as ethylenediaminetetraacetic acid (EDTA) and related compounds are likely too water soluble to accumulate in the solvent.

Phosphates

Alkyl phosphates with 12 or more carbon atoms can build up in the solvent. They interact with the modifier (trioctylamine), reducing its ability to solvate anions needed for charge balance with the cationic extractant-cesium complex. Tributyl phosphate (TBP) typifies this category (12 carbons). Dibutylphosphate (8 carbons) also interferes with stripping,⁴ but monobutylphosphate is likely too water soluble to accumulate in the solvent.

Alcohols

Alcohols with long aliphatic or aromatic chains may affect the CSSX process. Short chain homologs, such as methanol, ethanol, isopropanol, and butanol are too water soluble to build up in the solvent.

Amines

Amines with intermediate length alkyl groups may extract from the alkaline waste into the solvent as neutral molecules. Protonation in the acidic scrub stages allows extraction of the alkylammonium ion into the aqueous phase. The aqueous scrub stream returns to the last extraction stage where it combines with the alkaline waste. Deprotonation by the waste allows extraction to repeat, sending the amine back to the scrub section. This feed-back loop could produce high amine concentrations. Trimethylamine is an example of this class. Amines with longer alkyl chains show higher solubility in the solvent and are unlikely to participate in the feed-back loop, but could accumulate in the solvent. Tri-*n*-octylamine, a component of the solvent system, remains in the solvent and exemplifies the behavior of this class of compounds with longer alkyl chains.

RESULTS AND DISCUSSION

Results from Tank Farm Samples

Starting in 1998, a Potential Inadequacy in the Safety Analysis (PISA) related to flammability concerns in SRS waste tanks⁷ resulted in a program to sample and analyze SRS waste for volatile and semivolatile organic compounds. The program identified several organic compounds in the vapor space and waste.⁸ Table I lists the results of this program.

TABLE I. Organic Compounds Found in SRS Tank Farms

<u>Compound</u>	<u>Location*</u>	<u>Amount**</u>	<u>Reference</u>
<u>Alkanes and Aromatics</u>			
hexanes	Tank 32H vapor	0.2 µg/L	8g
<i>n</i> -paraffin	Tank 33F solution	37 mg/L	8d
	FPT-3 solution	77 mg/L	8f
toluene	HPT-5 surface	13 µg/disk	8b
	Tank 43H surface	1.2 mg/disk	8d
xylenes	FPT-3 vapor	0.8 ng/L	8b
	Tank 43H surface	400 µg/disk	8d
	FPT-3 surface	3 µg/disk	8f
1,2,4-trimethylbenzene	Tank 33F surface	1.9 µg/disk	8e
ethylbenzene	FPT-3 vapor	0.7 ng/L	8b
	FPT-5 vapor	0.1 ng/L	8b
1,3-diethylbenzene	HPT-5 vapor	61 µg/disk	8b
numerous 10 & 12 carbon benzyl and cyclohexyl fragments from polystyrene resins (example: 1-phenyl-2-butene, 800 µg/disk)	HPT-5 surface	24 to 800 µg/disk	8b, 8d
styrene	FPT-3 vapor	1.2 ng/L	8b
	HPT-5 vapor	0.1 ng/L	8b
biphenyl	Tank 38H solution	27 µg/L	8b
naphthalene	HPT-5 surface	170 µg/disk	8b
<u>Ester</u>			
tributylphosphate	FPT-3 solution	230 mg/L	8f
methyl 4-methylpentanoate	Tank 38H surface	8 µg/disk	8b
<u>Alcohols</u>			
<i>n</i> -butanol	Tank 33F vapor	1.3 µg/L	8g

* FPT = F-area Pump Tank; HPT = H-area Pump Tank

**Amounts listed as "µg/disk" were obtained from the Dip Filter Sampler in which an unspecified volume of liquid from the tank surface was filtered through a Solid Phase Extraction disk (47 mm diameter, C18-bonded silica particles impregnated in a Teflon filter disk). See Reference 8b for details.

TABLE I. Organic Compounds Found in SRS Tank Farms (continued)

<u>Compound</u>	<u>Location*</u>	<u>Amount**</u>	<u>Reference</u>
<u>Organic Acid Anions</u>			
formate	Tank 33F solution	1.3 g/L	8d
	FPT-3 solution	2.6 g/L	8f
<u>Aldehydes and Ketones</u>			
acetone	FPT-3 vapor	1.4 ng/L	8b
2-butanone	FPT-3 vapor	0.6 ng/L	8b
	FPT-5 vapor	0.5 ng/L	8b
4-methyl-2-pentanone	FPT-3 vapor	1.4 ng/L	8b
hexanal	HPT-5 surface	35 µg/disk	8b
<u>Miscellaneous Other</u>			
4,4-oxybisbenzenamine	Tank 38H solution	1 mg/L	8b
<u>Siloxanes</u>			
hexamethyl disiloxane	Tank 38H surface	280 µg/disk	8b
	Tank 26F surface	52 µg/disk	8e
	Tank 33F surface	44 µg/disk	8e
	FPT-3 surface	260 µg/disk	8b
methoxytrimethylsiloxane	Tank 38H surface	87 µg/disk	8b
trimethyl silanol	Tank 38H surface	31 µg/disk	8b
	Tank 26F surface	50 µg/disk	8e
	Tank 33F surface	95 µg/disk	8e
	FPT-3 surface	150 µg/disk	8b
methoxytrimethyl silane	Tank 26F surface	110 µg/disk	8e
	Tank 33F surface	270 µg/disk	8e
	FPT-3 surface	160 µg/disk	8b

* FPT = F-area Pump Tank; HPT = H-area Pump Tank

** Amounts listed as "µg/disk" were obtained from the Dip Filter Sampler in which an unspecified volume of liquid from the tank surface was filtered through a Solid Phase Extraction disk (47 mm diameter, C18-bonded silica particles impregnated in a Teflon filter disk). See Reference 8b for details.

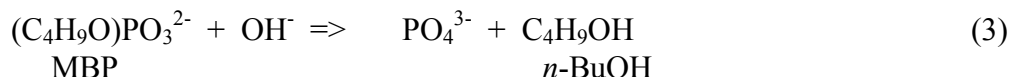
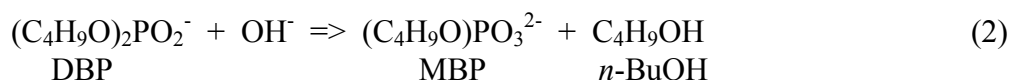
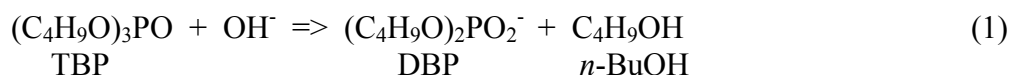
Process Chemicals from Canyons

The HLW at the SRS came from processing of nuclear materials by solvent extraction, ion exchange, and precipitation processes. Solvent extraction used tributyl phosphate (TBP) extractant dissolved in a paraffinic solvent. The original paraffinic solvent, called Ultrasene, contained branched chains and aromatic components. *n*-Paraffin containing 12- to 16-carbon chains replaced Ultrasene. Ion exchange processing used both anion and cation exchange resins. Head end operations for fuel dissolution used gelatin and gluconic acid. In addition, cleaning agents used in the canyons may also occur in waste sent to the tank farms.

Solvent Losses

Solvent (TBP and *n*-paraffin) may reach the tank farms dissolved or entrained in the aqueous waste stream. Canyon evaporators volatilize most of the *n*-paraffin and steam strip some of the TBP before transfer to the tank farms.⁹ Requirements on waste generators limit second (organic) phase transfers to less than 0.5 volume %.¹⁰ However, quarterly flushes of the evaporators to remove potential buildup of "red oil" sends some solvent directly to the tank farms. In addition, there have been occasional inadvertent transfers of larger amounts.¹¹ Table II lists estimated average annual losses for the entire 38-year operating life (1954 to 1992) based on entrainment of solvent in the aqueous process streams.¹² In 1984, M. C. H. Fong estimated significantly lower annual losses for 1954 to 1984 based on fresh solvent additions to the canyons over the previous few years (Appendix A). She estimated only 15% of the F Canyon and 3.4% of the H Canyon values shown in Table II. Based on modeling of evaporation of organic liquids, any *n*-paraffin that reaches the tank farm persists for only a few months due to the low burden and continuous tank ventilation.¹³

TBP that reaches the tank farm slowly hydrolyzes in the aqueous alkaline waste by the following reaction sequence.¹⁴



In addition, radiolytic degradation of paraffins during canyon processing produces primary carboxylic acids with 12 to 16 carbons and secondary carboxylic acids with 8 to 10 carbons. These non-volatile compounds are likely soluble in the alkaline waste.

TBP, *n*-BuOH, and *n*-paraffin have been reported in tank farm samples (Table I). Interestingly, the TBP was found in an F-area pump tank sample (e.g., in waste on its way to the tank farm) but not in actual waste samples, suggesting that hydrolysis may prevent

TABLE II. Canyon Solvent Losses

<u>Component</u>	<u>Amount (gal/yr)</u>	
	<u>F Canyon</u>	<u>H Canyon</u>
<i>n</i> -paraffin	13,613	7,005
TBP	8,880	2,182

significant accumulation in the waste tanks. Analyses for DBP did not reveal amounts above the relatively high detection limits (300 to 3000 mg/L). No analytical method was available for MBP.

Ion Exchange Resins

Canyon and B-line processes use both anion and cation exchange resins. These include the F Canyon Primary Recovery Column for recovery of Pu and Np (anion), H-Canyon frames for decontaminating and separating Pu and Np (anion), HB line for final Np purification (anion), F Canyon thorium removal column (cation), and FB line for concentration of Pu (cation). FB line cation resin goes to solid waste, but the others go to the tank farms. Relatively small amounts of the resin for thorium recovery have been used. Table III lists the types of ion exchange resins used in canyon operations and Figure 1 shows their structures. Most resins contained polymeric backbones made of polystyrene or styrene-divinylbenzene copolymer. Anion resins typically contained a quaternary amine functional group, although some contained a methylpyridinium group. Table IV lists the amounts of resins sent to the tank farms (Appendix A).

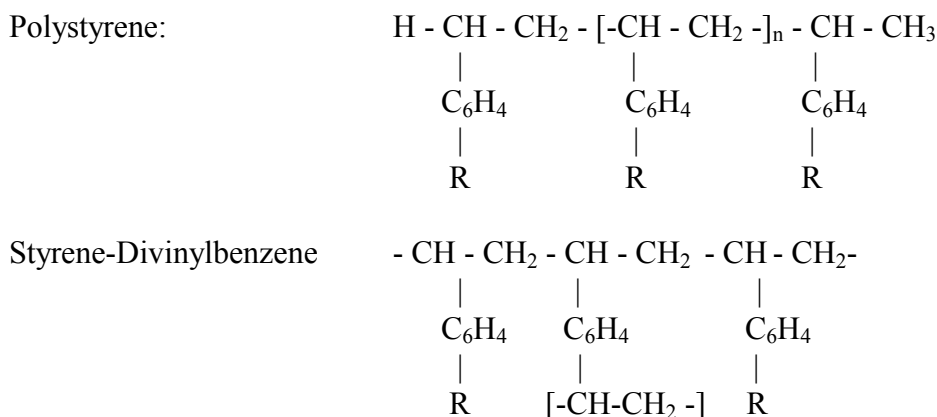
The majority of the resins were digested¹⁵ in alkaline permanganate before going to tank farms, although about 15% was sent undigested due to problems associated with the digestion process. Permanganate digestion breaks down the resins to short chains that

TABLE III. Types of Ion Exchange Resins Used in Canyon Operations

<u>Resin type</u>		<u>Application</u>
<u>Anion</u>		
Polystyrene gel	Dowex 1-X2 Dowex 1-X3	1960-74, all separations columns
Styrene-divinylbenzene macroporous	Dowex MSA-1 Dowex 21K Ionac A-641	1975-95, all separations columns
<u>Cation</u>		
Styrene-divinylbenzene	Dowex 50W	thorium removal and Pu concentration

TABLE IV. Ion Exchange Resins Sent to Tank Farms

<u>Resin Type</u>	<u>Amount (L)</u>	
	<u>F Area</u>	<u>H Area</u>
Anion, polystyrene, gel-type	18,000	26,000
Anion, styrene-divinylbenzene	25,000	55,000
Cation (Dowex 50W)	Unknown	0



where $-\text{C}_6\text{H}_4-$ = di-substituted phenyl group

R = Anion resins $-\text{N}(\text{CH}_3)_3^+$ or $-\text{C}_5\text{H}_4\text{N}(\text{CH}_3)^+$

Cation resins $-\text{C}_6\text{H}_5\text{SO}_3^-$

FIGURE 1. Structures of Ion Exchange Resins

contain alcohol and carboxylic acid groups. Depending on the length of the chain, the resulting fragments may be soluble in aqueous solution. Radiolysis will also contribute to the breakdown of the resins, eventually forming small organic molecules, hydrogen, carbon dioxide, and ammonia. Trimethylamine (TMA) forms from the quaternary amine functional groups. TMA and other volatile organic compounds occur occasionally in vapor samples taken from tank exhaust systems.¹⁶ Figure 2 shows potential non-volatile fragments and TMA formed from these processes.

Other Chemicals

In a few campaigns during the early 1950's, canyon operators added gluconic acid to solubilize head-end cake rather than transfer solid/liquid slurries. Gluconic acid (Figure 3) radiolytically decomposes to carbon dioxide and water.¹⁷ It is unlikely that any remains in the high-level waste.

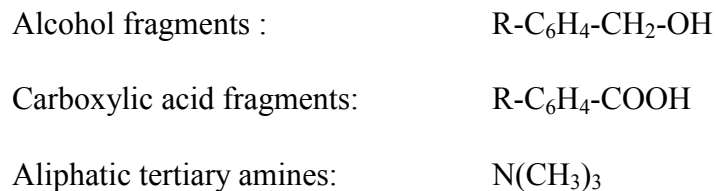


FIGURE 2. Potential Structures of Fragments Formed from Ion Exchange Resins

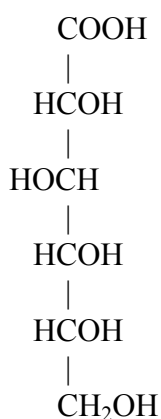


FIGURE 3. Structure of Gluconic Acid

Starting in the late 1950's, operators added gelatin as a flocculating agent to remove silica from nitric acid solutions of dissolved nuclear fuels.¹⁸ Gelatin, a protein, is a polymer of amino acids, primarily glycine, proline, and hydroxyproline. Proteins undergo rapid hydrolysis in strongly alkaline solutions, yielding the individual amino acids. Radiolysis will eventually reduce the amino acids to ammonia, carbon dioxide, and water.

The anionic powdered detergent Alconox[®], made by Alconox, Inc., White Plains, New York, contains alkyl aryl sulfonates.¹⁹ Figure 4 shows the general structure. This structure appears relatively stable to radiation and may exist for years in tank farm waste. Compounds of this general structure interfere with stripping in the CSSX process.⁵

Cleaning Chemicals from Equipment Decontamination

Decontamination of equipment in Building 299-H results in transfers of miscellaneous organic wastes to the tank farm. This includes decontamination chemicals, oils and greases, and gasoline from the 299-H waste collection tank. Although oxalic and nitric acid are most commonly used for decontamination, agents containing organic chemicals have also been used. Table V lists some of the cleaning agents used in the past few years.

Cleaning



where R = alkyl chains

Ar = phenyl or naphthyl groups

FIGURE 4. General Structure of Alkyl Aryl Sulfonates

TABLE V. Cleaning Agents Used in Equipment Decontamination

<u>Agent</u>	<u>Organic Components</u>
SC-200	2-butoxyethanol
Versene	EDTA
Turco 4324 NP	EDTA
Alconox	alkyl aryl sulfonates

agents containing EDTA are not currently recommended for use in this facility. With the exception of Alconox[®], these compounds are not expected to interfere with the solvent extraction process.

SRTC and Analytical Laboratories Waste

Laboratory facilities use a wide variety of organic chemicals, although most are used in small amounts. Aqueous radioactive waste containing these chemicals eventually transfers to the tank farms. In SRTC, aqueous waste sent to the High and Low Activity Drain systems is trucked to F Area (Building 211-F) where it is evaporated before transfer to the tank farm. Waste disposal procedures in the laboratories limit the amount of organic compounds disposed to the drains by requiring that all chemicals be water soluble. In addition, evaporative concentration of the waste in F Area will remove volatile organic compounds. For these reasons, SRTC and Analytical Laboratories likely do not contribute significant amounts of organic compounds to tank farm waste.

Scintillation cocktails used in radioactivity counting methods represent a possible exception to this argument. Since the early 1990's, scintillation cocktails made from mixtures of water soluble chemicals have been routinely sent to the high activity drain system in SRTC. Analytical Laboratories and Bioassay use similar scintillation cocktails. Packard Instruments Ultima Gold[™], a typical scintillation cocktail used at SRS, contains bis(1-methylethyl)naphthalene (65-70%) and a detergent, bis(2-ethylhexyl)hydrogen phosphate (9-12%) as the major ingredients.²⁰ Dr. David DiPrete of SRTC estimated the annual SRTC usage rate is 25-35 gallons per year. These two compounds would likely be scavenged by the CSSX solvent and the detergent could interfere with cesium stripping.

Chemicals from Tank Farm Operations

Corrosion inhibition

Sodium nitrite and sodium hydroxide are used to inhibit corrosion in the carbon steel waste tanks. Waste management personnel add these chemicals directly to the tanks and to "inhibited" water used in the tank farms. Site facilities also add these inhibitors to wastes prior to transferring into the tank farms. Since at least 1997, various SRS facilities (DWPF and F- and H Canyons) have purchased and used Repauno "Super Free Flowing"

technical grade sodium nitrite containing 0.05 wt % Petro AG. Petro AG is an alkylated naphthalene sulfonate salt added to the sodium nitrite as an anti-clumping agent. It is known to interfere with solvent extraction processing.⁵

In-Tank Precipitation Process (ITP): Tanks 48H, 49H, and 50H

In 1982 and 1995, SRS personnel decontaminated large batches of high-level waste in Tank 48H using tetraphenylborate to precipitate cesium. The decontaminated salt solution from both campaigns was sent to Tank 50H. The waste water from the 1982 campaign was stored in Tank 49H. In 2001-2002, the remaining phenylborates in Tank 49H were intentionally decomposed and the waste transferred to Tank 50H. The heel left after transferring the waste contained a small amount of sodium tetraphenylborate and phenol. At this time, Tank 48H continues to store tetraphenylborate waste, although methods for returning this tank to normal service are under study. Table VI lists the known organic compounds in Tank 48H and 49H. All solutions transferred to Tank 50H have or will be removed from the tank farm and sent to Saltstone.²¹

Evaporators

Waste management personnel use siloxane defoamers to prevent or minimize foaming in the tank farm evaporators. These are polydimethylsiloxane (PDMS) based, but may include minor amounts of other organics such as methylcellulose, methylated silica, mono- and di-glycerides (C14 to C18), and hydrogenated tallow glycerides. The PDMS chains vary in molecular weight between 5,000 and 10,000 g/mole. Dow Corning H-10 and Dow Corning Antifoam B have been used in the 2F and 2H evaporators.

TABLE VI. Organic Compounds from the In-Tank Precipitation Process*

<u>Compound</u>	<u>Amount (kg)</u>	
	<u>Tank 48H</u>	<u>Tank 49H**</u>
<u>Soluble</u>		
Sodium tetraphenylborate	<15	0.4
Phenol	830	24
<u>Insoluble</u>		
Biphenyl	Unknown	Unknown
Terphenyl isomers	Unknown	Unknown
Tetraphenylborate (present as K and Na salts)	25,000	None

*This list does not contain insoluble potassium and cesium tetraphenylborates.

** Estimated assuming a 10,000 gal heel and concentrations listed in reference.²²

PDMSs decompose from radiolysis and alkaline hydrolysis. Radiation results in crosslinking of PDMS molecules. Hydrolysis results in polydimethylsilanolates. Figure 5 shows the structures of PDMSs and silanolates.

DWPF

DWPF personnel use small amounts of organic chemicals in the analytical laboratory and organic defoaming agents in the Sludge Receipt Adjustment Tank (SRAT). Table VII lists chemicals used in the analytical laboratory. DWPF personnel used Dow Corning 544 defoamer (PDMS based) in the past and currently use IIT-747 (containing polyether-modified PDMS copolymers, polyether-modified heptamethyltrisiloxane, and allyloxypolyethyleneglycol methylether). The contents of the SRAT are sent to the DWPF melter where they likely decompose. Semivolatile decomposition products could be scrubbed in the DWPF off gas system and transferred to the tank farm in the DWPF recycle stream. However, the amounts reaching the tank farm are likely insignificant.

During startup of the DWPF in 1995, approximately 140,000 gallons of "Coupled Feed Cold Runs" Recycle transferred by truck to Tank 22H. This waste resulted from cold chemical tests of tetraphenylborate decomposition by the acid hydrolysis process. The waste produced was not analyzed for organic compounds, but a waste compliance plan indicated the compounds listed in Table VIII would be present.

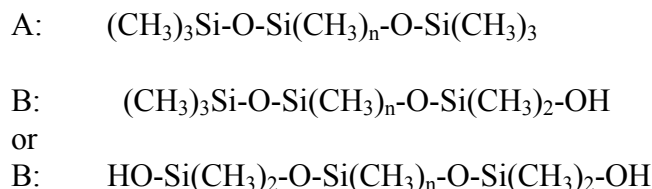


FIGURE 5. Structure of Polydimethylsilanols (A) and Polydimethylsilanolates (B)

TABLE VII. Organic Chemicals Used in the DWPF Laboratory

<u>Compound</u>	<u>Usage Rate (g/yr)</u>
succinic acid and disodium succinate	82
di- and trisodium cyclohexanediaminetetraacetate	46
EDTA	18
[ethylenebis(oxyethylenenitrilo)]-tetraacetic acid	2
methanol	Unknown
formic acid	Unknown
oxalic acid	Unknown
Alconox [®]	Unknown

TABLE VIII. Organic Compounds in the DWPF Cold Run-In Waste

<u>Compound</u>	<u>Amount (kg)*</u>
Benzene	0.5
Aniline	20
Nitrobenzene	0.1
Sodium phenoxide	50
Sodium 2- and 4-nitrophenoxide	70
Sodium 4-nitrosophenoxide	200
Sodium 2,4-dinitrophenoxide	<0.3
Sodium 2- and 4-phenylphenoxide	<0.5
Sodium 4-phenylazophenoxide	3
Dow Corning 544	8
Quinone	0.5
Biphenyl	2
o-, m-, and p-terphenyl	2
Diphenylamine	2
Triphenylamine	0.5
2- and 4-Nitrodiphenylamine	<1
N-Phenylformamide	<3
Diphenylformamide	0.5
Carbazole	<0.5
3H-phenoxazin-3-one	0.5

*Based on 140,000 gal of waste and concentrations listed in reference.²³

Future Tank Farm Operations

Plans for future tank operations include using monosodium titanate (MST) to remove strontium and actinides from waste prior to cesium removal. MST typically contains small amounts of methanol and isopropanol whose combined concentration is limited to 500 ppm by the purchase specifications.²⁴ Based on current projected usage rates (0.4 g MST/L of waste), the filtrate stream from the MST process going to the CSSX process will contain approximately 1.5 mg of methanol and isopropanol per liter of waste solution.

Other Sources

Ion Exchange Resins from RBOF

RBOF cleans and regenerates mixed bed ion exchange resins from the reactor cooling basins. This process includes removing fines and sorbed materials and sending them to the H Area tank farm (Tanks 21H, 22H, and 23H). Normally, the waste transfers contain

only small amounts of resin particles, but occasional equipment failures result in transfer of larger quantities of resin. A mixed bed ion exchange column contains both cation and anion resins. RBOF typically uses Amberlite IR-120 (cation) and Amberlite IR-400-1 (anion) resins. Both are styrene-divinylbenzene copolymers, containing either sulfonated benzene rings (cation) or quaternary amines (anion) as functional groups. Estimated amounts transferred to the tank farm are less than amounts added from the canyon and B-line processes.^{15b}

Coal

In 1970, three separate backwashings of the K Area sand filter were sent to Tank 7F.²⁵ Some sand and coal was inadvertently included in the third backwash. The total is unknown, but only a small fraction of the 17,000 lbs initially charged to K Area was assumed to have been sent to Tank 7F. Is it unlikely that coal introduces any significant amounts of organic compounds into the liquid portion of the waste.

CONCLUSIONS

Soluble high-level waste from the SRS tank farms potentially contains organic compounds that interfere in the CSSX process. This conclusion is based on records of materials sent to the tank farms and on analytical results from waste samples. However, the concentrations of these compounds are typically low or uncertain so it is not possible to conclude that they will degrade CSSX process performance. Table IX summarizes the compounds identified in this report. Few of these have actually been detected in waste samples. Tributylphosphate was present in a sample from a pump tank but has not been found in samples from waste tanks. Odors emitted through waste tank ventilation systems suggest the presence of trimethylamine (an ion exchange resin fragment). Semivolatile decomposition products of defoaming agents have been found, suggesting non-volatile fragments are likely present. The other compounds listed would not have been detected by the analytical methods used on SRS waste samples.

The presence and use of alkyl-aryl sulfonates (such as found in Alconox[®] and in Repauno sodium nitrite) are of concern since they are known to interfere in the CSSX process.⁵ Other chemically similar surfactants or emulsifying agents, such as components found in scintillation cocktails currently used at SRS, are also of concern because of their chemical similarity to the alkyl-aryl sulfonates. However, the process includes solvent washing to prevent accumulation and a suppressor (trioctylamine) in the solvent to improve tolerance to these compounds. It is unlikely that these compounds will exist in concentrations higher than those tested and found acceptable.⁵

TABLE IX. Organic Compounds Found in or Sent to the SRS Tank Farms that May Affect CSSX Processing

<u>Compound</u>	<u>Origin</u>
Tributylphosphate	Solvent used in F and H Canyons
Siloxanes and siloxanols	Defoaming agents used in DWPF and tank farm evaporators
Ion exchange resin fragments and trimethylamine	Ion exchange resins used in canyon process and RBOF
Alkyl-aryl sulfonates	Cleaning agents used in laboratories, decontamination, etc.; anti-clumping agent in sodium nitrite used by DWPF, F and H Canyons, and tank farm inhibited water.
Bis(2-ethylhexyl)hydrogen phosphate	Emulsifying agent used in scintillation cocktails

FUTURE WORK

It is recommend that the following additional investigations to improve understanding of the organic compounds in SRS high-level waste.

- Develop analytical methods for non-volatile, potentially interfering compounds and analyze additional samples of liquid wastes from selected tanks in F and H Areas.
- Investigate radiolytic and chemical breakdown pathways for high-risk compounds.
- Further investigate the amounts sent to tank farms by review of process records

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APPENDIX A. Memorandum "Organic Receipts to the Tank Farms from the F, H, and S Area Canyons" by M. C. H. Fong, 1984

OSR 3-4A

**INTER-OFFICE MEMORANDUM**

SAVANNAH RIVER PLANT

October 30, 1984

TO: P. J. SHIPPY, 703-H

FROM: M. C. H. FONG, 703-H
*MCHF*ORGANIC RECEIPTS TO THE TANK FARMS
FROM THE F, H, AND S AREA CANYONSSUMMARY

This memorandum discusses sources of organics from the F and H Area Separations Process to the waste tank farms and estimates total organic receipts since canyon startup. The estimates show that the expected DWPF S-Canyon annual organics contribution to the H-Area waste tank farm, ~ 2,300 pounds, will represent about 6% of total receipts in 1989 and about 0.2% of total estimated inventory.

DISCUSSION

Both F and H-Area Separations use a solution consisting of 70% n-paraffin and 30% tributyl-phosphate (TBP) to extract uranium and plutonium from dissolved fuel and target slugs. The majority of this solvent is recovered, but small amounts are lost to the waste stream. The TBP portion of the unrecovered solvent eventually ends up in the tank farm via the canyon evaporator bottoms. The n-paraffin portion is removed in the evaporator overheads.

Based on solvent additions made to the separations process in both areas over the last few years, an estimate can be made of the annual TBP additions to the tank farms. In F-Area it is estimated that 24,000 pounds per year of TBP is added to the tank farm^[1]. In H-Area the estimated addition rate is 2,200 pounds per year.^[2] Total inventory in the waste tank farms has been estimated based on these addition rates. The results are presented in Table 1.

P. J. Shippy
October 30, 1984
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Both F and H-Area Separations use a styrene based anion exchange resin in their respective processes. In F-Area, this resin is used in both the Primary Recovery Column (PRC), to recover plutonium and neptunium from unneutralized high activity waste, and in the frames process to decontaminate and separate the plutonium and neptunium recovered on the PRC. A small amount of styrene based cation exchange resin is used in one frame column to absorb and remove thorium. In H-Area the anion exchange resin is used in the frames process to recover plutonium from dissolved neptunium targets.

From 1960 through 1974, Separations used a polystyrene gel-type resin in all the columns (Dowex 1-X2 and Dowex 1-X3). The majority of this resin was digested before it was sent to the tank farm as high-heat waste in F-Area and as low-heat waste in H-Area. However, approximately 15% of the resin was sent to the tank farm undigested due to problems associated with the resin digestion process.

From 1975 to the present, a styrene-divinylbenzene macroporous resin is used in all of the columns (Dowex MSA-1 and Ionac A-641 in the anion exchange columns and Dowex 50W in the F-Area cation exchange column). In F-Area this resin has always been sent to the tank farm undigested. In H-Area the Separations Department stopped digesting the resin in 1982, and shut down the frames process all together in April, 1984. Table 2 lists the type and total amounts of each resin sent to the tank farms since startup of the PRC and frames process for each area.^[3,4]

Beginning in 1989, the H-Area waste tank farm will receive recycle solution from the DWPF S-Canyon. This solution is estimated to contain about 2,300 pounds of organic material primarily as sodium phenoxide.^[5] This represents about a 100% increase in current annual organic receipts to the H-Area waste tank farm. However, this amount of organic is only 6% of estimated total receipts (F, H, S-Area) in 1984 and 0.2% of the total estimated organics inventory received since F and H canyon startup through 1989.

MCHF:kpg
0008g

TABLE 1

TOTAL TBP RECEIPTS TO THE TANK FARMS

	<u>F-AREA</u>	<u>H-AREA</u>
1954-1955	24,000 lb	
1955-1959	96,000 lb	96,000 lb
*1959-1984	<u>600,000 lb</u>	<u>55,000 lb</u>
Total	720,000 lb	151,000 lb

*H-Area switched from the Purex to the HM Process in 1959.

TABLE 2

TOTAL ORGANIC RESIN RECEIPTS TO THE TANK FARMS

	<u>F-AREA</u>	<u>H-AREA</u>
Polystyrene Gel-Type Resin:		
Total	18,000 lb	26,000 lb
Undigested	3,000 lb	4,000 lb
Styrene-Divinylbenzene		
Macroporous Resin:		
Total	25,000 lb	55,000 lb
Undigested	25,000 lb	13,000 lb

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