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| 1                                                                        | 1         | Cog./Proj. Eng. J.W. Green     | <i>J.W. Green</i>   | 7-10-91  |          | C.M. Kronvall |                  |          |          | 3          |           |
| 1                                                                        | 1         | Cog./Proj. Eng. Mgr. R.D. Keck | <i>R.D. Keck</i>    | 7-10-91  |          | L.F. Wojdacz  |                  |          |          | 3          |           |
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| 1                                                                        | 1         | Safety G. Faulk                | <i>G. Faulk</i>     | 7-30-91  |          |               |                  |          |          |            |           |
| 3                                                                        | 1         | R.R. Borisch                   | <i>R.R. Borisch</i> | 7-30-91  |          |               |                  |          |          |            |           |
| 3                                                                        |           | M. Haas                        |                     |          |          |               |                  |          |          |            |           |

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7. Abstract

This document presents the results of an engineering study to evaluate methods for controlling the emission of carbon tetrachloride during the operation of the Plutonium Reclamation Facility solvent extraction system.

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**PFP CARBON TETRACHLORIDE  
EMISSION ABATEMENT  
ENGINEERING STUDY**

**1.0 SUMMARY**

A solvent extraction process (SX) is operated at the Plutonium Reclamation Facility (PRF) to recover and purify plutonium (Pu) from nitric acid solutions. In the PRF solvent extraction process, tributylphosphate is used as the solvent together with carbon tetrachloride (CCl<sub>4</sub>) as the diluent providing a heavy phase solvent for performing the necessary purifying separations of plutonium. Carbon tetrachloride is highly volatile and during operation of the solvent extraction process, CCl<sub>4</sub> emissions to the atmosphere are estimated to be between 75 and 400 lbs/day. The present method used to determine CCl<sub>4</sub> emissions is based on a physical inventory during the process campaigns. This exceeds the allowable regulatory limit (reportable quantity limit). There is legislation pending that may reduce the allowable limit to as low as one lb/day; therefore, CCl<sub>4</sub> losses to the atmosphere must be markedly reduced.

This document presents the results of an engineering study to determine the major sources of carbon tetrachloride air emissions from the PRF, and evaluates methods for reducing/abating those emissions during operation of the solvent extraction system. The anticipated life and operating plans for the PRF, and the production phase-out for carbon tetrachloride (as mandated by EPA, and shown in Table 1 below) are considerations which need to be weighed relative to the continued use of the present SX system and decisions as to which alternative(s) described herein should be implemented.

**TABLE 1 PRODUCTION PHASE-OUT SCHEDULE FOR CARBON TETRACHLORIDE**

| <u>Year</u> | <u>% Baseline Production</u> |
|-------------|------------------------------|
| 1991        | 100                          |
| 1992        | 90                           |
| 1993        | 80                           |
| 1994        | 70                           |
| 1995        | 15                           |
| 1996        | 15                           |
| 1998        | 15                           |
| 1999        | 15                           |
| 2000        | 0                            |

Due to the change in the mission, at the Hanford Site, from defense production to environmental restoration and remediation, the need for the PRF SX process as presently configured is uncertain. Plans are to operate the PRF to stabilize the current inventory of reactive material. This will require approximately two - 100 day campaigns for the solvent extraction system. If it is intended to continue use of the presently configured SX system, the diluent should be changed from  $CCl_4$  to a light phase organic such as dodecane which has little or no environmental liabilities. Replacing  $CCl_4$  with another heavy phase diluent was investigated because it would mean little change in equipment or operation. All of the known heavy phase solvents are either flammable or not environmentally acceptable (land ban).

This study evaluated short and long term alternatives for controlling the emissions of  $CCl_4$  from the PRF. It appears that none of the long term alternatives will be implemented due to the change in mission for the Plutonium Finishing Plant, and the PRF. Future stabilization of plutonium contaminated materials (if that option of the Hanford Chemical Processing Program Plan becomes the "record of decision") for the Hanford Site can be better served by processes other than the existing SX system. Other DOE sites utilize ion exchange or other processes for purification and stabilization of plutonium. There is a significant body of literature and operating experience to support the use of these other processes.

Based on the above discussion and the conclusions of this study it is recommended that only short term alternatives be implemented for controlling the emission of  $CCl_4$  to include:

- Installation of a diaphragm or water cap, or piston, between the air pulser control valve and the process solution ( $CCl_4$ ) to minimize the potential for the pulse air passing through the  $CCl_4$  and transporting the solvent out of the system;
- Replace air bubbler type level and specific gravity instrumentation with electronic instrumentation for those tanks which contain  $CCl_4$  solutions and can be readily refitted; and
- Installation of a silicone fluid scrubber system for the removal of  $CCl_4$  from the vent header system.

## 2.0 INTRODUCTION

### 2.1 PURPOSE

During operation of the solvent extraction process in the PRF,  $CCl_4$  air emissions are estimated to be between 75 and 400 lbs/day. This exceeds the allowable regulatory limit. The previous method used to determine these

emissions was based on a physical inventory during the process campaigns. There is legislation pending that may reduce the allowable limit to as low as one lb/day; therefore, CCl<sub>4</sub> losses to the atmosphere must be markedly reduced. The limits discussed above are RQ or reportable quantity limits. Carbon tetrachloride losses to air are the primary concern of this study since liquid losses are relatively insignificant and are not of concern here. Table 2 lists the physical properties of carbon tetrachloride [DOW 1989].

This document presents the results of an engineering feasibility study to investigate methods for reducing/abating CCl<sub>4</sub> emissions from the PRF during operation of the solvent extraction system.

TABLE 2 PHYSICAL PROPERTIES OF CARBON TETRACHLORIDE  
[DOW 1989]

|                                           |        |
|-------------------------------------------|--------|
| Molecular Weight . . . . .                | 153.82 |
| Specific Gravity, 25/25°C . . . . .       | 1.59   |
| Freezing Point, °C . . . . .              | -22.8  |
| Boiling Point, at 760 mm Hg, °C . . . . . | 76.5   |
| Vapor Pressure, at 20°C, mm Hg . . . . .  | 91.0   |
| Heat of Vaporization, cal/g . . . . .     | 46.4   |
| Specific Heat, at 20°C, cal/g/°C          |        |
| liquid . . . . .                          | 0.20   |
| vapor . . . . .                           | 0.13   |
| Flash Point . . . . .                     | None   |
| Flammable Limits . . . . .                | None   |
| Solubility, at 20°C, g/100 g              |        |
| in H <sub>2</sub> O . . . . .             | 0.08   |
| H <sub>2</sub> O in . . . . .             | 0.01   |

2.2 BACKGROUND

Solvent extraction columns are operated inside the Plutonium Reclamation Facility (PRF) canyon to recover, concentrate and purify plutonium (Pu) in nitric acid solution. The solvent extraction system receives the Pu bearing aqueous feed solutions from the miscellaneous PRF feed preparation systems which treat and bring into solution numerous types of Pu scrap materials received by the PRF from other plant site operations. The purified Pu nitrate solution is evaporated to a desired concentration in the product concentrator before being transferred from the PRF as Pu nitrate product. Gloveboxes are

located on the first two floors of the PRF and contain process piping, pumps, valves, flowmeters, and other equipment requiring frequent access. The access gloveboxes are located on the opposite side of a two foot thick concrete canyon wall. A remotely operated overhead crane can be used to remove or replace process canyon equipment.

The solvent extraction system utilizes a heavy phase solvent consisting of twenty volume percent tributylphosphate (TBP), with the formula  $(C_4H_9)_3PO_4$ , as the extractant and eighty volume percent carbon tetrachloride ( $CCl_4$ ) as the diluent. The diluent is used to favorably alter the properties of the extractant such as viscosity, density, and others. The primary solvent extraction system columns are the pulsed extraction column (CA column) and the pulsed stripping column (CC column).

In the CA column, the Pu containing aqueous feed solution is intimately contacted with the organic solvent to extract the plutonium from the aqueous phase into the organic phase. The heavier organic phase is introduced at the top of the column and gravitates downward, and the lighter aqueous phase is introduced at the bottom of the column and migrates upward towards the top. In the process, Pu is transferred, or extracted, into the organic (solvent) phase and exits the bottom to be introduced to the top of the CC, or strip column. The Pu depleted aqueous phase (or raffinate) which contains the metal salts and other aqueous waste is scrubbed and exits the top of the column and is transferred to a waste treatment facility.

In the CC column (also pulsed), the Pu rich organic phase from the CA column is intimately contacted with a continuous dilute nitric acid-hydroxylamine nitrate aqueous phase resulting in a reduced form of plutonium. With this chemical environment, Pu is stripped from the organic solvent to the aqueous phase. A portion of the CC column aqueous stream (CAIS stream) is returned to the CA column to improve the Pu product purity and content in the aqueous phase, and to reduce the boil-off load on the product concentrator.

The CC column waste (CCW) organic stream gravity flows to the top of the organic Pu wash column (CO) column for retrieval of retained Pu. Descending through the column it contacts a continuous, ascending stream of aqueous strip solution. This solution strips about 95% of the Pu retained by the TBP organic and up to 80% of the Pu retained by degraded organic leaving the CC column. The aqueous product (COP) is routed to the feed makeup tanks for solvent extraction rework.

The CO column organic waste (COW) is pumped to the top of the CU column for removal of nitric acid. The organic descends through a continuous, ascending stream of water. The water strips the nitric acid and trace Pu from the organic. The aqueous waste product (CUP) is continuously routed to waste receiver tanks where it is collected, sampled, and then depending on the Pu content, reworked or discarded to waste.

The CU organic waste (CUW) enters the CX column and descends through a dispersed, ascending stream of sodium carbonate solution. The carbonate

solution strips the organic degradation products and retained Pu from the organic. The aqueous waste is recycled back through the CX column and replaced before the solution pH decreases to ten. The final carbonate waste (CXP) is routed to a collection tank for storage, sampling, and discard to waste.

The CX column organic waste (CXW) is pumped to the OA column. The organic enters the column and descends through a continuous, ascending stream of nitric acid. This acidifies the organic and removes entrained carbonate solution from the CX column. The organic exits at the bottom of the column and gravity flows to the organic pump tank for recycle to the CA column as CAX.

### 2.3 CCl<sub>4</sub> EMISSION SOURCES AND MECHANISMS

All tanks, columns, and other equipment at PRF that contain CCl<sub>4</sub> are potential sources for loss or emissions because. Mechanisms that will be discussed in more detail in the following sections include: evaporation, air purging of dip tubes for level and specific gravity measurements, fluid heating caused by recirculation with pumps which cause elevated temperatures. The following identifies emission sources and briefly discusses the mechanisms that contribute to losses.

#### 2.3.1 Solvent Makeup Tank TK-114 and CCl<sub>4</sub> Head Tank TK-115

The solvent in TK-114, consisting of 20 volume% TBP and 80 volume% CCl<sub>4</sub>, is prepared in the AMU area of the PRF. The makeup tank is vented to a vent header that discharges to the stack via the primary ventilation system. The makeup tank contains MTS liquid level instrumentation [MTS 1990], which replaced the air bubbler instrumentation previously used for this service. The calculated CCl<sub>4</sub> loss from the makeup tank prior to installing the MTS instrumentation was 1.6 to 2.2 lbm/day [Wojdac 1990, LATA 1991].

TK-115 contains pure CCl<sub>4</sub> with negligible amounts of stabilizing agents. The tank is located adjacent to TK-114 and vents to the same vent header. Tank TK-115 has also been fitted with a solid state level indicator (MTS unit).

#### 2.3.2 Solvent Tanks: TK-27, TK-37, TK-38 and TK-120

Solvent from the makeup tank is transferred to the feed tanks. The feed tanks have air bubbler instrumentation for measuring liquid levels and specific gravity. The tanks also are equipped with recirculation pumps which serve to transport make-up solution to various points of use and to mix the contents of the tank. The feed tanks are vented to a header that enters the stack via the ventilation system. The calculated total CCl<sub>4</sub> loss from these tanks is 17 to 25 lbm/day [Wojdac 1990, LATA 1991].

### 2.3.3 Solvent Extraction Columns, CA, CC, and CU

Some of the solvent extraction columns use air pulsers to enhance interphase mass transfer. Air pressure is supplied to the bottom of the column during upstroke and is vented to the vent header via the column glovebox during downstroke. This is accomplished using a pressure reservoir and four-way valves. During upstroke, air is mixed with the solvent and  $\text{CCl}_4$  transfers into the air. During the downstroke, the  $\text{CCl}_4$  rich air exits a four-way valve which is vented into the respective column glovebox. The estimated  $\text{CCl}_4$  loss from each column due to pulsation is 9.8 to 19.4 lbm/day [Wojdac 1990, LATA 1991] which equates to a total pulsation loss of 29.4 to 58.2 lbm/day from the columns.

### 2.3.4 Loss by Diffusion

Diffusion losses can occur by two mechanisms, molecular diffusion and eddy diffusion. In molecular diffusion,  $\text{CCl}_4$  losses result from diffusion across the liquid-air interface and through the stagnant air above the liquid and into the vent system. This mechanism results in negligible losses of  $\text{CCl}_4$  from the PRF. Eddy diffusion occurs when the air pulsers cause the pulse leg to move up or down or "bounce", the result is that vapor laden air is pumped up the column at a rate that far exceeds molecular diffusion.

### 2.3.5 Entrainment

Entrainment losses occur in the tanks and columns that use air purgurator instrumentation. Perry [Perry 1984] indicates that drops forming from bubble dome collapse are virtually unavoidable. The bubbles formed are usually less than 25 microns and have very low terminal velocities and are easily entrained. Because of their small size, they contribute very little on a weight basis ( $< 0.001$  lb liquid/lb air). Perry also indicates that in the low velocity regime the entrainment is proportional to velocity and shifts to higher powers of velocity when the entrainment is  $0.0001$  lb liquid/lb air. For a four inch column, velocity is estimated at  $0.0032$  ft/sec-scfh air which is considered low velocity regime. Therefore, entrainment is estimated at  $0.0001$  lb liquid/lb air, the maximum entrainment in the low velocity regime. Losses from entrainment using the above value are estimated at approximately  $0.0002$  lb  $\text{CCl}_4$ /day per SCFH of air flow and is considered negligible compared to other mechanisms.

### 2.3.6 Other Losses

Other losses include those from spills and liquid leaks. In addition discarded aqueous waste streams are assumed to contain  $\text{CCl}_4$  at the solubility limit. The total losses from these mechanisms is estimated to be 10 lbm/day.

## 2.4 EMISSIONS VERIFICATION

This subsection explains how the  $\text{CCl}_4$  fume emission rate from the PRF columns/tanks can be calculated.  $\text{CCl}_4$  fume emissions can be attributed to:

pure  $\text{CCl}_4$  liquid under stagnant conditions; air bubbling through aqueous tanks (which also contain liquid  $\text{CCl}_4$ ); and  $\text{CCl}_4$  vapor emission due to the air pulsation of the PRF CA, CC, and CU solvent extraction columns.

Some mass transfer engineering models (and their associated custom in-house computer codes) have been researched, developed, and used to estimate the evaporation rates of  $\text{CCl}_4$  from the PRF columns and tanks of concern [Wojdac 1990, LATA 1991]. Consideration was given to evaporation mechanisms caused both by stagnant conditions and agitated conditions.

The PRF tanks which emit  $\text{CCl}_4$  due only to stagnant evaporation include: TK-48, TK-69, TK-114, and TK-115.

The PRF tanks which emit  $\text{CCl}_4$  due to agitation, either by air bubbling (liquid level instrumentation), or by air pulsation agitation (of the solvent extraction columns), include: TK-37 (air bubbling), TK-38 (air bubbling), TK-120 (air bubbling), TK-27 (air bubbling), TK-32 (CA column, air pulsation), TK-33 (CC column, air pulsation), and TK-123 (CU column air pulsation).

Appendix A illustrates additional detail on calculation methods used to establish the  $\text{CCl}_4$  emissions baseline for the PRF. Table 3 provides the worst case summary of  $\text{CCl}_4$  emissions and air flows from the PRF tanks of concern in this study.

### 3.0 SHORT TERM ALTERNATIVES

The following section identifies alternatives for short term solutions for  $\text{CCl}_4$  mitigation and also identifies methods of handling recovered  $\text{CCl}_4$  from processes that produce liquid  $\text{CCl}_4$ , or a secondary waste stream.

Short term alternatives are defined for this study as those requiring less than a year to design and install (under normal circumstances), require only minor canyon modifications, and a budget within the constraints of a CENRTC or GPP.

#### 3.1 REPLACE AIR BUBBLER DIP TUBE LEVEL INSTRUMENTATION

This alternative consists of replacing air bubbler dip tube type level instrumentation with electronic level instrumentation. This would be done in those tanks that could accommodate electronic level sensors. Air bubbler type level instruments measure hydrostatic head by purging a small amount of air, normally 0.5 scfh, into a tank length dip tube inserted in the tank. As the air escapes from the bottom of the dip tube (at zero level) the level sensor measures the back-pressure exerted by the height of liquid (hydrostatic head) and references it to atmospheric or tank pressure, translating the hydrostatic head to tank level.

TABLE 3 CCl<sub>4</sub> EMISSIONS AND AIR FLOWS FROM SOME PRF TANKS

| Source Vessel              | Total Vent Flow Rates scfh | Vent Stream CCl <sub>4</sub> Concentration, PPM | Total CCl <sub>4</sub> Losses, lbs/day | Air Bubbler/Pulsar Contribution to Total Vent Flow, scfh |
|----------------------------|----------------------------|-------------------------------------------------|----------------------------------------|----------------------------------------------------------|
| TK-48                      |                            |                                                 | 0.07                                   |                                                          |
| CU vent                    |                            |                                                 | 0.04                                   |                                                          |
| TK-120                     | 2.9                        | 487,619                                         | 4.6                                    | 2.5                                                      |
| CU pulse                   | 750                        | 135,001                                         | 19.4                                   | 64.1                                                     |
| CA vent                    |                            |                                                 | 0.04                                   |                                                          |
| CC pulse                   | 750                        | 135,001                                         | 19.4                                   | 64.1                                                     |
| CC vent                    |                            |                                                 | 0.04                                   |                                                          |
| CA pulse                   | 750                        | 135,001                                         | 19.4                                   | 64.1                                                     |
| CO vent                    |                            |                                                 | 0.10                                   |                                                          |
| TK-37 Bubbler <sup>1</sup> | 5.3                        | 481,077                                         | 8.1                                    | 4.5                                                      |
| TK-38 Bubbler <sup>1</sup> | 5.3                        | 481,077                                         | 8.1                                    | 4.5                                                      |
| TK-69                      |                            |                                                 | 0.10                                   |                                                          |
| TK-27 Bubbler <sup>1</sup> | 2.9                        | 487,619                                         | 4.6                                    | 2.5                                                      |
| TK-115 <sup>2</sup>        |                            |                                                 | 2.2                                    |                                                          |
| TK-114 <sup>2</sup>        |                            |                                                 | 2.2                                    |                                                          |
| misc. air                  | 116                        | 0                                               | 0                                      | 116.00                                                   |
| TOTAL                      | 330.4                      | 107,879                                         | 88.4                                   | 322.3                                                    |

<sup>1</sup> Limiting case calculations are assumed to apply to both tanks.

<sup>2</sup> A limiting case calculation is used as a basis for both tanks.

The tanks which use air bubbling instruments to measure liquid levels of  $\text{CCl}_4$ , or mixtures of  $\text{CCl}_4$  with other chemicals include: a) TK-27 (CAR), b) TK-120 (CAP), and TKs-37 & 38 (CAX).

Contact and non-contact liquid level detection systems were evaluated. Replacing air bubbler liquid level instrumentation with electronic level instrumentation would require the following:

- Removal of the old air bubbler system;
- Installation of new liquid level system, either contact or non-contact as appropriate for the tank (note: the existing air bubbler type level instrumentation utilizes electronic transmitters with air (pneumatic) input and current output (10-50 ma) which feed associated electronic readouts/controls);
- Tank nozzle modification;
- Piping and valving; and
- Electrical power and control cable.

### 3.1.1 Contact Liquid Level Sensors

Types of contact liquid level (i.e., in contact with the liquid being measured) systems include:

- MTS liquid level system;
- In-tank pulse echo;
- Radio frequency level system;
- Resistance level sensing;
- Time domain reflectometry (TDR); and
- Flange mounted/sealed diaphragm Level Transmitter.

The magnetostrictive (MTS) liquid level system [MTS 1990] is a variation of the linear variable displacement transducer (LVDT) [Schaevitz] concept that utilizes the principle of magnetostriction. The position of a permanent magnet (in the float) on a probe in the tank determines the liquid level in the tank. An electronic pulser sends a current pulse down a wire in the tank level probe, the probe also serves as a waveguide. The interaction of the magnetic field from the float together with the magnetic field generated by the current pulse traveling down the waveguide produces a strain pulse which also travels down the waveguide and is detected by a coil at the end of the probe. The position of the float, and the level, is detected by measuring the lapsed time between launching of the current pulse and arrival of the resulting strain pulse at the detector coil [MTS 1990]. Tank TK-114 in the PRF aqueous make-up area uses an MTS liquid level system.

The in-tank pulse echo liquid level system has an ultrasonic sound transducer mounted on (or in) the bottom of the tank holding the liquid. The liquid level is measured using the sonar principle. Thus, the transducer is electronically excited to send out a short pulse longitudinal sound burst. The

electronics then waits for the two way return echo from the top surface of the liquid, e.g.,  $\text{CCl}_4$  or  $\text{CCl}_4$  mixed with other liquids. Solution inconsistencies could present a problem for this liquid level option. This option could also result in numerous maintenance problems.

The radio frequency level sensing system, also called a capacitive sensing system, is commonly used in industry and is also used in the Aqueous Makeup (AMU) areas of the PFP. The capacitance sensor probe is immersed in the liquid and its electrical capacitance monotonically increases as the liquid level (inside the tank) increases and vice versa. The probe is attached to an oscillator circuit and acts as a variable electrical capacitance. For materials that tend to coat the level probe, the capacitance of the probe and the material coating the probe are measured in a measurement known as "admittance" which in effect cancels out the effect of the coating [Schuler 1987].

The electrical contact resistance liquid level method is also used in industry. This method works by measuring the total electrical resistance around a cable loop. The sensing cable resistance is a direct function of the liquid level. The conducting liquid makes the electrical contact. Since  $\text{CCl}_4$  is a poor conductor, this contact level method is a poor option.

The Time Domain Reflectometry (TDR) method [Tektronix 1989] is commonly used to determine faults in electrical and fiber optic (FO) cable. TDR, also called wire radar, works by sending out an electrical pulse. The injected TDR pulse travels down the wire and is conducted across the top surface of the liquid (in the tank) to and through the tank wall and back to TDR electronics. This contact level detection method is considered to be too costly and more complex than is necessary.

The electronic flange mounted/sealed diaphragm liquid level transmitters are similar to other electronic differential pressure (DP) transmitters in that a liquid filled DP sensor measures the difference between two pressure signals, and translates - transmits that variable current signal to a receiver. The difference here is that the diaphragm itself is sealed by welding/soldering such that it can be mounted into the tank near the bottom, or at "zero" level via a flange. The diaphragm itself is exposed to the process solution in the tank. The flange mounted electronic level sensor-transmitter measures the hydrostatic head directly, instead of measuring the back-pressure exerted by a bubble escaping from a dip tube located inside the tank. This type level sensor functions the same as the existing electronic level transmitters without the need of dip tubes. Foxboro, and Leeds and Northrup are two companies that supply these type level transmitters.

### 3.1.2 Non-contact Liquid Level Systems

Non-contact or non-wetted liquid level systems may have an application at the PRF. Some of these techniques include: a) ultrasonic, and b) external tube liquid level systems.

Non-contact ultrasonic liquid level systems use ultrasonic sound transmitted through air from a send/receive transducer mounted at the top of the tank [ASC 1990]. Some of these non-contact ultrasonic methods operate by electronically pulsing/exciting an ultrasonic transducer - transceiver which then transmits ultrasound pulses vertically downward from the transceiver - transducer which is mounted into the top of a tank. The ultrasonic pulse travels through the air-vapor above the liquid inside the tank, until it hits the liquid surface inside the tank. Most of the pulse energy is reflected, back from the surface through the air-vapor to the transceiver (which is now in a receiving mode). The transceiver - transducer converts the reflected ultrasound pulse into an electrical pulse which is in turn converted to represent liquid level. These type level sensors are not applicable to tanks that may foam in that the sensor "sees" the level of foam as the liquid level which may be critically different than the actual liquid level. [National Sonics, Nusonics]

Another general type of liquid level system uses an external wet well, or sight gauge, connected to the tank whereby a level system can monitor the level in the wet well. One system utilizes an automatic servo system to determine the liquid level in the wet well, which in turn should be the level in the tank. Liquid level resolutions around 1/2 mm are predicted with this system [Skan-A-Matic 1989]. This method requires added plumbing and an automatic control positioning system which makes this option too costly and complex to be considered further. Furthermore, the connections to the tank could become restricted such that changes in level would either not be detected or be slowly detected.

### 3.2 MITIGATE LOSSES FROM AIR PULSERS

This alternative consists of replacing the air pulsers on the three SX columns so equipped (CA, CC and CU) with mechanical pulsers. This eliminates the potential for the pulse leg air passing through the  $CCl_4$  and causing the emission by this mechanism. Mechanical pulsers can be used for direct pulsing of extraction columns [Weech 1961]. Mechanical pulsers consist of three types: diaphragm, piston, and bellows [Long 1978].

#### 3.2.1 Diaphragm Pulser

Diaphragm type pulsers are basically diaphragm pumps without check valves that impress pulses by flexing the diaphragm. The diaphragm is in direct contact with the fluid. A type of diaphragm pump is shown in Figure 1 [Pulsafeeder]. The diaphragm can be either mechanically connected to the pump or indirectly actuated by the pump via air or other means. The latter type causes less wear and maintenance on the diaphragm, but the former provides a sharper shaped pulse which may enhance operations.

### 3.2.2 Piston Pulsers

Piston type pulsers are basically reciprocating piston pumps without check valves. A typical piston pump pulser is shown in Figure 2. A hydraulic fluid, normally oil, between the piston and a diaphragm is pulsed by the piston which in turn transmits pulses to the process liquid on the other side of the diaphragm producing the desired pulse. Piston type pulsers generally utilize a diaphragm to isolate the hydraulic fluid from the process solution. Piston type pulsers are generally reliable, but internal lubricant leakage may be a concern. In addition, failure of the diaphragm would introduce hydraulic fluid into the process solution. However, the diaphragm failure rate for this type pulser is expected to be lower than that of the mechanically connected diaphragm pulsers described above.

### 3.2.3 Bellows Pulsers

Bellows pulsers basically consist of a bellows that is flexed with an eccentric cam or using a hydraulic pulse generated by a reciprocating piston. The flexing action of the bellows, containing the fluid, provides the pulse action. Bellows pulsers are very effective for controlling pulse amplitude and frequency in pilot plant pulse column operation but bellows failure from cyclic fatigue may be too frequent for an operating facility.

### 3.2.4 Summary of Pulser Options

Although technically feasible, mechanical pulsers have some operational disadvantages when compared to air pulsers. Air pulsers do not require moving parts within a glovebox and may be more efficient than mechanical pulsers because they have fewer mechanical parts. The advantages of mechanical pulsers for this application include requiring less energy to operate since no compressible fluids like air are involved, but more importantly, the emission of  $\text{CCl}_4$  caused by air pulsers will be reduced/eliminated during operation of the SX system. Replacing the air pulsers with mechanical pulsers would require installation of the following equipment for the CA, CX, or CU columns:

- Pulser pumps;
- Piping modifications to disconnect the air and install the pumps;
- Electrical connections for power and instrumentation; and
- Instrumentation and pressure control valves.

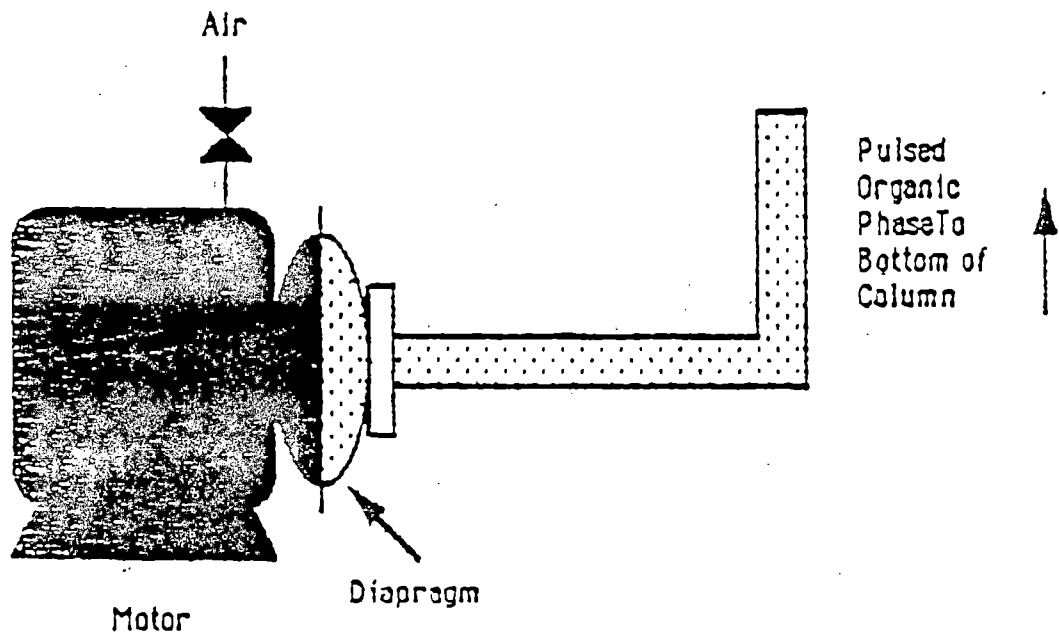


Figure 1 Air Operated Diaphragm Pulsifier

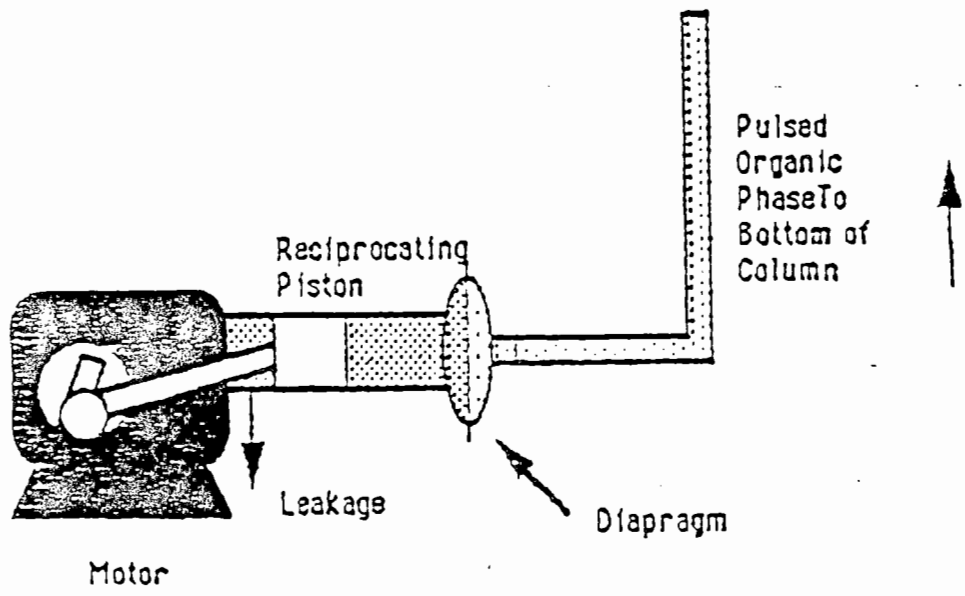


Figure 2 Piston Operated Diaphragm Pulser

### 3.3 WATER CAP ON PULSE LEG

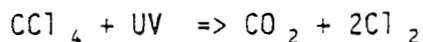
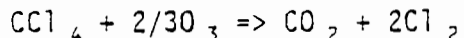
Instead of installing mechanical pulsers to eliminate  $\text{CCl}_4$  emissions from the air pulser source as described 2.3.3 and 3.2 above, it has been proposed to install a water "cap" on the  $\text{CCl}_4$  to act as a water piston between the air and the  $\text{CCl}_4$  [Wojdac 1990]. It is thought that the water cap would reduce emissions due to the low solubility of  $\text{CCl}_4$  in water, and more importantly, is a method that could be readily implemented at little or no cost.

### 3.4 OFFGAS VENT TREATMENT

These alternatives consist of chemically destroying/altering or physically removing  $\text{CCl}_4$  from the gas stream. The  $\text{CCl}_4$  will either be destroyed, or quantitatively removed for recycle back to the process. These alternatives, for the short term, will be limited to minimal unit processes. All the alternatives discussed below include tying the  $\text{CCl}_4$  vent piping together into a common header prior to treatment.

#### 3.4.1 Ozone or UV Light

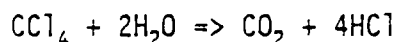
Ozone ( $\text{O}_3$ ) and ultraviolet light (UV) are both known to decompose or oxidize  $\text{CCl}_4$  at ordinary temperatures. An example of the reactions that may occur include:



With adequate residence time, UV light alone will decompose carbon tetrachloride completely based on tests [Chemical Engineering, January 1982] where C-Cl bonds (dissociation energy = 81.0 kcal/gm-mole) are broken by UV light at standard low-pressure mercury-vapor lamp wavelengths of 184.9 nm and 253.7 nm. Ultrox International has developed a process that combines ozone (or hydrogen peroxide) with UV light to create a powerful oxidizing regime to destroy gas-phase volatile organic compounds (VOC's) from gases/vapors. It is claimed that reaction rates of the Ultrox process exceed those of ozone oxidation alone [Waterworld News 1987]. A system is being designed for installation in ventilation systems. [Chemical Engineering 1991]. Most of the testing to date for UV and/or ozone destruction of organic compounds has been conducted on wastewaters. A typical Ultrox system consists of an ozone generator or hydrogen peroxide feed system, a UV/oxidation reactor and an ozone decomposition chamber. The UV/oxidation reactor is the heart of the process. Reactor sizes range from 75 to 6000 gallons, and flow rates from 1 to 1000 gpm.

### 3.4.2 High Temperature Steam Decomposition

When  $\text{CCl}_4$  is mixed with excess water and heated to  $250^\circ\text{C}$ , the  $\text{CCl}_4$  decomposes to carbon dioxide and hydrochloric acid as follows:



This could be accomplished by injecting high temperature steam concurrent with the entering gas stream. However, if the quantity of water is limited, phosgene is produced [Kirk & Othmer 1979]. This alternative consists of installing a continuous gas phase reactor where the  $\text{CCl}_4$  vapors in the common vent header, as described above, are directed to the reactor for decomposition of the  $\text{CCl}_4$ . This alternative requires the design and installation of the following:

- Gas phase reactor system;
- Water injection system; or
- High temperature saturated steam generator;
- Steam and drain piping and fittings;
- Instrumentation including process control; and
- Electrical connections for instrumentation and steam generator power.

### 3.4.3 Plasma Arc

This alternative utilizes a plasma arc system to dehalogenate  $\text{CCl}_4$ . The plasma arc creates ultra-high temperatures by passing process gas through an electric arc. The gas molecules are ionized and exist as a plasma and as they continue losing electrons they are converted to simple atomic and molecular compounds. Temperatures generally exceed  $5,000^\circ\text{F}$  and may reach  $21,000^\circ\text{F}$ . This technology is currently being developed for solid and liquid wastes. Westinghouse Plasma Systems (a unit of the Environmental Technology Division, Madison, PA) has a mobile unit currently being tested for the EPA, and have demonstrated destruction removal efficiencies (DRE's) of 99.99996 to 99.9999998 for PCB's (on test runs of 1 gpm feed at times of 60 to 300 mins.). They also have performed tests on  $\text{CCl}_4$  [Westinghouse Electric 1988]. Other plasma arc test results [Freeman 1989] for  $\text{CCl}_4$  indicate organic compound destruction efficiencies range from 99.9999 to 99.99996 per cent. The major components for a plasma arc system are the plasma torch, reaction chamber, scrubber, power unit and monitoring equipment. The simple gasses (among others, carbon monoxide, hydrogen, carbon and hydrogen chloride) that exit as off-gas could be burned with a flare or used in heat recovery. For this alternative  $\text{CCl}_4$  would be condensed, or adsorbed on activated carbon, in a pretreatment step followed by destruction via the plasma arc system.

### 3.4.4 Condensation

Condensation using refrigeration and/or cold traps is a viable method for condensing VOC's from air, particularly where the VOC concentration is very high, e.g. 100,000 ppm, and the air flow rate is low [USAF/DOE 1990]. Thermodynamic cycle condensation such as the reverse Rankine (like a household refrigerator) and Brayton cycles (like a heat pump) are also methods for condensing high concentrations of VOC's and can also handle higher flow rates (2,000 to 9,000 scfm) [Reynolds 1977, Scheiting 1989]. Condensation, can be used as an effective method to remove  $CCl_4$  from the vent air. Water is first removed from  $CCl_4$  laden air to prevent freezing. The air is then contacted with a heat transfer surface cooled by a refrigerant. The  $CCl_4$  would reach its dew point and condense as a liquid. It is estimated that the  $CCl_4$  removal efficiency is approximately 97% at a stream concentration in the range of 100,000 ppm. This alternative consists of condensing  $CCl_4$  from the vent gas using multi-staged refrigerated cold traps (cryogenic condensation) or mechanical methods (mechanical refrigeration) [Polycold 1990, Nucon 1990, Edwards Engineering 1990]. The recovered  $CCl_4$  would be collected in sealed collection/storage tanks and recycled, or treated as discussed elsewhere.

### 3.5 REPLACE DILUENT WITH HEAVY PHASE SOLVENTS

This alternative consists of replacing the  $CCl_4$  diluent with a different heavy phase diluent (solvent with a density greater than that of water). This would be a relatively easy alternative to implement in that the  $CCl_4$  would just be replaced by a different solvent. It would require recalibration of the instrumentation to account for a different specific gravity. The other properties of the solvents listed below, particularly tetrachloroethylene (TCE) and bromo benzene, are relatively close to that of  $CCl_4$ . Heavy-phase solvents used as diluents for TBP in nuclear processing have been studied previously. Several solvents with densities greater than that of water have been investigated and recommended as replacements for  $CCl_4$  by Barney [Barney 1977]. The heavy phase solvents and some of the properties considered in this evaluation are shown in Table 4 below.

TABLE 4 - HEAVY PHASE DILUENTS

|                                      | <u>Flashpoint</u><br>(°C) | <u>Vapor Press.</u><br>(mm Hg) | <u>Viscosity</u><br>(cp) | <u>Density</u><br>(gm/cm <sup>3</sup> ) |
|--------------------------------------|---------------------------|--------------------------------|--------------------------|-----------------------------------------|
| • Carbon Tetrachloride ( $CCl_4$ )   | None                      | 123                            | 0.97                     | 1.59                                    |
| • Carbon Tetrabromide ( $CBr_4$ )    | None                      | N/A                            | 17                       | 3.42                                    |
| • Tetrachloroethylene ( $C_2Cl_4$ )  | None                      | 20.6                           | 0.88                     | 1.62                                    |
| • Trichloro Benzene ( $C_6H_3Cl_3$ ) | 110                       | <1                             | 1.97                     | 1.45                                    |
| • Bromo Benzene ( $C_6H_5Br$ )       | 51                        | ≈5                             | 1.2                      | 1.5                                     |

The properties of  $C_2Cl_4$  (TCE) and  $C_6H_5Br$ , from a process point of view, are similar enough to those of  $CCl_4$  that very few other changes (other than recalibration) would be expected in replacing  $CCl_4$  with either solvent. However,  $C_6H_5Br$  may not be suitable based on its low flash point of  $51^\circ C$ , whereas  $C_2Cl_4$  has no flashpoint like  $CCl_4$ . Long [Long 1978] does not recommend a diluent with a flashpoint less than  $72^\circ C$  for fire safety reasons. However, TCE ( $C_2Cl_4$ ) and Bromobenzene ( $C_6H_5Br$ ) are the two diluents which are technically feasible based on the relative transfer unit height (HTU) calculated in Appendix B. An equation from Long [Long 1978], which accounts for the effects of viscosity, density, and other key parameters, was used by LATA [LATA 1991] in ratio form to determine the relative HTU's that might be expected using other diluents (LATA calculated the HTU using  $CCl_4$  to be 1.657).

The relative HTU calculated (with  $CCl_4$  referenced as 1.0) for using  $C_6H_5Br$  as a diluent is approximately 20% (1.25) greater than the HTU for  $CCl_4$ . This indicates that the effectiveness of using  $C_6H_5Br$  would be less than that of  $CCl_4$  and may be unacceptable. The relative HTU for using  $C_2Cl_4$  is less than the HTU for  $CCl_4$  (0.91) which indicates that TCE could be very effective based on this criterion. The vapor pressure of TCE is a factor of six lower than  $CCl_4$  (20.6 mm Hg versus 123 mm Hg), and the estimated vapor loss rate of TCE (at 8 lb/day) compared to  $CCl_4$  (at 48 lb/day) is correspondingly lower. These facts, together with the closeness in densities, viscosities, and solubilities in water seem to indicate that TCE could provide a short term solution to the mitigation of  $CCl_4$  vapor losses. Other factors must be considered when deciding to replace a diluent, and it has been shown that the distribution coefficient, and radiolysis stability for TCE to be better than  $CCl_4$  [Barney 1977].

Since a land ban exists for  $C_2Cl_4$ , as well as  $CCl_4$ , it may not be advisable to recommend changing to TCE as a diluent replacement. However, since the vapor loss for TCE is so much lower than for  $CCl_4$ , and in the event a hammer date or emission limit is imposed on PRF emissions for  $CCl_4$ , it would be worth considering the use of TCE, particularly since it is likely there will only be two (proposed) 100 day campaigns remaining in the life of the PRF.

#### 4.0 LONG TERM SOLUTIONS

Long term solutions for this study take a year or longer to design and install, require significant modifications, and exceed a specified dollar amount.

#### 4.1 REPLACE DILUENT WITH LIGHT PHASE SOLVENTS

Solvents used as diluents with densities less than water are common in solvent extraction systems and have been studied extensively in nuclear reprocessing. When solvent extraction was first recognized as a desirable method for purifying nuclear energy metals, much effort was spent on evaluating the effects of type and structure of the diluents on extraction performance [Long 1978]. As a result of these studies, the light-phase diluents that are in common usage are refined kerosenes, aviation naphthas, and n-dodecane. The aromatic, xylene, has been shown to be an effective diluent but its flashpoint (63°F) is far too low to consider [Blake 1963].

Use of a simple, pure, stable hydrocarbon such as n-dodecane is recommended. Also, supplies of n-dodecane can be obtained with consistent compositions. For this and other reasons (research and data collection consistency), n-dodecane is becoming more widely accepted at DOE sites as the preferred light phase diluent for solvent extraction operations.

Equipment changes would be required to change from a heavy phase diluent ( $\text{CCl}_4$ ) to a light-phase diluent (n-dodecane). The equipment modifications include modifying hydraulic systems because of density and viscosity changes. Piping changes would also be required since the flow sheet would be inverted relative to the  $\text{CCl}_4$  flow sheet. Column insert changes would likely be required to accommodate the new continuous/dispersed phases. Since n-dodecane has a moderate flash point (170°F), a safety analyses would be necessary.

Operating experience at PUREX shows relative HTU's of 1.1 to 1.25. It has been estimated that the height of transfer unit (HTU) will increase by 10-25 percent by replacing the  $\text{CCl}_4$  diluent with an aliphatic hydrocarbon [Richardson 1964]. LATA [LATA 1991] also indicates higher HTU's. Further engineering study is needed on process operating parameters if this alternative is to be implemented. In addition, the rate of extraction may be slower for an aliphatic hydrocarbon than for  $\text{CCl}_4$ . Data indicate that the rate of extraction of  $\text{UO}_2(\text{NO}_3)_2$  by TBP in an aliphatic hydrocarbon is generally slower.

The literature indicates that n-dodecane has the following favorable diluent properties:

- Flash point 78°C
- Vapor pressure < 1 mm Hg
- Viscosity 1.35 to 1.8 cp
- Density difference 0.25 (dodecane = 0.75 gm/cm<sup>3</sup>)
- Low solubility
- Radiolytic stability
- Chemical stability
- Favorable extractability, compared to other aliphatics [Long, 1971]

This alternative is considered the most favorable for meeting regulatory requirements if it is decided to upgrade and use the existing PRF solvent extraction system. The emissions of  $\text{CCl}_4$  would be eliminated. In addition, very little light-phase solvent will be emitted since n-dodecane has a very low vapor pressure. However, other extraction methods, such as ion exchange, have been perfected in recent years for the purification of plutonium and have proven to be very efficient and are in use at other sites.

Changing the diluent to a solvent with a density less than that of water would require design, equipment and process engineering modifications as follows:

- Piping modifications redirecting the flow to the SX columns because the aqueous phase will be heavier than the organic phase (although the CA and CC columns could be reversed and flows would be correct);
- Replacing/installing new instrumentation;
- Other hardware changes; and
- Replacing some column inserts.
- Recalculating the flow sheets and preparing new process engineering operating parameters and operating procedures.

#### 4.2 REMOVE $\text{CCl}_4$ FROM OFFGAS

The following alternatives consist of removing  $\text{CCl}_4$  from, or destroying/converting the  $\text{CCl}_4$  in, the process off-gas. This alternative requires routing all of the vent piping containing  $\text{CCl}_4$  vapors to a common header for routing to removal or treatment equipment. The treatment equipment would be located upstream of the main exhaust system. If the specified treatment does not destroy the  $\text{CCl}_4$ , it must be processed in a disposal treatment system described in Section 4.3 below.

##### 4.2.1 Incineration

The re-routed  $\text{CCl}_4$  vent would be directed to an incinerator for destruction of the organics of concern ( $\text{CCl}_4$ ). The incinerator off-gas would be quenched, scrubbed, dewatered, adsorbed with activated carbon (if necessary), and filtered with HEPA filters prior to discharge out the stack. Secondary wastes would be treated as necessary as discussed in Section 4.3.

The incinerator would be a controlled-air incinerator where the gasses or any other materials would be burned (sometimes described incorrectly as pyrolysis) in the primary chamber at near or sub-stoichiometric conditions where all the wastes would be converted to gasses. The primary chamber provides a quiescent atmosphere to minimize turbulence, turbulence causes the formation of particulates which would increase the burden of downstream off-gas treatment systems. The gasses from the primary chamber are then directed to the secondary chamber where excess air is introduced to create turbulence and provide sufficient oxygen for burning of the gasses. Generally the primary chamber temperatures are maintained at 1400-1600°F, while those of the

secondary chamber are maintained at 2000-2200°F. Secondary combustion chamber offgas would then be routed through refractory lined pipe to a quench tower then to a venturi scrubber. The offgas would be cooled in the quench tower to its saturation temperature via evaporative cooling. The high energy venturi scrubber would maintain a liquid seal and would feature a differential pressure to pneumatic jack leg controller to control pressure drop. Offgas scrubbing would occur in the venturi scrubber followed by a packed column utilizing a caustic scrub solution for neutralizing the acidic off-gas solutions resulting from burning organics. The offgas would exit through a demister at the top of the packed column. Level controls, raschig rings or other type tower packing and an overflow line at the bottom of the packed column would be utilized to maintain critically safety.

The offgas would be superheated before passing through the HEPA filter assembly. The HEPA filter assembly would be preceded by roughing filters which could be sintered metal or ceramic blow-back filters for removing particulates. If it is thought that the organics might not be fully destroyed in the incinerator, they could be further removed from the HEPA filtered offgas via an activated carbon bed.

An induced draft blower would convey continuously monitored purified offgas through the exhaust stack. A continuous emissions monitoring station would monitor all critical offgas components exiting the exhaust stack in compliance with EPA and RCRA source emission requirements. The Los Alamos National Laboratory has been operating just such a system for over a decade. Design and installation of the following is required for this alternative:

- incinerator and feed system;
- quench tower/column;
- venturi scrubber followed by a packed column scrubber;
- demister;
- Blow-back sintered metal filters;
- activated carbon bed (if required);
- HEPA filters;
- Induced draft (Roots or Spencer Turbine) blower;
- piping, valves, and pumps;
- instrumentation; and
- regulatory emission monitoring equipment.

#### 4.2.2 Granular Activated Carbon (GAC) Adsorption

This alternative consists of using granular activated carbon (GAC) to remove  $CCl_4$  from the vent gas. Activated carbon adsorbs contaminants from the gas/vapor on the surface of pores in/on the activated carbon. GAC systems have been successfully applied for a wide variety of volatile organics (VOC's), especially when combined with an upstream water vapor removal system, and is applicable for gas phase treatment/removal for compounds such as  $CCl_4$  with molecular weights ranging from 50-200 and boiling points ranging from

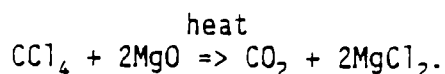
20°C to 175°C. Carbon systems have been successfully applied for a wide variety of VOCs from such hydrocarbon classifications as fluorocarbons, chlorinates, aliphatics, aromatics, alcohols, ketones, esters, or combinations of these solvents [VIC 1989, ESI 1990].

Activated carbon systems can achieve VOC recovery efficiencies of 99% or greater. Depending on the organic of concern, several carbon columns may need to be connected in series to achieve these efficiencies. Activated carbon systems can be in the form of removable cartridges, canisters, thin beds, thick beds, or pleated dry processed carbon composites [Kinkheed 1989].

Two GAC columns/beds should be installed to operate in parallel with one being on-line while the other is either dormant or being regenerated. Regenerant gas (either nitrogen or steam), containing eluted/extracted  $\text{CCl}_4$  and water vapor would be condensed, decanted and recycled back to the feed tanks. Secondary wastewater from the water removal step mentioned above containing  $\text{CCl}_4$  would be treated as described in Section 4.3.

#### 4.2.3 MgO Adsorption/Reaction

Magnesia ( $\text{MgO}$ ) or magnesium hydroxide  $\text{Mg}(\text{OH})_2$  particles placed on supports in a bed could be used to adsorb/react  $\text{CCl}_4$  from the gas stream according to the following chemical reaction:



The solid  $\text{MgO} - \text{CCl}_4$  reaction occurs at approximately 700°C. At temperatures above 714°C the resulting  $\text{MgCl}_2$  melts and could be drained from the bed and disposed. If the temperature of the reactor is kept below the melting point of the  $\text{MgCl}_2$ , the reactor can be cooled and the packing material, consisting of unreacted  $\text{MgO}$  and  $\text{MgCl}_2$ , can be washed with a water spray. The  $\text{MgO}$ , which is insoluble in water, will be separated from the soluble  $\text{MgCl}_2$  and can be placed back in service. The  $\text{MgCl}_2$  solution will be handled according to methods discussed in Section 4.3.

#### 4.2.4 Molecular Sieves

Molecular sieves are a group of porous crystalline aluminosilicates whose pores are uniform in size and of molecular dimensions [MDI 1989, Baker 1990]. Molecular sieves are "activated" by being dehydrated, and as such have a strong tendency to recapture the water molecules lost during dehydration. This tendency is so strong that in the absence of water, molecular sieves will accept any material that can diffuse into the interstitial spaces which are then adsorbed. Based on their pore size, molecular sieves can adsorb smaller molecules while molecules larger than the pore size will be rejected. This sieving or screening action makes it possible to separate gases, vapors and liquid species. As an example, sieves whose pore diameters are less than 3Å ( $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$ ) will selectively adsorb water vapor, and reject larger sized molecules such as  $\text{CCl}_4$  vapor. A molecular sieve whose pore diameters are 5Å

would not only adsorb water vapor but would also adsorb  $\text{CCl}_4$  vapor. This same sieve would reject larger (larger than 5Å) molecules such as aromatic hydrocarbon molecules because they cannot physically get inside the pores.

Molecular sieves can be made of activated carbon and other materials, such as synthetic crystal zeolites [MDI 1989].

#### 4.2.5 Gas-Phase Membranes

The use of gas-phase membranes could be used for reducing  $\text{CCl}_4$  in the vent system. The dense phase  $\text{CCl}_4$  would be recycled to the feed tanks for reuse. Membranes are substances (polypropylene, ceramics, glass fibers, polycarbonates, and polyethersulfones) that utilize small pores to separate, by diffusion or micro-filtration, vapors (or liquids) from air (or water). Membranes could be used to separate  $\text{CCl}_4$  from air or dissolved/emulsified  $\text{CCl}_4$  from liquid water.

Gas separation (permeation) membranes act as molecular-scale type filters where a relatively high pressure (150 psi) is applied to the solution/gas being "filtered" to overcome the osmotic pressure to cause the solvent to diffuse from the solution through a permeable or semi-permeable membrane while leaving the solute behind. One principle for their selectivity is based on mobility and solubility. Mobility or diffusivity into and through a selective membrane favors smaller molecules, while solubility favors the more condensible molecules. This is thought to be a slow process [Baker 1990]. Another principle is based purely on diffusion where the inverse square root ratio of the molecular weights of two gas components predicts the effectiveness of their separation. This method is used in the gaseous diffusion plants for the enrichment of uranium. The pore size for these membranes range from 50 to 100 angstroms (angstrom =  $1 \times 10^{-10}\text{m}$ ) in diameter. This method is not used for volatile organic separations because of its inefficiency. Ultramicroporous membranes (generally smaller pore sizes than those mentioned above) operate by exploiting the higher diffusion rates of the smaller molecules and utilize smaller pore size membranes to affect separation. Membrane pore sizes range from 2 to 50 angstroms [Baker 1990]. This latter type membrane is used for most gas separation membrane systems.

The membranes are manufactured in three basic configurations: spiral wound, hollow fiber, and plate and frame. Spiral wound membrane modules consist of alternate layers of membrane and spacer wound around a perforated collection tube. The membrane favors the smaller molecular weight substance which diffuses into the collection tube and is carried away. This assembly is installed into a circular pressurizable vessel. Typical modules are 36-40 inches in length and 4-12 inches in diameter [Osmonics 1990, Baker 1990]. Hollow fiber membrane modules are fabricated similar to shell and tube heat exchangers in that hollow membrane tubes are bundled together in a circular pressurizable vessel such that the fume laden air enters one end, passes through and exits the other end. The vapors, e.g.  $\text{CCl}_4$ , diffuse outward (or permeate radially) and are collected from the "shell" side through a port where the highly enriched  $\text{CCl}_4$  exits. The less permeable gas (air) passes

through the tubes and exits the "residue" end. Hollow fiber membrane units typically operate at differential pressures of 150 psi [Baker 1990]. Plate and frame modules are the earliest types and consist of circular membrane "plates" stacked alternately with spacers/separators with a hole in the middle. They are assembled to the permeate pipe in the middle and placed in a pressure vessel with spacers between the edge of the plates and inner vessel wall. The vapor laden air enters the vessel on the "shell" side and the more volatile component ( $\text{CCl}_4$ ) diffuses radially inward toward the permeate collection pipe at a faster rate than the air thereby leaving the cleaned air behind. The high input pressure (approximately 150 psi) creates a high differential pressure between the shell side input and 1) the permeate pipe outlet, and 2) the residue end (opposite the input end). The air is "scalped" from the periphery of the stack and out the residue end pipe outlet, and the  $\text{CCl}_4$  is collected and discharged out the permeate pipe [Osmonics 1990, Baker 1990].

Although many different membrane modules are available, spiral wound types are generally favored. A spiral wound module available from Membrane Technology and Research, Inc. (MTR) is manufactured for separating  $\text{CCl}_4$  from air. MTR utilizes asymmetric membranes of composite structures made by coating a tough relatively open microporous support membrane with a very thin, dense film. The strong support membrane provides mechanical strength while the thin, dense coating performs the gas separation. MTR claims this construction reduces surface fouling and pore plugging [MTR 1990]. The use of gas membranes for  $\text{CCl}_4$  recovery would require from one to four modules cascaded together to achieve the EPA and other regulatory emission standards or requirements, and would require some form of condensation to concentrate the  $\text{CCl}_4$  prior to recycling.

#### 4.2.6 Scrubbing

Scrubbing is a very common mass transfer unit operation used for the removal of a wide array of contaminants from the gas-phase [Tri-Mer 1990]. Dry scrubbing (bag, filters, electrostatic, etc.) is thought not to be effective for removing  $\text{CCl}_4$  unless packed with some type of adsorbent or oxidizer which must be periodically replaced. Wet scrubbers are thought to be somewhat more effective. Effectiveness depends largely on the driving force and solubility of the contaminant and scrubbing media. If a component is highly insoluble in the scrubbing media, then scrubbing would not be effective. Cooled water was shown to be approximately 50% efficient in a liquid column where a saturated (saturated with  $\text{CCl}_4$ ) process gas was bubbled through the column [PNL 1991]. However, an unsaturated process gas stream bubbled through the same liquid column was only 13% efficient. This shows the effect of limited driving force on removal efficiencies. Wet scrubbing may require further treatment of the scrub solution to separate dissolved  $\text{CCl}_4$  from water.

Early test results by PNL utilizing DOW CORNING silicone fluid have been quite successful, being 90+% efficient [PNL 1991]. The  $\text{CCl}_4$  can easily be removed from the silicone fluid for recycle. Further tests are being

performed to determine the equilibrium amount of silicone fluid that reports with the  $\text{CCl}_4$  and its effect on separation effectiveness in the SX operation, if it were to be reused/recycled. The  $\text{CCl}_4$  could be removed and destroyed by one of the processes described herein.

#### 4.3 RECOVERED LIQUID $\text{CCl}_4$ OR SECONDARY WASTE TREATMENT

Some of the processes described above generate either liquids or solids, or a secondary waste stream that may require additional processing or treatment. The liquids may or may not contain  $\text{CCl}_4$ .

##### 4.3.1 Recycle

Liquids from the processes mentioned above that contain  $\text{CCl}_4$  will be further processed to recover the  $\text{CCl}_4$ . The recovered  $\text{CCl}_4$  will then be recycled back to tanks TK-37, TK-38 and TK-120. Recycling  $\text{CCl}_4$  may be feasible for the following alternatives: gas-phase membranes, condensation, scrubbing, activated carbon, and molecular sieves. Generally, all that would be required for recovering the  $\text{CCl}_4$  is to install a decanter. The resulting aqueous phase from the decanting operation, containing dissolved  $\text{CCl}_4$ , may require further treatment or may be disposed. Recycling of recovered  $\text{CCl}_4$  will require the design and installation of the following:

- collection tanks;
- piping to tanks TK-37, TK-38 and TK-120;
- pumps and valves;
- decanter (membranes, GAC, and condensation);
- distillation column (scrubbing);
- instrumentation and control; and
- piping, pumps, and valves for transfer of waste liquid to disposal or treatment facility.

Recycling has been identified by regulatory agencies as one of the preferred waste management options. The EPA's hierarchy of waste management options is as follows [CEP 1989]:

- source reduction: reducing the amount of wastes at the source through process changes;
- recycling: reusing and recycling wastes as substitutes for feedstocks/ingredients for other industrial processes;
- treatment: destroying, detoxifying, or neutralizing wastes (including separation, volume reduction, or energy recovery);
- disposal: discharging wastes into ambient water or air or injecting or depositing wastes into or onto the land.

Source reduction has been a major consideration in this study, resulting in several of the alternatives discussed herein (e.g. changing diluents, replacing pulsers, and replacing instrumentation).

#### 4.3.2 Disposal

Liquids that contain minor amounts of  $\text{CCl}_4$  (acceptable for discharge) and/or solids must be properly disposed via approved methods. The only solids generated from alternatives discussed thus far are the  $\text{MgCl}_2$  solids (section 4.2.3) that will be considered low-level radioactive waste (LLW) for the purposes of this study. Liquids are generated from most of the alternatives discussed thus far. Liquid disposal options might include discharge to the soil column, the river, the Treated Effluent Disposal Facility (TEDS), a treatment plant, or injection to underground wells. Depending on the selected process, secondary liquid wastes known to contain higher concentrations of  $\text{CCl}_4$  would require treatment as described in Section 4.3.3 below. Solids would be disposed to a LLW burial site. This alternative requires design and installation of the following:

- Monitoring systems;
- collection tanks/sumps;
- pumps; and
- instrumentation and control

#### 4.3.3 Treatment

Numerous treatment technologies are available to effectively reduce  $\text{CCl}_4$  in liquid wastes and include:

- UV- $\text{H}_2\text{O}_2$  oxidation unit process;
- Ozonation;
- Biochemical Oxidation;
- GAC Adsorption;
- High temperature water reaction;
- Distillation;
- Supercritical Extraction; and
- Membrane Technology.

##### 4.3.3.1 UV- $\text{H}_2\text{O}_2$ Oxidation

As discussed in Section 3.3.1, UV light alone (mercury-vapor lamps issuing wavelengths of 184.9 nm and 253.7 nm) will break the carbon-chloride bonds thereby destroying carbon tetrachloride with sufficient time [Chemical Engineering, 1982]. However, a number of ozone manufacturing firms including Ultrox International are investigating waste treatment technologies using UV light and hydrogen peroxide and/or ozone, to increase the destruction efficiencies of organic wastes in wastewaters. Ultrox International is looking for increased uses for their ozone generating business. It is thought that the UV light excites/breaks the chemical bonds of the chlorinated

hydrocarbons in a photo-oxidation step and then the  $H_2O_2$  and/or ozone oxidizes the simpler organics resulting from the photo-oxidation.

#### 4.3.3.2 Ozonation

Los Alamos Technical Associates, Inc. (LATA) have performed preliminary bench scale tests on organic compound destruction using a proprietary ozone generating unit where the tests were conducted by mixing one liter of ozonated water containing approximately 11 mg ozone with an equal volume of waste water containing from 18 to 37 mg of the organic compound of interest. Carbon tetrachloride destruction efficiency was 77% [LATA 1991].

Ozone can be generated either in-situ or externally then introduced into the water similar to chlorination. The ozone supply or generation system must be in close proximity to the treatment system since ozone has a half-life of only one-half hour.

Ozonation may not be practical in an organic destruction system by itself, particularly for chlorinated hydrocarbons because if there is insufficient ozone, intermediates such as dioxin and others may be formed which are of as much concern as the chlorinated hydrocarbons. Ozonation is more suited for oxidation of organics when combined with UV light in a more complete oxidation system as described in Section 4.3.3.1 above.

#### 4.3.3.3 Biochemical Treatment

Biochemical, or biological treatment systems utilize facultative (facultative, meaning the same microorganism can be both aerobic or anaerobic) micro-organisms to digest  $CCl_4$  in activated sludge treatment systems or facultative lagoons as a method for removing  $CCl_4$  from wastewaters. The dilute  $CCl_4$  in a wastewater is fed to these organisms in a biological treatment system which utilize the  $CCl_4$  as a food source. Normally high concentrations of organics, like  $CCl_4$ , would destroy the microorganisms, but by gradually increasing the organic concentrations from dilute to the expected waste concentration the microorganisms become "acclimated" and then can consume the organic of concern. Shuckrow, et. al., reports that biological treatment was 100% effective in removing  $CCl_4$  from industrial wastewaters utilizing a biological aeration pond. The mechanisms for removal were not clearly described, but it probably was a combination of air-stripping and assimilation by microorganisms in the aeration pond. Kobayashi, et. al., state the following: "in contrast to naturally occurring compounds, man-made compounds are relatively refractory to biodegradation. One reason is that organisms that are naturally present often cannot produce the enzymes necessary to bring about transformation of the original compound to a point at which the resultant intermediates can enter into common metabolic pathways and be completely mineralized" [ES&T 1982]. They also indicate that  $CCl_4$  is degraded by sewage sludge microorganisms but the mechanism is questionable. However, Eckenfelder has shown that almost any organic can be assimilated by microorganisms once they have been acclimated to the organic [Eckenfelder 1966]. Being rather simple structures, the microorganisms generally

assimilate the simpler organics which are the "intermediates" described by Kobayashi above.

When using the normal activated sludge process, waste is fed to an aeration basin where blowers provide sufficient dissolved oxygen content and mixing for the aerobic organisms. The mixed liquor flows to a clarifier to allow 1) settling of the mixed liquor solids for recycle (underflow) back to the aeration basin, and 2) clarification of the effluent which overflows the clarifier. In facultative lagoons, the whole process takes place in one tank where aeration devices (floating aerators, blowers with diffusers or rotating brushes) provide mixing and air for the oxygen requirements. But the difference here is that the mixed liquor that settles is anaerobically converted to solids much like in a septic tank. A typical biological waste treatment system would include the following:

- Collection tanks and piping;
- facultative lagoon or aeration basin;
- pumps and/or aeration system;
- clarifier(s);
- sterilization system;
- monitoring systems; and
- instrumentation and control.

This type of system can be supplied in totally self contained, turnkey units in sizes to 1 million gallons per day as a package treatment plant by companies such as Met-Pro and others.

#### 4.3.3.4 Granular Activated Carbon (GAC) Adsorption

Activated carbon adsorption can be used to remove a wide variety of contaminants from liquid streams [Freeman 1989]. GAC adsorption is relatively non-specific and is commonly used on wastewaters that are not fully characterized or that have varying organic concentrations. GAC adsorption should be considered as a potential removal process for organic contaminants that are nonpolar, of low solubility, or of high molecular weight [Freeman 1989].

Activated carbon can be purchased as a powder or in granular form, and can be purchased in all types of containers for direct connection to a system, or can be supplied in bulk form. Virtually any desired particle size and size distribution can be obtained. Comparisons between carbons and their adsorption capacities are usually made through use of such indexes as the iodine or molasses numbers. Large iodine numbers generally meaning good capacity for low molecular weight organics, and large molasses numbers generally meaning good capacity for high molecular weight organics. Adsorption isotherms generally can provide a good indication as to the kinetics and capacity of a carbon for a particular organic, if a sample of wastewater and carbon can be obtained to run the isotherms.

Currently, both granular and powdered activated carbon adsorption systems are used for water and wastewater treatment. Powdered carbon is usually used as an additive in an activated sludge treatment system for additional organic removals (PACT Process). Granular carbon systems are generally used in tertiary treatment systems as a polishing step.

For the activated carbon alternative granular activated carbon is recommended as the primary treatment step because the organics are the principal waste of concern. The spent carbon could be regenerated on-site or disposed depending on carbon usage. Most regeneration systems incorporate a thermal step, where water is driven off and adsorbed organics are pyrolyzed. Regeneration costs are about one-tenth the cost of new carbon, and about 5 to 10 percent of the carbon is lost during each regeneration cycle.

This alternative technology could be used to remove  $\text{CCl}_4$  from secondary wastewaters. Two GAC beds would be connected in parallel with one being on-line while the other is either on standby or being regenerated/unloaded. The polished wastewater would be discharged in accordance with section 4.3.2. If it was decided to utilize the regeneration option for the activated carbon, the  $\text{CCl}_4$  could be recovered for recycle. For the airflows and  $\text{CCl}_4$  concentrations expected for this application, it would seem prudent to use activated carbon in disposable canisters.

#### 4.3.3.5 High Temperature Water Reaction

This alternative is essentially the same as the High Temperature Water Reaction discussed in Section 3.3.2 and consists of collecting waste  $\text{CCl}_4$  solutions for reaction with water in high temperature batch reactors. The solution is mixed with excess water in a batch reactor and the temperature is increased to  $250^\circ\text{C}$  producing  $\text{HCl}$  and  $\text{CO}_2$ . High temperature steam could form chloromethanes, hexachloroethane and perchloroethylene [Kirk & Othmer 1979]. If excess water is not used, phosgene is produced [Kirk 1979]. The resulting effluent would have to be neutralized to a pH of 7, cooled, and discharged. Since  $\text{HCl}$  is produced, the materials of construction would need to be Hastelloy B or other material known to be capable of handling  $\text{HCl}$ .

There is insufficient information available to adequately size system equipment and to determine system effectiveness. Therefore, this alternative is not recommended for treatment of the secondary wastes.

#### 4.3.3.6 Distillation

Azeotropic distillation is a very common unit process, especially in the petrochemical industry. It is a separations technology that has recently been applied to wastewater treatment. Azeotropic distillation could be used for the treatment of secondary wastes generated from some of the primary treatment technologies described above.

The  $\text{CCl}_4$  - water system forms a heteroazeotrope. A heteroazeotrope is defined as a mixture of two (or more) liquid compounds whose boiling point

does not change as vapor is generated and removed; and is synonymous with "constant-boiling mixture" [Perry 1950]. All reported heteroazeotropes are minimum boiling mixtures - the boiling point of the mixture is less than the boiling points of either component. For the  $\text{CCl}_4$  - water system the vapor composition from a boiling mixture would be 95.9%  $\text{CCl}_4$  - 4.1% water (the azeotropic composition). A batch type evaporator could be utilized to separate and purify  $\text{CCl}_4$  for recycle back to the organic storage tanks. Carbon tetrachloride and water have low solubilities for each other. Table 1, above, shows that the solubility of  $\text{CCl}_4$  in water is 0.08g/100g, or 0.08% (@20°C), and that the solubility of water in  $\text{CCl}_4$  is 0.01g/100g, or 0.01%. It would be assumed that by condensing the azeotropic composition vapor coming from the evaporator overheads, and then decanting the resulting immiscible mixture; that the  $\text{CCl}_4$  would contain approximately 100ppm (0.01%) water, and the water would contain approximately 800ppm (0.08%)  $\text{CCl}_4$ . However, laboratory tests by PNL [PNL 1991] have demonstrated that by extending the operating period of a batch evaporator, sub-ppm levels of  $\text{CCl}_4$  can be achieved. Azeotropic distillation/evaporation could be utilized for removing dissolved and undissolved liquid  $\text{CCl}_4$  in liquid water.

Distillation (not azeotropic distillation) is also fairly effective for treating secondary wastewaters containing  $\text{CCl}_4$ . A typical efficiency of 98% has been reported [MDC 1987]. With this removal efficiency, the discharge  $\text{CCl}_4$  concentration is estimated to be 0.0016 gm/100 gm water or approximately 16 ppm. The overheads will be at the azeotropic composition of approximately 96%  $\text{CCl}_4$  but upon subcooling will form two phases which could be decanted for recycle of the  $\text{CCl}_4$  [LATA 1991]. Industrial batch or continuous distillation units are commercially available specifically for solvent recovery processing [Glitsch 1990, DEC 1989].

A typical azeotropic distillation system would include the following:

- Batch type azeotropic evaporator;
- Condenser;
- Chiller;
- Utilities including water and steam;
- Piping, pumps, valves, and other hardware; and
- Instrumentation.

#### 4.3.3.7 Supercritical $\text{CO}_2$ Extraction/Oxidation

Supercritical organic extraction systems are commercially available that can remove  $\text{CCl}_4$  from waste water. The technology is available in sizes from 5 to 100 gpm [WHC 1989]. Data indicates that supercritical extraction is in excess of 99.9 percent efficient in removing  $\text{CCl}_4$  from water. Supercritical  $\text{CO}_2$  is used to extract organic compounds from water. In the supercritical state,  $\text{CO}_2$  is a powerful solvent and can remove organics very rapidly and effectively. The recovered  $\text{CCl}_4$  can then be recycled.

Supercritical organic oxidation is similar to extraction except water is compressed to its supercritical state where the organics are very soluble and air or oxygen is injected to oxidize the organic material. While this technology shows promise for destroying halogenated hydrocarbons, no commercial systems are yet available [Freeman 1989].

#### 4.3.3.8 Membrane Technology

This alternative consists of using membrane technology to remove  $\text{CCl}_4$  from secondary wastewater generated from other primary processes, e.g., scrubbing, azeotropic distillation. Reverse osmosis or pervaporation are two membrane technologies that might be utilized to separate and recover  $\text{CCl}_4$  from wastewater prior to discharge [Leeper 1984]. Reverse osmosis operates under pressure forcing water through a semi-permeable membrane while the contaminants are concentrated in the reject stream. Pervaporation uses a vacuum on the other side of the membrane to provide the driving force allowing the desired liquid solute to permeate across the membrane and vaporize. The problem with membrane systems is the fragility of the membranes. Membranes generally cannot tolerate solids, organics or radiolytic materials, and require pretreatment of most wastes prior to passing through membrane systems. Newer membranes are continually being formulated, and there is a possibility of finding a membrane suitable for this application.

## 5.0 RECOMMENDED ALTERNATIVES

### 5.1 SHORT TERM ALTERNATIVES

Since there has been a major change in the mission for the PRF, and since the continued use of  $\text{CCl}_4$  is not environmentally acceptable, it does not seem prudent, nor fiscally responsible, to install high cost or long term  $\text{CCl}_4$  abatement systems for the presently configured solvent extraction battery. The near term mission calls for two 100 day stabilization campaigns, after which there will be limited use of the SX system. Future scrap recovery work is more amenable to other, batch or lower throughput, purification processes, e.g. ion exchange or small mixer settler solvent extraction systems using dodecane as the diluent. Therefore, the following recommendations are short term alternatives that can be implemented to support the near term mission of the PRF.

#### 5.1.1 Water Cap on Pulse Leg

This alternative, as briefly described in Section 3.3, provides installation of a water "cap" on the  $\text{CCl}_4$  such that it acts like a water piston between the air and the  $\text{CCl}_4$ . The water cap essentially eliminates the  $\text{CCl}_4$  losses from the pulse legs of the extraction columns. There is basically no cost to implement this alternative.

### 5.1.2 Replace Column Air Pulsers with Mechanical Pulsers

This alternative consists of replacing the air pulser with a mechanically operated diaphragm pulser on each of the three solvent extraction columns (CA, CC, and CU). The emissions from these three columns is debatable, it has been estimated to be as high as 58.2 lbs  $\text{CCl}_4$ /day [LATA 1991] and as low as 0.0004 lbs.  $\text{CCl}_4$ /day if a water cap is present [Wojdac 1990]. It is estimated that installation of this alternative would reduce emissions from the columns by 96%. This alternative borders on being cost prohibitive.

An alternative to this option would be to install a sealed diaphragm between the air and the  $\text{CCl}_4$  to provide separation between them such that there is no pathway for the air to pass through the  $\text{CCl}_4$ .

### 5.1.3 Replace Tank Air Bubblers With Sealed Diaphragm Level Transmitters

This alternative consists of replacing the tank air bubbler level instrumentation with a sealed diaphragm type level system in each of four tanks (TK-27, TK-37, TK-38, and TK-120). This type level system does not bubble air into the process liquid to measure the back pressure caused by the height of liquid, instead a diaphragm is placed at "zero" level and the pressure exerted by the height of liquid is thus measured. This type transducer-transmitter functions just like air bubbler type level instruments. The transducer-transmitter could be mounted inside the glovebox with a pipe installed from the tank (in the tank canyon) penetrating the bottom port into the glovebox. This would make the instrument accessible for maintenance and calibration. It is estimated that eliminating the air bubbler type instruments from these four tanks will reduce  $\text{CCl}_4$  emissions by approximately 25.0 lbs/day, or 86% of the estimated 28.9 lbs  $\text{CCl}_4$ /day presently emitted from these tanks.

### 5.1.4 Replace $\text{CCl}_4$ Diluent with Tetrachloroethylene

As discussed in Section 3.5 above, based on the work of Barney [Barney, 1977] replacing  $\text{CCl}_4$  with another heavy phase diluent would be rather straight-forward, and is highly recommended. It is thought that the use of tetrachloroethylene (TCE) would be almost a direct substitute as regards solvent extraction system operation. However, as previously mentioned, although TCE is a land ban chemical it is not on the list of chlorinated hydrocarbon ozone depleters and may be more environmentally acceptable. Tetrachloroethylene also exhibits a lower vapor pressure/volatility resulting in significantly lower emission losses than  $\text{CCl}_4$ . For these reasons, replacing  $\text{CCl}_4$  with TCE is worthy of recommendation. It should be noted that most all other heavy phase organics that would be considered as a replacement diluent are as equally detrimental to the environment as  $\text{CCl}_4$  and TCE.

## 5.2 LONG TERM ALTERNATIVE

The only desirable long term alternative worthy of recommendation is to change the diluent from  $\text{CCl}_4$  to a light phase organic, like n-dodecane. This would reduce  $\text{CCl}_4$  emissions by 100%. Furthermore,  $\text{CCl}_4$  is being phased out of production, and by 1995 production will be only 15% of current levels, and by the year 2000 production will cease. The only reason for selecting this alternative would be based on a decision to continue operation of the presently configured solvent extraction system for some future mission.

## 6.0 RECOMMENDATIONS FOR FURTHER WORK

### 6.1 SOLVENT EXTRACTION

The analysis in Section 4 indicated there may be a reduction in the rate of extraction on changing the  $\text{CCl}_4$  diluent to n-dodecane, a light phase aliphatic hydrocarbon. There are methods to compensate for this reduced efficiency. One way would be to install centrifugal contactors after the columns. Another way is to conduct laboratory evaluations on scaled down models in order to predict operating efficiencies and parameters. Since this alternative is so attractive in other aspects, additional studies to compensate for reduced efficiencies are recommended.

### 6.2 PRF STACK AND PROCESS AREA MONITORING

Various techniques are available to continuously monitor/analyze  $\text{CCl}_4$ , and other vapors/gases of regulatory concern at the PRF.

$\text{CCl}_4$  emissions are monitored to determine the effectiveness of the various  $\text{CCl}_4$  mitigation methods and to ascertain whether or not PRF stack gases meet EPA and other regulatory requirements.

Available  $\text{CCl}_4$  vapor detection methods (some of which are EPA approved) include the following [Aldrich 1989, Ametek 1990, EG&G Ortec 1990, Rosemount 1989, Teledyne 1990]:

- Fourier Transform Infrared (FTIR) Analysis;
- gas mass spectrometry;
- gas chromatography (using both flame ionization and thermal conductivity detectors);
- near infrared (IR) photometric gas analysis;
- ultraviolet (UV) light photometric gas analysis;
- nuclear magnetic resonance (NMR) gas analysis.

### 6.3 RECOVERY PROCESSES OTHER THAN SOLVENT EXTRACTION

Two types of extraction methods that are fully developed and presently used at other sites include: 1) ion exchange, 2) solvent extraction using centrifugal contactors, and 3) solvent extraction using mixer settlers. The latter solvent extraction methods normally use light phase organics. A considerable engineering effort would be required to change the diluent to, for example, n-dodecane. It might prove to be more feasible to convert to a method such as ion exchange which would be suited to an operation that would minimize waste generation and be more suited to the waste stabilization mission of PFP.

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APPENDIX A  
EXISTING EMISSIONS BASELINE SUMMARY

PLUTONIUM RECLAMATION FACILITY (PRF)  
EMISSIONS BASELINE SUMMARY

The purpose of the emission baseline summary is to:

1. Document the major  $\text{CCl}_4$  emission sources (and associated equipment, i.e. vents, filters, etc.) on engineering schematics;
2. Develop (or use) analytical models (and their associated computer codes) to estimate the  $\text{CCl}_4$  fume emission rates from the  $\text{CCl}_4$  source tanks;
3. Evaluate potential reductions (to the extent possible) in emissions for selected alternatives as applied to the major sources (not all sources are amenable to a single alternative);
4. Assist with the determination of cost and schedule requirements associated with each alternative;

The baseline schematics (Figures A-1 and A-2) depict the top (plan) and elevation (side) views of the major  $\text{CCl}_4$  fume emitters. Figure A-3 details the physical mechanisms which can produce and/or enhance the  $\text{CCl}_4$  fume emission.

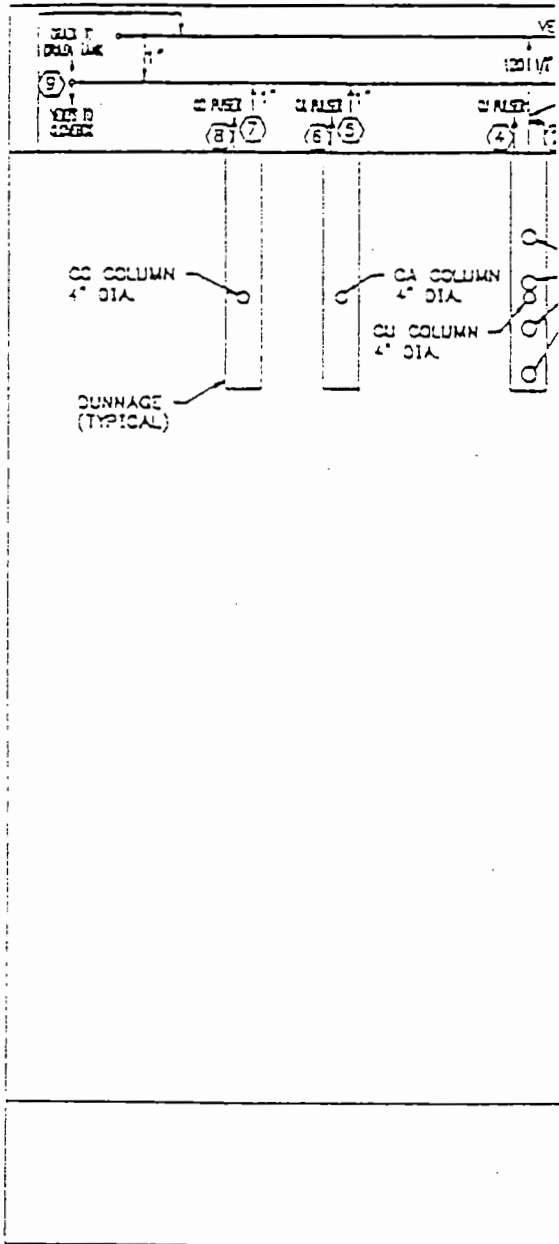
The flow rates shown on the bottom of Figure A-1 were calculated using the worst case  $\text{CCl}_4$  fume emission rates obtained using the equations for fume emission due to: a) stagnant tank conditions, b) agitated (by air bubbles), tanks, and c) pulsed solvent extraction columns.

STAGNANT TANK CONDITIONS

The tanks which can emit  $\text{CCl}_4$  fumes under stagnant conditions with very low air flow rates across the top of the liquid  $\text{CCl}_4$  inside the tanks are TK-48, TK-69, TK-114, and TK-115. Refer to Baseline Schematics, Figures A-1 and A-2.

The mass transfer equations that were used to acquire the best estimate for the purely diffusion,  $\text{CCl}_4$  fume emission rate is given by the TRANSPORT PHENOMENA equation (Bird, Stewart, and Lightfoot) [Bird 1960]:

$$N_{AZ} = \frac{(P_A)(D_{AB})}{(Z_2 - Z_1)(R)(T)} \ln \left[ \frac{(P_{B2})}{(P_{B1})} \right] \quad (\text{A-1})$$



|                                                  |            |   |
|--------------------------------------------------|------------|---|
| VENT SYSTEM FLOW STREAM                          | ①          | < |
| VENT SYSTEM STREAM DESCRIPTION                   | TK-48 VENT | ✓ |
| VENT SYSTEM FLOW RATE (SCFM)                     |            |   |
| FLOW STREAM SO <sub>2</sub> CONCENTRATION (ppm)  |            |   |
| FLOW STREAM CUMULATIVE SO <sub>2</sub> MASS (lb) |            |   |

Figure A-1 Baseline Schematic, Plan View

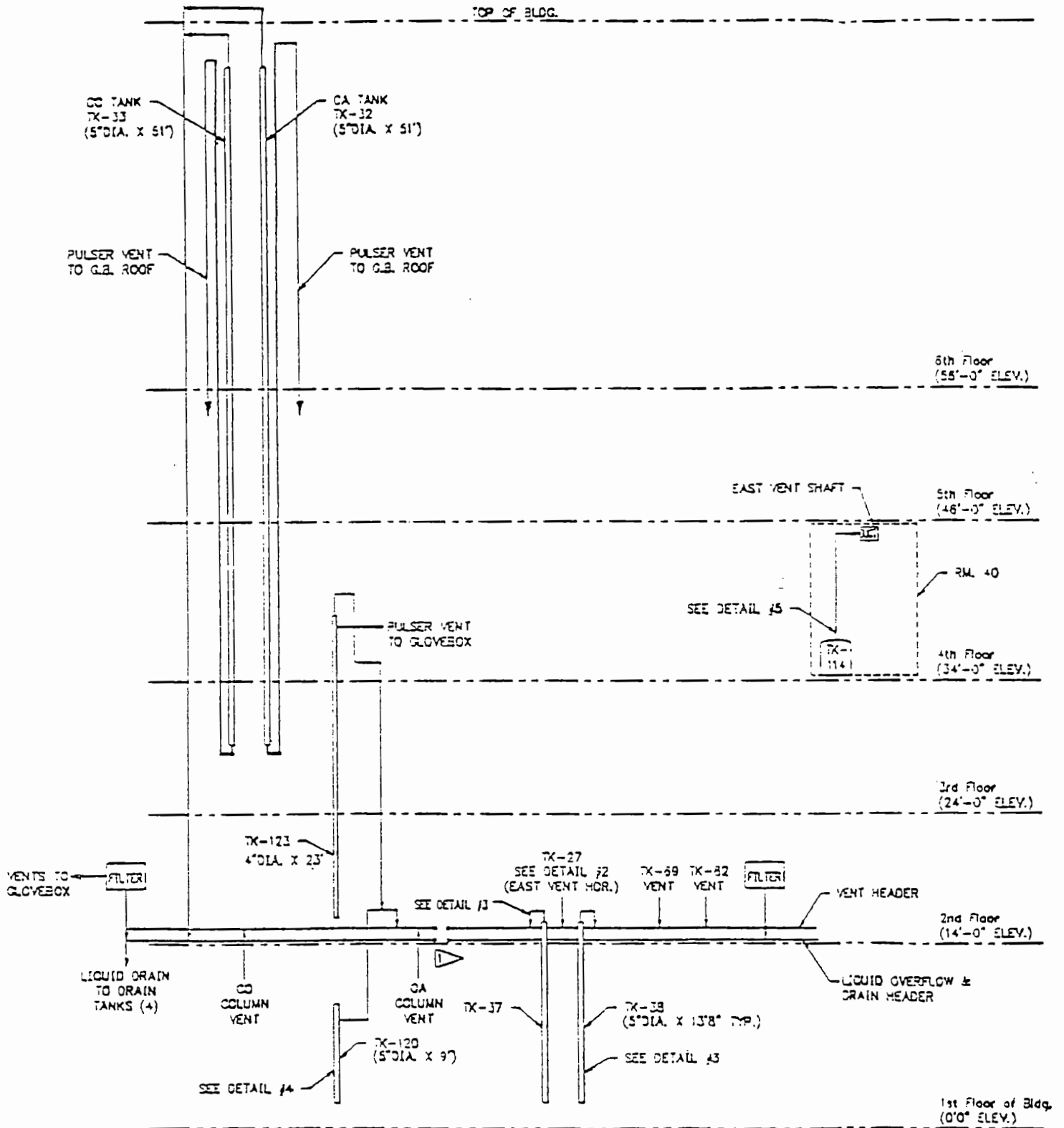
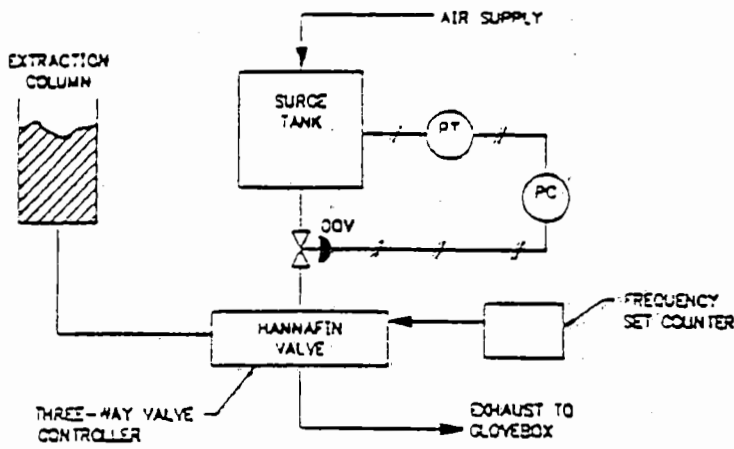
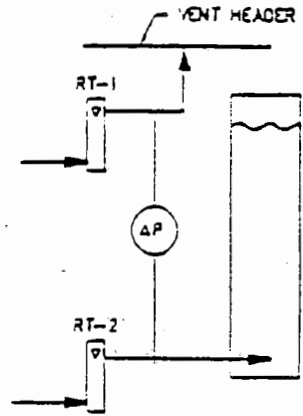


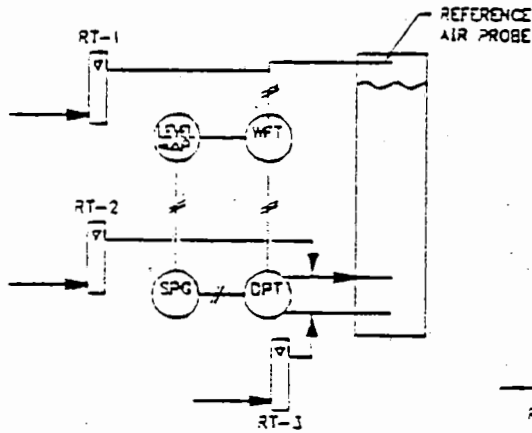
Figure A-2 Baseline Schematic, Elevation View



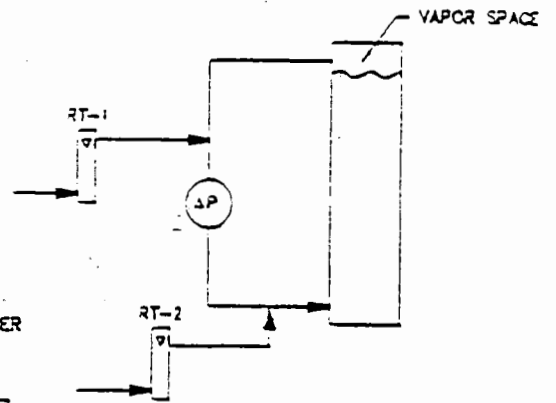
**DETAIL #1**  
COLUMN PULSER CONTROL SYSTEM



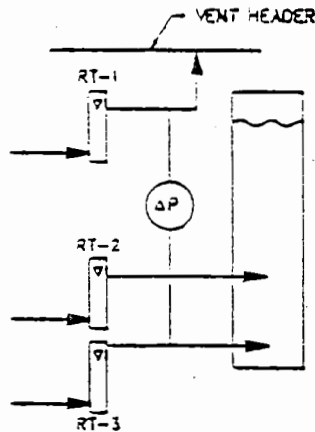
**DETAIL #4**  
LIQUID LEVEL INSTRUMENT  
(TYP. 2)



**DETAIL #2**  
LEVEL AND DENSITY INSTRUMENT



**DETAIL #5**  
LIQUID LEVEL INSTRUMENT  
(TYP. 2)



**DETAIL #3**  
LEVEL AND DENSITY INSTRUMENT  
(TYP. 2)

Figure A-3 Baseline Schematic, Details

Where,

- $N_{AZ}$  is the gas stagnation evaporation flux  $\left(\frac{\text{lbm-mole}}{\text{ft}^2\text{-s}}\right)$ ,  $N_{AZ}$  is a point function;
- $P_A$  is the total ambient (A) air pressure around (and entering) the tank;
- $D_{AB}$  is the binary mass diffusivity between  $\text{CCl}_4$  (A) and air (B)  $\left(\frac{\text{ft}^2}{\text{s}}\right)$ ;
- $Z_1$  is the elevation of the top liquid surface inside the tank;
- $Z_2$  is the elevation of the intersection of the vent header and the connecting pipe;
- $R$  is the universal gas constant (1,545)  $\left(\frac{\text{lb}_m\text{-ft}}{\text{lbm-mole}\text{-}^\circ\text{R}}\right)$ ;
- $T$  is the absolute temperature ( $^\circ\text{R}$ );
- $P_{B2}$  is the air partial pressure in the upper pipe intersection;
- $P_{B1}$  is the partial pressure of air at the gas-liquid boundary layer interface inside the tank; and
- $\ln$  is the natural logarithm.

Now, assuming that,

$$P_{B2} = P_A \text{ at the pipe intersection } (Z=Z_2), \text{ refer to Figure A-4.}$$

Also, 
$$P_{B1} = P_A - P_{\text{CCl}_4} (Z=Z_1)$$

Where,

$P_{\text{CCl}_4} (Z = Z_1)$  is the  $\text{CCl}_4$  vapor pressure (partial pressure of  $\text{CCl}_4$  vapor) at the liquid surface-gas interface.

It was also assumed that  $Z_2 - Z_1 = 2$  ft for conservative fume emission estimates.

$D_{AB}$  is calculated using the following equation,

$$D_{AB} = \frac{(a)}{(P)} \left[ \frac{T}{\sqrt{T_{CA} \cdot T_{CB}}} \right]^b (P_{CA} \cdot P_{CB})^{1/3} (T_{CA} \cdot T_{CB})^{5/12} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad (\text{A-2})$$

Where,

- $D_{AB}$  is the mass diffusivity for nonpolar gas-pairs
- $a = 2.745 \times 10^{-4}$
- $b = 1.823$

- P is the total pressure due to CCl<sub>4</sub> vapor and air
- T is the temperature of the CCl<sub>4</sub>-air mixture
- T<sub>CA</sub> is the critical (c) temperature of CCl<sub>4</sub>
- T<sub>CB</sub> is the critical temperature of air
- P<sub>CA</sub> is the critical pressure of CCl<sub>4</sub>
- P<sub>CB</sub> is the critical pressure of air
- M<sub>A</sub> is the molecular weight of CCl<sub>4</sub>
- M<sub>B</sub> is the molecular weight of air

The model used for the CCl<sub>4</sub> fume emission from the aqueous tank (tanks containing H<sub>2</sub>O and organic liquids), was based on Henry's law. The following equation is the final form of the CCl<sub>4</sub> fume emission rate:

$$W_{\text{CCl}_4} = \dot{m}_{\text{CCl}_4} = \frac{y * V_{\text{Total}}}{v_{\text{CCl}_4}} \quad (\text{A-3})$$

$$= \frac{(H_{\text{CCl}_4}) (\chi_{\text{CCl}_4}) * V_{\text{Total}}}{v_{\text{CCl}_4}} \quad (\text{A-4})$$

Where,

- W<sub>CCl<sub>4</sub></sub> is the CCl<sub>4</sub> fume emission rate ( $\frac{\text{lbm}}{\text{hr}}$ );
- y is the mole fraction of CCl<sub>4</sub> in the vapor = P<sub>o</sub>/P<sub>T</sub>;
- H<sub>CCl<sub>4</sub></sub> is the Henry's Law constant for CCl<sub>4</sub> and H<sub>2</sub>O at 25°C, 1 atm = 0.84;
- v<sub>CCl<sub>4</sub></sub> is the specific volume ( $\frac{\text{ft}^3}{\text{lbm}}$ ) of CCl<sub>4</sub> at 70°F and 1 atm; and
- x is the mole fraction of CCl<sub>4</sub> in the liquid.

Henry's law applies for dilute solutes (here liquid CCl<sub>4</sub> in an aqueous mixture), and is computed using,

$$P_i = (\chi_i) (H_i) \quad (\text{A-5})$$

where,

- P<sub>i</sub> is the vapor pressure of the i-th dilute component in a liquid mixture;
- χ<sub>i</sub> is the molar fraction of the i-th dilute liquid component in a liquid mixture; and
- H<sub>i</sub> is the Henry's constant for the i-th liquid (dilute) component.

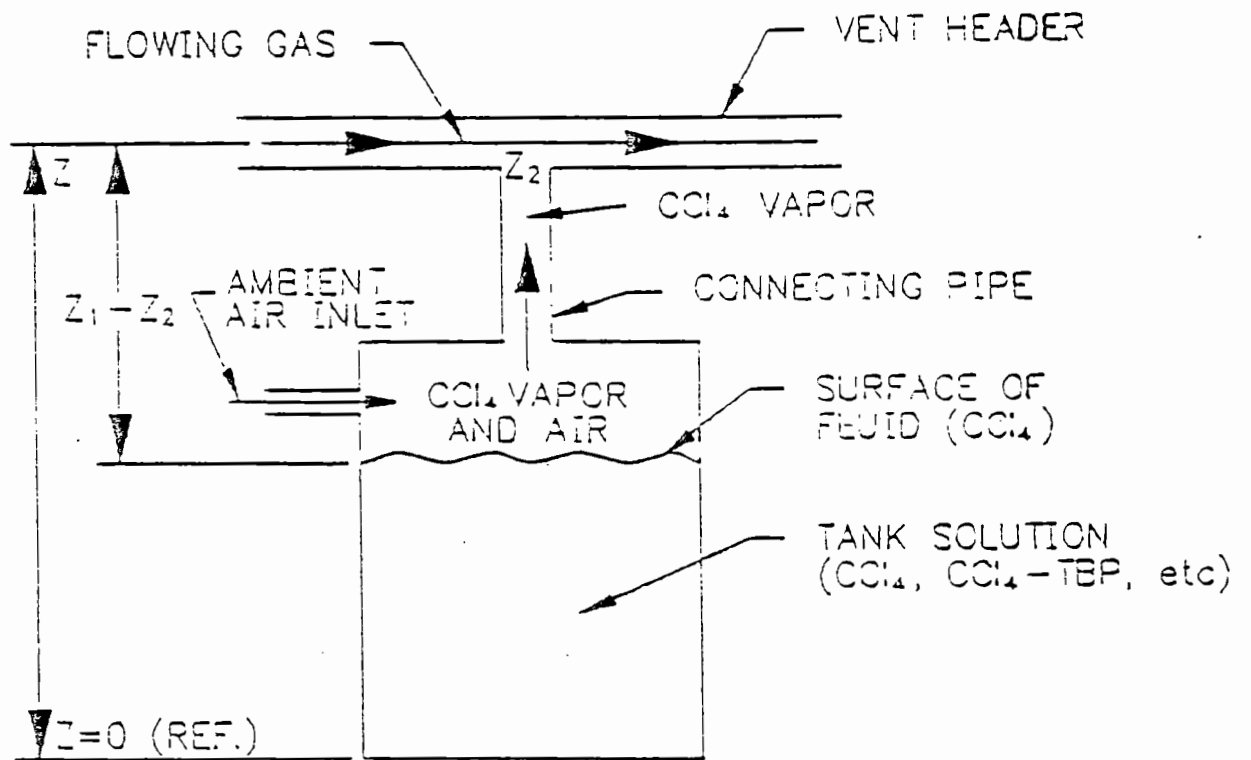


Figure A-4 Geometric Layout for CCl<sub>4</sub> Stagnation Evaporation Model

PPM CCl<sub>4</sub> VAPOR FROM AIR AGITATED TANKS

The primary PRF tanks emitting CCl<sub>4</sub> fumes due to air bubbling (used for liquid level measurement instruments) are: TK-27 (CAR), TK-37 (CAX), TK-38 (CAX), and TK-120 (CAP). Figures A-1 and A-2 (sheet 1 of 2) depict the approximate scale locations of these tanks. Figure A-2 (sheet 2 of 2) depicts some of the mechanical configurations of the air bubbling liquid level instruments. The driving force for CCl<sub>4</sub> fume evaporation is the total air flow rate emitted from the one or more air bubblers inside the tanks.

The model for the CCl<sub>4</sub> fume concentration for non-stagnant tanks is given by the following equation:

$$PPM = \frac{(\dot{m}_c) (10^6)}{(\dot{m}_c + \dot{m}_a)} \quad (A-6)$$

Where,

PPM is the CCl<sub>4</sub> fume concentration in parts per million;  
 $\dot{m}_a$  is the total air bubbling mass flow rate; and  
 $\dot{m}_c$  is the CCl<sub>4</sub> fume mass flow rate.

DETERMINATION OF CCl<sub>4</sub> VAPOR MASS FLOW RATE DUE TO MECHANICAL AGITATION

Carbon tetrachloride fumes are emitted by part of the mechanism used to air pulse the three solvent extraction columns. The three pulsed columns are TK-32 (CA column), TK-33 (CC column) and TK-123 (CU column). Refer to Baseline Schematics Figures A-1 and A-2.

Detail #1 on Figure A-3 (Baseline Schematic, Details) depicts the mechanism used to control the air driven pulsing of the extraction column liquid components. The CCl<sub>4</sub> fumes are released by the Hannifin valve to the respective column glovebox volume from the surging CCl<sub>4</sub> inside the pulse leg tube.

Wojdac [1990], developed a one dimensional eddy diffusion model which treats the pulse column as a series of displacement zones where the action of the Hannifin valve transfers the mass of one zone into the zone below in the form of a parabolic velocity wave. During the relaxation phase of the pulse the parabola is inverted and travels upward resulting in the mixing of a portion of the lower zone volume into the upper zone (eddy diffusion). Predictions based on the eddy diffusion model indicate that approximately 30 pounds of CCl<sub>4</sub> per day can be expected to be lost from the three pulse columns (CA, CC and CU) by this mechanism.

LATA used two mass transfer models [Bird 1960] to estimate the  $\text{CCl}_4$  fume emission from the valve and the worst case model was used as a basis for  $\text{CCl}_4$  emissions. The fumes are thought to be emitted by a liquid  $\text{CCl}_4$  paraboloid which occurs within the pulse leg.

The model for the worst case  $\text{CCl}_4$  fume emission rate is given by the following equation:

$$W_{\text{CCl}_4\text{-AVD}} = (\text{CF}_{\text{PAR}}) (S_A) (X_{\text{AO}}) \sqrt{\frac{D_{\text{AB}}}{\pi}} (\text{CF}_{\text{STP}}) \quad (\text{A-7})$$

Where,

$W_{\text{CCl}_4\text{-AVD}}$  is the emitted  $\text{CCl}_4$  vapor mass flow rate from the three extraction columns.

$\text{CF}_{\text{PAR}}$  is the correction factor to correct for the surface area of the paraboloid.


$S_A$  is the planar surface area of the motionless liquid  $\text{CCl}_4$  inside the surge tube.

$X_{\text{AO}}$  is the mole fraction of liquid  $\text{CCl}_4$ .

$D_{\text{AB}}$  is the binary mass diffusivity for  $\text{CCl}_4$  vapor diffusing from the liquid interface, (see Eq. A-2).

$\text{CF}_{\text{STP}}$  is the correction factor to correct to standard temperature and pressure (STP).



|                                                                                                                                                                                                                                                                                                                                                                               |                                                              |                                                                                                                                                                                                                                                                                                                                                             |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Date Received:<br><i>6/18/93</i>                                                                                                                                                                                                                                                                                                                                              | <b>INFORMATION RELEASE REQUEST</b>                           | Reference:<br>WHC-CM-3-4                                                                                                                                                                                                                                                                                                                                    |
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| Title <b>PFP Carbon Tetrachloride Emission Abatement Engineering Study</b>                                                                                                                                                                                                                                                                                                    |                                                              | Unclassified Category<br>UC-                                                                                                                                                                                                                                                                                                                                |
| Impact Level <i>5</i>                                                                                                                                                                                                                                                                                                                                                         |                                                              |                                                                                                                                                                                                                                                                                                                                                             |
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| Title of Conference or Meeting                                                                                                                                                                                                                                                                                                                                                |                                                              | Group or Society Sponsoring                                                                                                                                                                                                                                                                                                                                 |
| Date(s) of Conference or Meeting                                                                                                                                                                                                                                                                                                                                              | City/State                                                   | Will proceedings be published? <input type="checkbox"/> Yes <input type="checkbox"/> No<br>Will material be handed out? <input type="checkbox"/> Yes <input type="checkbox"/> No                                                                                                                                                                            |
| Title of Journal                                                                                                                                                                                                                                                                                                                                                              |                                                              |                                                                                                                                                                                                                                                                                                                                                             |
| CHECKLIST FOR SIGNATORIES                                                                                                                                                                                                                                                                                                                                                     |                                                              |                                                                                                                                                                                                                                                                                                                                                             |
| <u>Review Required per WHC-CM-3-4</u>                                                                                                                                                                                                                                                                                                                                         | Yes    No                                                    | Reviewer - Signature Indicates Approval<br>Name (printed)    Signature    Date                                                                                                                                                                                                                                                                              |
| Classification/Unclassified Controlled Nuclear Information                                                                                                                                                                                                                                                                                                                    | <input checked="" type="checkbox"/> <input type="checkbox"/> | <i>W. F. Russell</i> <i>W. F. Russell</i> <i>6-9-93</i>                                                                                                                                                                                                                                                                                                     |
| Patent - General Counsel                                                                                                                                                                                                                                                                                                                                                      | <input checked="" type="checkbox"/> <input type="checkbox"/> | <i>S. W. Berglin</i> for Barbara Williamson 6/19/93                                                                                                                                                                                                                                                                                                         |
| Legal - General Counsel                                                                                                                                                                                                                                                                                                                                                       | <input checked="" type="checkbox"/> <input type="checkbox"/> | <i>S. W. Berglin</i> for Barbara Williamson 6/19/93                                                                                                                                                                                                                                                                                                         |
| Applied Technology/Export Controlled Information or International Program                                                                                                                                                                                                                                                                                                     | <input type="checkbox"/> <input checked="" type="checkbox"/> |                                                                                                                                                                                                                                                                                                                                                             |
| WHC Program/Project                                                                                                                                                                                                                                                                                                                                                           | <input checked="" type="checkbox"/> <input type="checkbox"/> | <i>D. B. Cartmell</i> <i>D. B. Cartmell</i> <i>6-9-93</i>                                                                                                                                                                                                                                                                                                   |
| Communications                                                                                                                                                                                                                                                                                                                                                                | <input type="checkbox"/> <input checked="" type="checkbox"/> |                                                                                                                                                                                                                                                                                                                                                             |
| RL Program/Project                                                                                                                                                                                                                                                                                                                                                            | <input checked="" type="checkbox"/> <input type="checkbox"/> | <i>J. E. Mecca</i> <i>J. E. Mecca</i> <i>6/10/93</i>                                                                                                                                                                                                                                                                                                        |
| Publication Services                                                                                                                                                                                                                                                                                                                                                          | <input type="checkbox"/> <input checked="" type="checkbox"/> |                                                                                                                                                                                                                                                                                                                                                             |
| Other Program/Project                                                                                                                                                                                                                                                                                                                                                         | <input type="checkbox"/> <input checked="" type="checkbox"/> |                                                                                                                                                                                                                                                                                                                                                             |
| Information conforms to all applicable requirements.    The above information is certified to be correct.                                                                                                                                                                                                                                                                     |                                                              |                                                                                                                                                                                                                                                                                                                                                             |
| <b>References Available to Intended Audience</b><br><input type="checkbox"/> Yes <input checked="" type="checkbox"/> No                                                                                                                                                                                                                                                       |                                                              | <b>INFORMATION RELEASE ADMINISTRATION APPROVAL STAMP</b><br>Stamp is required before release. Release is contingent upon resolution of mandatory comments.<br><br>                                                                                                      |
| <b>Transmit to DOE-HQ/Office of Scientific and Technical Information</b><br><input type="checkbox"/> Yes <input checked="" type="checkbox"/> No                                                                                                                                                                                                                               |                                                              |                                                                                                                                                                                                                                                                                                                                                             |
| Author/Requestor (Printed/Signature)    Date<br><i>CS Hammack</i> <i>CS Hammack</i>                                                                                                                                                                                                                                                                                           |                                                              |                                                                                                                                                                                                                                                                                                                                                             |
| Intended Audience<br><input type="checkbox"/> Internal <input type="checkbox"/> Sponsor <input checked="" type="checkbox"/> External<br>Responsible Manager (Printed/Signature)    Date<br><i>PK Vacca</i> <i>PK Vacca</i> <i>6-9-93</i>                                                                                                                                      |                                                              |                                                                                                                                                                                                                                                                                                                                                             |
| Date Cancelled                                                                                                                                                                                                                                                                                                                                                                |                                                              | Date Disapproved                                                                                                                                                                                                                                                                                                                                            |

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|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------|---------------|----------------------------------------------------|---------------------------|------|
| Lead Author                                                                                                                                                                        | Phone<br>3-3280           | MSIN<br>T4-18 | Other Author(s) or Requestor<br><i>[Signature]</i> |                           |      |
| Project or Program<br>PFP                                                                                                                                                          | Lead Org Code<br>15550    |               | Sponsor Agency (DOE, DOT, NRC, USGS, etc.)         |                           |      |
| Editor                                                                                                                                                                             | Phone                     | MSIN          | DOE/HQ Program (DP, EH, EM, NE, etc.)              |                           |      |
| Mandatory Comments (Only mandatory comments are to be documented. All other comments should be made on a copy of the information submitted for review and returned to the author.) | Reviewer Name & Signature | Date          | Resolution                                         | Reviewer Name & Signature | Date |
|                                                                                                                                                                                    |                           |               |                                                    |                           |      |
|                                                                                                                                                                                    |                           |               |                                                    |                           |      |
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|                                                                                                                                                                                    |                           |               |                                                    |                           |      |

Legends/Notices/Markings (required per WHC-CM-3-4 or guidance organization.) (Reviewer initials)

|                                | Affix |     |                                                               | Affix |     |
|--------------------------------|-------|-----|---------------------------------------------------------------|-------|-----|
|                                | Yes   | No  |                                                               | Yes   | No  |
| Applied Technology             | [ ]   | [ ] | Predecisional Information                                     | [ ]   | [ ] |
| Business-Sensitive Information | [ ]   | [ ] | Programmatic Notice                                           |       |     |
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Additional Information \_\_\_\_\_

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