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The Fate of Organics from Hot Semiworks in CR Vault

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The Fate of Organics from Hot Semiworks in CR Vault

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LIST OF TERMS

CASN	Chemical Abstract Services Number
DOE-RL	U.S. Department of Energy, Richland Operation Office
NPH	normal paraffin hydrocarbon
PAS	PUREX acidified sludge
PUREX	Plutonium Uranium Reduction Extraction
REDOX	Reduction oxidation
SCFM	standard cubic feet per minute
TBP	tributyl phosphate

1.0 INTRODUCTION

The 244-CR vault contains four tanks: two 40,000-gallon carbon steel tanks and two 15,000-gallon stainless steel tanks. On occasion, the waste from 201-C Semiworks was routed through the tanks in 244-CR. This had the potential for mixing the organics from 201-C Semiworks and a residual heel in 244-CR which may be acidic.

The purpose of this study is to determine if there is a possibility that a reactive waste could be present in 244-CR vault.

2.0 FACILITIES AND PROCESSES

The 201-C Process Building was constructed in 1949 as a pilot plant for reprocessing reactor fuel using the reduction and oxidation (REDOX) process. It was converted to a pilot plant for the PUREX process in 1954 and continued in this capacity until it was shut down in 1956. It was put back into operation for the recovery of strontium from fission product waste. It has been inactive since 1967, and decommissioning activities began in 1983. During this time various waste streams were generated. The 241-CX-70 and 241-CX-72 storage tanks (in 201-C Semiworks) received high-level process wastes between 1952 and 1957. Tank 241-CX-71 received acidic wastes from 201-C Semiworks prior to discharge to the 216-C-1 Crib.

The 244-CR vault was built in 1952 to support the uranium metal recovery program, which began in the early 1950's. The 244-CR vault and associated tanks and cells were used for uranium sludge recovery and distribution for the 241-C Tank Farm (Grams et al. 1999). The 244-CR Vault was also used for the interim storage and transfer of waste from B-Plant, PUREX, Hot Semiworks between PUREX and B-Plant.

The 244-CR Vault contains two carbon steel 40,000-gallon tanks, 244-CR-001 and 244-CR-011, and two stainless steel 15,000-gallon tanks, 244-CR-002 and 244-CR-003. All of the tanks are equipped with agitators, pumps, samplers, and appropriate instrumentation (Buckingham 1967).

From 1968 to 1978 tanks 244-CR-003 and 244-CR-002 were used to receive the sluiced PUREX acidified sludge (PAS) waste from the AR vault which was then transferred to B-Plant. After 1983, the 244-CR vault was used for sluicing operation of Hot Semiworks tank CX-70. The supernatant from tank CX-70 was pumped out in the late 1970's to tank 244-CR-011. In 1987, the sludge from Tank CX-70 was pumped into 244-CR-003, agitated and then transferred to double-shell tanks.

Prior to 1970's, the Semiworks sent waste either to cribs or directly to the large storage tanks without going through CR vault. Apparently only two CR vault tanks received

waste from the Semiworks: 244-CR-011 and 244-CR-003. The waste received into CR-011 must have been neutralized waste since it is a carbon steel tank. A sample from 1981 (Grams et al. 1999) shows this waste to be 0.155 grams of carbon per liter of waste. This is well below any concerns for organic-nitrate reactions that could occur above 4.5 weight percent total organic carbon (Meacham et al. 1998).

Tank 244-CR-003 was considered to contain sludge from both PAS and Hot Semiworks tank CX-70 sludge. The PAS was an acid waste while the CX-70 waste was basic. This tank was reported to have been agitated in 1987 and the sludge transferred to double-shell tanks (Grams et al. 1999). This should have effectively neutralized the waste. Then in 1995, CR-003 was used as the double-contained receiver tank for stabilizing 241-C-102, 241-C-107, and 241-C-110. A total of 103,000 gallons of waste (Hanlon 1998) and approximately 40,000 gallons of flush water went through the 15,000-gallon CR-003. It is difficult to see how any acid could survive these transfers.

3.0 ORGANICS FROM HOT SEMIWORKS

DOE-RL (1993) and Klem (1990) present an exhaustive search of the chemicals that were used in the 201-C Semiworks. However, neither reference documents quantities of the various chemicals used or the time period that they were used. DOE-RL (1993) and Klem (1990) were used to extract the tables of organics shown in this study.

Table 3-1. Organic Chemicals Used in the 201-C Semiworks (2 Sheets)

No.	Species [CASN ¹]	Formula	
1	Caustic Tartrate		Not volatile, water soluble
2	Citric acid [77-92-9]	C ₆ H ₈ O ₇	Not volatile, water soluble
3	Di-2-ethylhexyl phosphoric acid [298-07-7]	C ₁₆ H ₃₅ O ₄ P	Separable phase
4	Ethylenediamine tetraacetate (EDTA) [60-00-4]	C ₁₀ H ₁₆ N ₂ O ₈	Not volatile, water soluble
5	Glycolic acid [79-14-1]	C ₂ H ₄ O ₃	Not volatile, water soluble
6	Hexone [108-10-1]	C ₆ H ₁₂ O	Separable phase, volatile
7	Hydrazine [302-01-2]	H ₄ N ₂	Water soluble, degrades
8	Kerosene [8008-20-6]		Separable phase
9	Nitrilotriacetic acid (NTA) [139-13-9]	C ₆ H ₉ NO ₆	Not volatile
10	Nonylphenoxy polyethoxy ethanol [9016-45-9]	(C ₂ H ₄ O) _x .C ₁₅ H ₂₄ O	Surfactant
11	Normal paraffin hydrocarbon (NPH)		Separable phase
12	Oxalic acid [144-62-7]	C ₂ H ₂ O ₄	Not volatile, water soluble
13	Pentasodium diethylene Triamine penta acetate (DTPA) [67-43-6]	N ₃ (CH ₂) ₄ (COONa) ₅	Water soluble

Table 3-1. Organic Chemicals Used in the 201-C Semiworks (2 Sheets)

No.	Species [CASN ¹]	Formula	
14	Shell spray base	C ₁₀ H ₂₂ to C ₁₆ H ₃₄	Separable phase, Product Name
15	Shell E-2342	Naphthene and Paraffins	Separable phase, Product Name, 80% naphthene, Used 1955 to 1961*
16	Soltrol-170	C ₁₀ H ₂₂ to C ₁₆ H ₃₄	Separable phase, Product Name, Used 1961 to 1966*
17	Sugar [57-50-1]	C ₁₂ H ₂₂ O ₁₁	
18	Sulfamic acid [5329-14-6]	H ₃ NO ₃ S	Not an organic
19	Tartaric acid [87-69-4]	C ₄ H ₆ O ₆	
20	Tetrasodium ethylene diamine-tetra acetate (EDTA)	Na ₄ C ₁₀ N ₂ H ₁₂ O ₈	
21	Tributyl phosphate (TBP) [126-73-8]	C ₁₂ H ₂₇ O ₄ P	Separable phase
22	Trisodium hydroxyethyl ethylene-diamine triacetate (HEDTA) [150-39-0]	C ₁₀ H ₁₈ N ₂ O ₇	
23	Turco 4128A		Product Name
24	Chloroform [67-66-3]	CHCl ₃	Separable phase
25	1-Butanol [71-36-3]	C ₄ H ₁₀ O	

*Sederburg et al. (1994)

¹CASN = Chemical Abstract Services Number

3.1 SEPARABLE PHASE ORGANICS

A number of the above species were used in liquid-liquid extraction and were chosen because they were immiscible with aqueous solutions. These chemicals have the potential of forming a separate phase in a waste tank. The chemicals do have some finite solubility in the aqueous phase but it is low.

Table 3-2 is a list of those chemicals that have the potential of forming a separable phase.

Table 3-2. Separable Phase Organics (2 Sheets)

No.	Name [CAS]	Formula	Boiling Point, °C
3	Di-2-ethylhexyl phosphoric acid [298-07-7]	C ₁₆ H ₃₅ O ₄ P	not available
6	Hexone [108-10-1]	C ₆ H ₁₂ O	117
8	Kerosene [8008-20-6]	C ₁₀ to C ₁₅	151-325
11	Normal paraffin hydrocarbon (NPH)	C ₁₀ to C ₁₅	174-252
14	Shell spray base	C ₁₀ H ₂₂ to C ₁₆ H ₃₄	193-260

Table 3-2. Separable Phase Organics (2 Sheets)

No.	Name [CAS]	Formula	Boiling Point, °C
15	Shell E-2342	Naphthene (cyclopentane and cyclohexane) and Paraffins	49-81
16	Soltrol-170	C ₁₀ H ₂₂ to C ₁₆ H ₃₄	208-239
21	Tributyl phosphate (TBP) [126-73-8]	C ₁₂ H ₂₇ O ₄ P	289
24	Chloroform [67-66-3]	CHCl ₃	61.7

Kerosene, normal paraffin hydrocarbon (NPH), Shell spray base, Shell E-2342, and Soltrol-170 all have very similar properties and were all used as diluents. The vapor pressures of these species are less than that of pure water at any given temperature. Still, if only 25 percent of the vapor pressure is used, about 12 gallons per day will evaporate in 150 SCFM airflow from waste at 40 °C (Kirch 1983). The chloroform is very volatile and would not remain in a tank for years. The boiling points of the chemicals are shown in Table 3-2 to illustrate the relative volatility of the materials.

Hexone, Di-2-ethylhexyl phosphoric acid, and tributyl phosphate (TBP) were used as solvents in liquid-liquid extraction. Hexone has a high vapor pressure and is expected to evaporate rapidly. The other two have very low vapor pressures because of the phosphate atom. Typically, a mixture of NPH and TBP will tend to enrich in TBP over time as the more volatile NPH evaporates.

3.2 AROMATIC ORGANICS

The only aromatic organics on the list is nonylphenoxy polyethoxy ethanol. Nonylphenoxy polyethoxy ethanol has a phenyl group in a rather large molecule. It is used as a surfactant and an emulsifier. Therefore, it was not used in appreciable quantities in the Hot Semiworks.

3.3 MISCELLANEOUS ORGANICS

Sugar is used for denitrating the nitric acid prior to neutralizing and sending the waste to the tank farm. Ideally, the sugar is consumed in the denitrating reaction and does not get to the waste tanks. Any degradation product or sugar not reacted is water-soluble.

The Turco-4128A is a commercial cleaning agent. It is common for the Turco™ products to contain organics as detergents, solvents, and emulsifiers. However, the exact organics in this particular formulation is unknown.

Two chemicals in Table 3-1 are not technically organics. These are hydrazine and sulfamic acid. Hydrazine is a reducing agent that cannot persist in alkaline solutions. Sulfamic acid was used in the PUREX process to adjust valence state of plutonium. It is consumed in that reaction and only trace quantities are introduced to the waste.

The remaining chemicals in Table 3-1 are salts of organic acids. These were introduced into the process to complex various elements. All are water-soluble ions. Therefore, they are not volatile. Indications from the rest of the tank farms are that these organic ions tend to degrade with time under the radiation fields and temperature. The degradation products are more stable organics. The final degradation products are carbonate and oxalate ions.

3.4 VOLATILE ORGANICS

Only chloroform and 1-butanol in Table 3-1 can be considered volatile organics. Chloroform is discussed above. The 1-butanol is an alcohol and very soluble in water. Butanol was not used as a process chemical but is a degradation product of TBP. Even though it is volatile, it is common in waste streams because it is soluble in water and is made in the waste from degradation of TBP.

4.0 CONCLUSIONS

The organics used in the Hot Semiworks were similar to those found in the process streams. The separable phase organics do volatilize over time. The soluble organics degrade under the radiation fields to stable products such as carbonate. The problem is that the quantities of organics used are not given in the references. Also, the rate at which the organics degrade or evaporate is a function of temperature and radiation dose. These are not readily available for the waste storage tanks.

However, there were only two tanks in CR vault that received any Hot Semiworks waste. CR-011 still contains some Hot Semiworks waste from the clean out. The sample reported in 1981 shows that the organics are too low to be of concern. This is a carbon steel tank so only neutralized waste can be stored in the tank. There is no chance of nitration of organics to take place there. CR-003 perhaps received Hot Semiworks waste on top of acidic PAS sludge. Since that time, this 15,000-gallon tank has been swept with over 100,000 gallons of caustic waste from the Retrieval program. There is no chance that the PAS sludge could remain acidic under that condition. Neither of these tanks should be considered as having an organic-nitrate problem under current or foreseeable conditions.

Two of the CR vault tanks were inactive before the Hot Semiworks clean out and did not receive any waste from Hot Semiworks. These tanks are CR-001 and CR-002.

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