An Alternative to Storage of Spent Dry Cleaner Filters as Mixed Waste

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Abstract

A portable treatment unit has been developed by Pacific Gas & Electric Company (PG&E) to extract Freon 113® from radioactively-contaminated dry cleaner filters. In addition, the PG&E unit is also effective for extraction of alcohol and acetone from contaminated paper wipers. Filters and wipers of this type are currently classified as mixed waste. Storage of these wastes at many nuclear power plants has been required because no treatment, storage, and disposal facility (TSD) has accepted this kind of solid mixed waste. The PG&E unit was built after commercial paint solvent recovery systems were tested and found to be ineffective.

Separation of the hazardous volatile component from solid mixed wastes by thermal desorption is an EPA-approvable treatment. Recovery of the solvent enables it to be recycled. Evaluation of a commercial solvent recovery unit was performed by treating unused filters and wipers that had been spiked with solvent to simulate mixed waste. This unit proved to be unsuitable for use with Freon® and did not remove alcohol or acetone from 30 spiked paper wipers below 1.5% residual (by weight). The PG&E unit reduced the acetone or alcohol residue to well below 1% in 75 wipers. This made the flash point of the treated wipers greater than 140°F; a condition that allows them to be incinerated. The PG&E unit also removed Freon® from the filters to <30 mg/kg, enabling it to be used to treat filters in accordance with the disposal regulations for a listed waste.

Based on this work, a portable treatment unit constructed by PG&E has been shown to successfully remove the volatile hazardous component of some simulated mixed wastes. Should appropriate offsite treatment facilities not be permitted to handle mixed wastes, the unit discussed may be valuable as an alternative to prolonged storage.

Introduction

Diablo Canyon Power Plant (DCPP) currently stores fourteen drums of spent dry cleaner filters from the laundry facility and two drums of paper wipers generated by maintenance activities. The filters contain Freon® 113 and the wipers contain either acetone or denatured alcohol (ethanol made unfit for consumption; referred to as alcohol from here forward). Both media contain radionuclides, and as such are classified as "mixed wastes." Only one facility is currently permitted to accept solid mixed wastes. To date, this facility has not accepted the waste discussed here. Faced with the possibility of permanent storage, alternatives were investigated.

Extractions of volatile solvent spikes from simulated mixed wastes using a commercial paint solvent recovery unit were performed at Technical and Ecological Services (TES) in San Ramon, California during 1992. Those tests (1) showed that the commercial unit could recover the majority of denatured alcohol or acetone from paper wipers that had been spiked with one of these fluids. However, two major limitations were apparent from the results of preliminary tests with Freon® 113. First, the seal design of the commercial unit did not allow efficient capture of this fluid. Second, the commercial unit was unable to accept a full size filter. Even if recovery of Freon® 113 had been successful, cutting the filter in half to fit it into the commercial unit would not be desirable for filters containing radioactive particles because of the potential for spreading contamination.

More testing of the commercial solvent recovery unit was subsequently performed to determine if the solvent could be extracted sufficiently from the treated wipers to render them non-hazardous. In those tests, the wipers still smelled of solvent after treatment. Assuming that the wipers treated with the first unit remained hazardous, another commercial unit was tested. When the second commercial solvent recovery unit proved unsatisfactory, TES designed and constructed a new unit instead of trying to adapt what was available. The resulting PG&E mixed waste treatment unit (MWTU) was specifically designed for extracting Freon® from filters. The MWTU also worked well at removing acetone or alcohol from paper wipers. The investigation that led to development of the MWTU and our preliminary tests of its efficiency will be discussed.

Commercial Solvent Recovery Unit Performance Test Methods

Initial tests of a commercial solvent recovery unit (Siva International Inc., Recyclene model R-2A, designated Unit C-1 in this paper) had shown that it could recover acetone or alcohol from spiked paper wipers (Wypalls®). Despite the inability of Unit C-1 to recover Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane; referred to as Freon® below), testing was performed to determine if the extraction of acetone or alcohol rendered the Wypalls® non-hazardous.

To spike Wypalls® for the tests described, ten to fifteen were placed in a 2-liter beaker after unfolding and then crumpling each to simulate its having been used. Acetone or denatured alcohol (400 ml total; in appropriate portions) was then added to the Wypalls® in the beaker. A few seconds were allowed for the solvent to soak completely into the Wypalls®, which were then placed inside the chamber of Unit C-1. More Wypalls® were spiked as described until the planned number had been loaded into Unit C-1 with 400 ml of solvent evenly distibuted among them. After loading was completed, the lid was closed and secured. Following this, the heating cycle was started; generally at a setting of 125°C for acetone or 150°C for alcohol. It should be noted that the manufacturer of Unit C-1 recommended temperature settings 20 to 40°C above the boiling point of the solvent to be recovered from a liquid matrix (2). However, it was necessary to make these settings 70°C above the boiling points of acetone and denatured alcohol (56°C and 78°C, respectively) to allow extraction of these solvents from the solid matrix of the Wypalls®.

Extraction times of up to 7.5 hours were used during tests of Unit C-1 that were run to minimize the residual solvent in spiked Wypalls®. Unit C-1 was limited by its microprocessor to heating cycle lengths of up to 5 hours. For this reason, it had to be restarted manually between the successive heating cycles of a test to give treatment times longer than that. Overnight runs were not used because an operator was needed to add ice to the closed-loop system that cooled Unit C-1's condenser. This closed-loop system had been installed at TES to replace the manufacturer's setup because it was incompatible with water conservation practices required at the time of testing. When Unit C-1's heating cycle(s) for a given run was finished, the machine was cooled to an indicated temperature of 120°F (49°C). At that temperature, the automatic release of Unit C-1's safety interlock enabled the machine to be opened for collection of samples from the Wypalls®. Tests that followed this generic plan were run with batches of 10 and 30 wipers, at various temperatures from 125 to 155°C, and with total heat cycle durations of 1.25 to 7.5 hours.

Upon completion of a test such as those described above, sections were cut from at least half of the Wypalls® and packed in a 50-ml glass sample vial so that the headspace in the vial was minimized. The vial was then sealed with a Teflon-lined closure. Duplicate samples were also taken periodically and submitted as "blinds" to monitor the consistency of the analyzing laboratory's

results. After collection, all samples were labeled and refrigerated until they were transferred to the laboratory for solvent residue analysis by EPA method 8015 (modified) or 3510 (3). From the results of these analyses (described below and shown in Tables 2 and 3), it was seen that the solvent residues in the Wypalls® (after tests with either acetone or alcohol) exceeded 1.5% by weight after up to 7.5 hours heating in Unit C-1. It was assumed that this concentration of residue was in excess of that required to render the Wypalls® non-hazardous because it was evident (by the odor) that the solvents were not completely removed by treatment.

A commercial solvent recovery unit that had a positive seal design (Siva International Inc., Recyclene model S-8V; designated Unit C-2) was rented in late 1992 to test it with simulated mixed wastes. Where Unit C-1 could be moved by one person, Unit C-2 was as large as a refrigerator laid on its side and had to be moved with a forklift. It was first tested to determine if Freon® (500 ml, no filter present) could be evaporated and recovered successfully; a simple, but critical test. Unit C-2 did evaporate the Freon® with which it had been loaded in less than an hour. However, only half the Freon® was recovered and the mass of Unit C-2 made it a lengthy process to cool the device after the test had been completed. Specifically, about 12 cubic feet of ice had to be added over a period of 6 hours to the closed-loop system in order to cool it from the 90°C temperature set point to 50°C. At 50°C, Unit C-2's safety interlock allowed it to be opened so that the volume of solvent which remained after the test could be measured. After the 8-hour heating and cooling cycle described, about 5 ml of Freon® still remained. Based on Unit C-2's cost (more than $10k), the presence of a significant amount of residual solvent in the chamber after heating, and its requirement of an external cooling system, further testing was rejected. These results and tests of Unit C-1 led to a proposal by TES to design a unit specifically for extracting Freon® from the type of dry cleaner filters used at DCPP.

Quantitative extraction of the Freon® in DCPP's stored dry cleaner filters was chosen as the primary design objective for the PG&E Mixed Waste Treatment Unit (MWTU) because the filters take up much more space than the Wypalls® at the plant. The MWTU was designed to require minimal operator attention and is intended in most cases to be loaded one day, allowed to run, and shut down for unloading and reloading the next day. It should be noted that the MWTU's technical specifications are currently proprietary. For this reason, three types of enhancement to its basic thermal desorption technology are designated E-1, E-2, and E-3, when used below.

PG&E Mixed Waste Treatment Unit (MWTU) Performance Test Methods; Freon®-Filter Extractions

Testing of the MWTU was begun in late April of 1994. The objective of these tests was to qualitatively evaluate its efficiency for extracting Freon® from spiked dry cleaner filters. The filters are 0.5-micron-nominal-porosity, cartridge-type (Kleen-Rite model KR-221) units with steel end-caps and core support. They are 14-inches in length with an 8-inch outside diameter and a 1-inch inside diameter. In performance tests of the MWTU, an unused dry cleaner filter was plugged at one end and spiked with 400 ml of Freon® 113 by pouring portions into the filter's core while rotating it around its long axis. After the Freon® had soaked in, the plug was removed from the filter end. The filter was then mounted in the MWTU chamber and the chamber lid secured.

After treatment had been completed and the MWTU had returned to ambient temperature, the filter was removed and cut in half with a band saw. Samples of the inner core were promptly removed and packed in a 50-ml glass vial so as to minimize headspace. The vial was then sealed with a

Teflon-lined closure. As before, duplicate samples were collected and submitted for analysis as unknowns. All samples were refrigerated until analysis by EPA solid waste analysis method 8015 (modified) (4).

Results of MWTU Freon®-Filter Extractions

Table 1 shows the results of the Freon®-filter extractions that have been done using the MWTU. Freon® 113 (boiling point 48°C) was successfully extracted from the spiked filters at temperature set points of 70 and 80°C. All extractions done at the higher temperature resulted in residual concentrations at or below 30 milligrams of Freon® per kilogram of filter core material (mg/kg in Table 1; samples 94-MW-1, 4, 5, and 6). One sample (Table 1; sample 94-MW-1) that had been processed with a first type of enhancement (E-1) showed a residual Freon® concentration of 25 mg/kg after only 5 hours. A longer, 19-hour E-1 extraction (Table 1; sample 94-MW-5) further reduced the residual Freon® concentration to 15 mg/kg in the filter. A run (Table 1; samples 94-MW-2 and 3) was also made with a second type of enhancement (E-2), as was one (Table 1; sample 94-MW-6) with a third type of enhancement (E-3). The use of E-3 extraction appears to have allowed an additional reduction of the residual Freon® concentration by a factor of two over E-1 extraction with the MWTU.

Table 1. Results of Extracting Dry Cleaner Filters Spiked With 400 ml of Freon® Using the PG&E Mixed Waste Treatment Unit (MWTU).

Sample Number	Freon® Residue (mg/kg of filter core)	MWTU Temperature Setpoint (°C)	Extraction Enhancements Used*	Extraction Time (hours)	Duplicated Sample (number)
94-MW-1	25	80	E-1	5	no
94-MW-2	40	70	E-1, E-2	20	no
94-MW-3	48	70	E-1, E-2	20	yes (94-MW-2)
94-MW-4	30	80	none	22	no
94-MW-5	15	80	E-1	19	no
94-MW-6	7	80	E-1, E-3	21	no

*Enhancements of basic technology are proprietary.

To briefly summarize the results of Freon®-filter extractions with the MWTU:

- At a temperature set point of 80°C, E-1 extraction of 400 ml of Freon® from a spiked dry cleaner filter resulted in a residual concentrations of less than 30 mg Freon per kg of filter core in as little as five hours or 15 mg/kg if E-1-extracted overnight;

and

- E-3-enhanced extraction allowed the residual Freon® concentration to be further reduced to less than 10 mg/kg in an overnight run.

MWTU Performance Test Methods; Acetone-/Alcohol-Spiked Wypalls®

Following the Freon®-filter extractions with the MWTU that have been described, experiments were performed to extract acetone and denatured alcohol spikes from Wypalls®. In the first few tests, acetone- or alcohol-spiked Wypalls® were simply placed in the MWTU for treatment. Only 26 Wypalls® could be loaded in this manner. With success at reaching residual alcohol levels in

Wypalls® that had not been acheived with commercial Unit C-1 (described under comparative results), our attention was turned to improving the efficiency of the MWTU for that process. It was found that the capacity of the MWTU for Wypalls® could be increased by modifying the system's chamber.

Comparative Results of Extracting Acetone- or Alcohol-Spiked Wypalls®

Extractions of acetone from Wypalls® with the MWTU were more effective than those done for alcohol. Unenhanced MWTU extraction of Wypalls® for acetone (Table 2; sample 94-MW-10) was marginally more effective than the extractions with the R-2A had been (Table 2; samples 3, 5, (93)-MW-5, and (93)-MW-6). In an overnight E-1 extraction, acetone residues in the MWTU-processed Wypalls® were reduced by roughly an order of magnitude (Table 2; samples 94-MW-11 and 12) over those acheived with commercial Unit C-1 (Table 2; samples 3, 5, (93)-MW-5, and (93)-MW-6).

Table 2. Results of Extracting Wypalls® Spiked with 400 ml of Acetone With Commercial Solvent Recovery Unit 1 and PG&E Mixed Waste Treatment Unit (MWTU).

Sample Number	Treatment Unit	Acetone Residue (weight %)	Number of Wypalls®	Temperature Setpoint (°C)	Extraction Enhancements Used*	Extraction Time (hours)	Duplicated Sample (number)
3	Unit C-1	2.4	10	155	n/a	2	no
5	Unit C-1	1.9	30	125	n/a	4	no
(93)-MW-5	Unit C-1	1.5	30	125	n/a	5	no
(93)-MW-6	Unit C-1	1.5	30	125	n/a	7.5	no
94-MW-10	MWTU	0.73	26	80	none	23	no
94-MW-11	MWTU	0.11	26	80	E-1	24	no
94-MW-12	MWTU	0.18	26	80	E-1	24	yes (94-MW-11)
94-MW-16	MWTU	n/a; flash pt. >140°F	75	85	E-1	24	no
94-MW-17	MWTU	n/a; flash pt. >140°F	75	85	E-1	24	yes (94-MW-16)

*Enhancements of basic technology are proprietary.

The result of an initial unenhanced alcohol-Wypalls® extraction (Table 3; sample 94-MW-7) with the MWTU was similar to the results obtained with commercial Unit C-1(Table 3; samples 1, 2, (93)-MW-1, and (93)-MW-3). In E-1 MWTU extractions of alcohol spikes from Wypalls®, this solvent was removed to around 1% residual (by weight in the processed Wypalls®) in 24-hour runs at 80 and 85°C (Table 3; samples 94-MW-8, 9, and 13). Residual concentrations of alcohol in Wypalls® of 1% or below had been arbitrarily set as a milestone in the MWTU project because in all the runs with test Unit C-1, extraction to that level had not been attained. After modification of the MWTU's sample chamber, the batch of 75 alcohol-spiked Wypalls® that had been extracted at 85°C for 72 hours showed a residual alcohol concentration of less than 1% by weight (Table 3; samples 94-MW-14 and 15).

Table 3. Results of Extracting Wypalls® Spiked with 400 ml of Denatured Alcohol With Commercial Solvent Recovery Unit 1 and PG&E Mixed Waste Treatment Unit (MWTU).

Sample Number	Treatment Unit	Alcohol Residue (weight %)	Number of Wypalls®	Temperature Setpoint (°C)	Extraction Enhancements Used*	Extraction Time (hours)	Duplicated Sample (number)
1	Unit C-1	3.2	10	150	n/a	1.25	no
2	Unit C-1	2.3	30	155	n/a	3.5	no
(93)-MW-1	Unit C-1	2.7	30	150	n/a	5	no
(93)-MW-1	Unit C-1	1.5	30	155	n/a	7.5	no
94-MW-7	MWTU	2.02	26	85	none	26.25	no
94-MW-8	MWTU	1.35	26	85	E-1	22.5	no
94-MW-9	MWTU	1.17	26	85	E-1	22.5	yes (94-MW-8)
94-MW-13	MWTU	0.83	26	80	E-1	24	no
94-MW-14	MWTU	0.56	75	85	E-1	72	no
94-MW-15	MWTU	0.75	75	85	E-1	72	yes (94-MW-14)
94-MW-18	MWTU	n/a; flash pt. >140°F	75	85	E-1	72	no
94-MW-19	MWTU	n/a; flash pt. >140°F	75	85	E-1	72	yes (94-MW-18)

*Enhancements of basic technology are proprietary.

Discussion

In the tests described here, replication of conditions between tests was purposely left for a later time. This was done because the immediate goal of the project was to construct the MWTU and develop basic operating methods that were sufficient for DCPP to begin treatment of its solid mixed wastes. Due to the lack of replicate tests, no statistical uncertainties for the results presented are available. Despite this, variations in the residual solvent concentrations reported for all tests were consistent with variations in the test parameters. For example, solvent residue concentrations after E-1-plus-E-3 extractions were lower than those resulting from E-1(only) extraction, which in turn were lower than those resulting from unenhanced extractions. In addition, the results of quantitative, blind duplicate analyses (samples 94-MW-2 and 3 in Table 1, 94-MW-11 and 12 in Table 2, and 94-MW-8 and 9 and 13 and 14 in Table 3) showed no differences large enough to indicate gross errors in the sampling or performance of these analyses. Understanding the shortcomings of this approach, it is believed that enough data has been collected to prove the efficiency of the MWTU and permit development of effective operating procedures.

The final objective originally assigned to the project described here was the determination of whether the DCPP mixed wastes could be rendered non-hazardous by treating them using the alternate hazardous debris treatment standards specified by the Resource Conservation and Recovery Act. Freon® 113 and acetone are regulated as "listed" solvents; Waste Codes F001, F002, and F003 (5). Alcohol is regulated as a "characteristic" waste (D001; ignitable). The resulting (6) Freon®, acetone, and alcohol residues in solid waste are currently limited to approval of the treatment technology for the "non-hazardous" determination.

In the tests performed, E-1-enhanced MWTU extraction (at the 80°C setpoint) of Freon® from dry cleaner filters for 5 hours or longer resulted in residual Freon® concentrations below 30 mg/kg (Table 1; samples 94-MW-1, 5, and 6). E-1 MWTU extraction (at the 85°C setpoint) of acetone or alcohol from batches of 75 Wypalls® for 24 and 72 hours, respectively, resulted in the processed Wypalls® exhibiting a flash point above 140°F (Table 2; samples 94-MW-16 and 17, Table 3; samples 94-MW-18 and 19). Based on the above criteria for acceptable residual solvent concentrations in solid wastes, both E-1- and E-1-plus-E-3-enhanced extraction with the MWTU removed sufficient Freon® from filters to permit disposal under the debris rule. In addition, both of these processes removed sufficient acetone/alcohol from Wypalls® to render them non-hazardous.

Extraction of hazardous solvents from mixed wastes using the MWTU falls under treatment defined as, "thermal desorption," in Title 40 of the *Code of Federal Regulations* (7). As an EPA-approvable treatment technology that has been shown to extract solvents from simulations of DCPP's mixed wastes, application for a permit to use the MWTU in actual treatment has been made. If a permit is granted, a waste analysis plan will be submitted for approval. At that point in time, it should become clear if repetitive extractions of non-radioactive spiked materials, pilot tests with actual wastes at DCPP, or other steps toward preparing for routine mixed waste treatment are required.

Conclusion

There is currently only one facility permitted to accept solid mixed wastes for disposal. There are severe restrictions on the acceptability of waste by this facility. These restrictions prevent disposal of some as-generated wastes. Options for on-site extraction of hazardous solvents from solid mixed wastes at Diablo Canyon Power Plant (Freon® in dry cleaner filters and acetone or alcohol in Wypalls®) were requested as an alternative to continued storage. Two commercial solvent recovery systems were evaluated for this purpose and found to be unsuitable. Instead of continuing adaptation of existing commercial units to DCPP's needs, TES built the PG&E mixed waste treatment unit (MWTU) specifically to handle DCPP's solid mixed wastes. This portable unit is simple to operate and has removed the hazardous solvents from simulated wastes to levels that would allow off-site disposal of the filters and incineration of the Wypalls®.

References

1. Gans, C. D. Mixed Waste Treatability Study. San Ramon, CA: Pacific Gas & Electric Company Technical and Ecological Services. 420DC-92.826; 1992. (Please contact author to request copies)

2. Siva International Inc. Recyclene R-2A Solvent Recovery System Operating Manual. South San Francisco, CA; 1990

3. USEPA (United States Environmental Protection Agency). Test Methods for Evaluating Solid Waste. SW846, 3rd ed., Update 1. Washington, D.C.: Office of Solid Waste and Emergency Response; 1992.

4. USEPA, ibid.

5. USEPA (United States Environmental Protection Agency). 40CFR260, 40CFR261, Subpart D Fed. Reg. 46:4617; 1981.

6. USEPA (United States Environmental Protection Agency). 40CFR261, Subpart C Fed. Reg. 45:33119; 1980, 1990.

7. USEPA (United States Environmental Protection Agency). 40CFR268.45 Fed. Reg. 57:37277; 1992.