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**RECOVERY STUDIES FOR PLUTONIUM
MACHINING OIL COOLANT**

Chemistry Research and Development

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SUBJECT DESCRIPTORS

Lathe Coolants
Plutonium
Plutonium Recovery
Separation Processes
Tetrachloromethane

ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ROCKY FLATS PLANT
P.O. BOX 464
GOLDEN, COLORADO 80401

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RECOVERY STUDIES FOR PLUTONIUM MACHINING OIL COOLANT

James D. Navratil and Charles E. Baldwin

Abstract. Lathe coolant oil, contaminated with plutonium and having a carbon tetrachloride diluent, is generated in plutonium machining areas at Rocky Flats. A research program was initiated to determine the nature of plutonium in this mixture of oil and carbon tetrachloride. Appropriate methods then could be developed to remove the plutonium and to recycle the oil and carbon tetrachloride. Studies showed that the mixtures of spent oil and carbon tetrachloride contained particulate plutonium and plutonium species that are soluble in water or in oil and carbon tetrachloride. The particulate plutonium was removed by filtration; the nonfilterable plutonium was removed by adsorption on various materials. Laboratory-scale tests indicated the lathe-coolant oil mixture could be separated by distilling the carbon tetrachloride to yield recyclable products.

INTRODUCTION

Lathe coolant oil, having a carbon tetrachloride (CCl_4) diluent and contaminated with plutonium (Pu), is generated in plutonium machining areas at Rocky Flats. Each month, spent lathe-coolant oil mixture is filtered ($3\ \mu\text{m}$) and stored in two tanks. In addition to the oil, the mixture contains approximately 50 percent carbon tetrachloride and $10^{-3}\ \text{g/l}$ Pu, which exists in soluble forms or as $<3\ \mu\text{m}$ particles. After appropriate analyses have been obtained, the oil is shipped to a waste treatment facility for disposal. The disposal process consists of mixing the oil and carbon tetrachloride with a synthetic, hydrous, calcium silicate powder to produce a solid that can be packaged in 55-gallon drums for storage.

To reduce solid wastes for storage and to conserve materials, a research program was initiated to examine the feasibility of recycling lathe coolant oil and carbon tetrachloride. Since plutonium was

not desired in the recycled products, methods to remove plutonium from the spent mixture also were studied. A determination of plutonium species in the oil mixture was therefore needed to assist in the development of plutonium decontamination methods.

EXPERIMENTAL

Materials and Equipment

Samples of spent lathe-coolant oil containing carbon tetrachloride were obtained from either of two storage tanks, V-30 or V-31, in the plutonium machining area at Rocky Flats. The tanks' contents were mixed with an air sparge for 20 minutes before the samples were taken from taps at the bottom of the tanks.

Other materials used in the studies are described in Table 1. Filter holders and 0.01-, 0.1-, and $0.8\text{-}\mu\text{m}$ Millipore® filters* were used as was Whatman 1PS phase separating paper.

Procedures and Methods

Plutonium decontamination experiments consisted of filtration and adsorption tests. In the filtration tests, mixtures of used lathe-coolant oil were filtered under vacuum through Millipore filters. Plutonium concentrations in the mixtures underwent radio-metric, pulse height, and alpha analysis before and after filtration. In the analysis, eight aliquots per original oil sample and four aliquots per filtered sample were counted at least three times each, and the counts were averaged.

For the adsorption tests, 15-ml volumes of the adsorbents were covered with used lathe coolant under static conditions. The oil mixtures with

*Manufactured by Millipore Filter Corp., Bedford, Massachusetts.

TABLE 1. Description of Chemicals Used in Experiments

Chemical	Form and/or Purity	Manufacturer
Alumina	80-200 mesh powder	Fisher Scientific Co.
Antioxidant Agent (2,6-Di- <i>tert</i> -butyl-4-methylphenol)	Practical	Chem Service
Calcium Oxide	B&A reagent	Allied Chemical Co.
Calcium Sulfate (Drierite®)	10-20 mesh	W. A. Hammond Drierite Company
Carbon Tetrachloride	Analytical reagent	Mallinckrodt
Cellulose, Cellex N-1	Non-ionic powder	Bio-Rad Laboratories
Charcoal	Activated (¼ in.)	Barnabeey Cheney
JM Chromosorb®	Calcined diatomite type 80-100 mesh	Johns-Manville
Charcoal	Activated, 6-14 mesh	Fisher Scientific Co.
Corn Starch	Powder	Kingman
DMP (2,2-dimethoxypropane)	Reagent grade	Eastman Organic Chemicals
Fullers Earth	—	—
Molecular Sieve	Activated, Type 13X, ⅛ in.	Linde
Nitric Acid	B&A reagent grade	Allied Chemical Co.
Oil, Texaco 643®	—	Texaco Oil Co.
Polyethylene, Lot 3-17-174-2	Beads, 200-600 micron	The Dow Chemical Co., Louisiana Division
Polystyrene	Beads, 20-24 mesh	—
Silica Gel	6-16 mesh	Sargent
Sodium Carbonate	Reagent grade, powder	Allied Chemical Co.
Sodium Hydroxide	B&A reagent grade, pellets	Allied Chemical Co.
Sucrose	Granular	Great Western Sugar Co.
Teflon®	Powder	Carl Roth OHG
TEOF (triethyl-orthoformate)	Reagent	Eastman Organic Chemicals

and without (for control) adsorbents were stored for various periods of time. The entire oil mixtures (samples) were filtered (0.01 μm) separately and then analyzed for plutonium. The difference between analyses of the treated oil and the control oil samples was used to calculate the percent of soluble plutonium removed.

Column tests also were used to test the adsorbents. Fractions (15 ml) of the oil mixtures were passed through a 1.4-cm-diameter by 3.2-cm-high column of the adsorbent at a 10 ml/hr flow rate. Each oil fraction was filtered through a 0.01- μm filter and analyzed for plutonium.

Tests with dehydrating reagents consisted of storing 2 ml of either DMP or TEOF with 5 ml of oil mixture in sealed vials. The oil mixture was filtered (0.01 μm) and analyzed for plutonium.

Plutonium decontamination tests with 10M sodium hydroxide (NaOH) or with 7M nitric acid (HNO_3) and 0.1M hydrofluoric acid (HF) consisted of mixing equal volumes of both phases for 5 minutes. The phases were then separated for 10 minutes, and each phase was analyzed for plutonium.

Experiments were conducted to measure the effect of the antioxidant agent (2,6-Di-*tert*-butyl-4-methylphenol) on the growth of nonfilterable plutonium in mixtures of oil and carbon tetrachloride. The experiments consisted of dissolving 0, 100, 1000, and 10,000 mg/l of antioxidant agent in duplicate batches of Texaco 643 oil (free of antioxidant) containing 50 vol % CCl_4 and 0.1 vol % water (H_2O). Plutonium metal coupons (0.1-cm thick by 2.4-cm diameter), free of surface oxidation, were stored in the oil and carbon tetrachloride batches—some for 15 days and others for 66 days. After storage, the batches were filtered through a 0.2- μm Millipore filter and sampled in triplicate for plutonium.

The spent lathe coolant and recovered oil and carbon tetrachloride samples were characterized by analysis. Relative hydrocarbon oxidation was measured as volume percent dibutyl sebacate by infrared spectroscopy. Observed degradation was determined by comparing relative differences in the infrared spectra of 0.1-mm films of a fresh oil sample and of sample oils after volatile constituents had been removed. Subtle differences were detected in the 1300- to 670- cm^{-1} region indicating chain cleavage, dehydrogenation, oxidation, and nitration. Volume percent of carbon tetrachloride was determined by measuring the percent volatiles. The pH and chloride contents of the oils were determined by potentiometric methods after a

1:1 water extraction. Water content was determined by Karl Fisher coulometric titration.

Characterization of soluble plutonium species in the oil was attempted by chromatographic mass-spectroscopy techniques. Filtered oil mixtures were introduced into a 1.3-cm-diameter column packed with alumina. That was followed by slow elution with 50 ml CCl_4 . The discolored portion of the alumina was heated and the outgas analyzed by mass spectroscopy to obtain fragmentation patterns of the adsorbed species.

The corrosion tests were accomplished by the conventional weight-loss method. The method involved storing treated plutonium coupons (surface area of about 7 cm^2) in each oil sample at ambient temperatures. After storage, the coupons were treated as before storage, i.e., wire brushed to remove surface corrosion, rinsed in 1,1,1-trichloroethane, dried, and weighed to the nearest 0.1 mg. The weight difference of the coupon before and after storage was used to calculate the corrosion rate.

X-ray diffraction techniques were used to identify the plutonium species filtered from the oil. The oil was filtered through $0.05\text{-}\mu\text{m}$ Millipore filters, and the filter and residue were subjected immediately to X rays without removing the oil coating from the residue. Nuclear track techniques were used to determine the physical form of plutonium in the filtered oil mixtures.

Carbon tetrachloride was separated from spent lathe-coolant mixtures by simple distillation techniques. The distillation equipment consisted of a 500-ml flask connected to an air-cooled condenser. The distillation occurred at a vapor temperature of $\sim 80^\circ\text{C}$ under atmospheric pressure ($\sim 610 \text{ mm Hg}$).

RESULTS AND DISCUSSION

Plutonium Form in Lathe Coolant

Oil samples were taken over a period of several months from the plutonium machining storage tanks and were characterized by chemical analysis.

Plutonium decontamination experiments were also conducted to determine whether plutonium in the lathe coolant oil was present as suspended particulate or as a form that is soluble in water or in a mixture of oil and carbon tetrachloride.

Characterization and decontamination results are shown in Tables 2 and 3. The original samples taken in September contained a large amount of visible particulate matter (V-30 more so than V-31) compared to the October samples. These observations correlate with the decrease in plutonium concentration after filtering the oil samples through an $0.8\text{-}\mu\text{m}$ Millipore filter. In most cases, the plutonium concentration did not decrease significantly by filtering with 0.1- or $0.01\text{-}\mu\text{m}$ Millipore filters when compared to $0.8\text{-}\mu\text{m}$ filtering. The plutonium concentration also did not change significantly after filtering through phase separating paper; however, after storage over anhydrous calcium sulfate for six days, and subsequent filtering through $0.01\text{-}\mu\text{m}$ filters, the alpha count was near background of available radiometric counting equipment ($\sim 1 \mu\text{g/l Pu}$).

These results show that particulate and soluble plutonium species are present in mixtures of oil and carbon tetrachloride. The nonfilterable (soluble) plutonium remaining in the monthly samples of oil and carbon tetrachloride averaged $50 \times 10^{-5} \text{ g/l}$ over a period of a year. Nuclear track techniques confirmed the filtered oil was free of plutonium-containing particulate matter. The concentration and percentage of nonfilterable plutonium, shown in Tables 2 and 3, varied over a wide range. No correlation was found with the chemical analysis that was performed except perhaps in chloride content. A statistical test showed no significant correlation between the amounts of nonfilterable plutonium and chloride concentrations, but because each sample had a different history and length of plutonium and carbon tetrachloride interaction time, a real correlation may have gone undetected.

The amount of nonfilterable plutonium in the samples of oil and carbon tetrachloride decreased, and the chloride concentration and pH generally increased after 3 to 10 months storage in sealed polyethylene bottles (see Appendix 1). The decrease

TABLE 2. Results of Decontamination Experiments

Description	Average Plutonium Concentration (10^{-5} g/l) $\pm$ Standard Deviation				
	Sept V-30	Sept V-31	Oct V-30	Oct V-31	Jan V-30
Sample date and tank number					
Untreated oil sample	886 $\pm$ 274	116 $\pm$ 26	157 $\pm$ 11	143 $\pm$ 36	57 $\pm$ 4
Filtered (0.8 μ m)	164 $\pm$ 1	35 $\pm$ 2	71 $\pm$ 1	63 $\pm$ 6	1.2 $\pm$ 0.2
Filtered (0.1 μ m)	144 $\pm$ 4	23 $\pm$ 2	78 $\pm$ 4	62 $\pm$ 7	1.8 $\pm$ 0.3
Filtered (0.01 μ m)	144 $\pm$ 2	22 $\pm$ 2	81 $\pm$ 4	81 $\pm$ 5	1.2 $\pm$ 0.3
Filtered through 0.01- μ m Millipore and Whatman 1PS phase separating paper	144 $\pm$ 7	25 $\pm$ 2	81 $\pm$ 7	83 $\pm$ 1	—
Stored over calcium sulfate, Filtered (0.01 μ m)	0.5 $\pm$ 0.2	0.3 $\pm$ 0.1	0.3 $\pm$ 0.3	0.2 $\pm$ 0.5	0.1 $\pm$ 0.1

Description	Average Plutonium Concentration (10^{-5} g/l) $\pm$ Standard Deviation				
	Jan V-31	Apr V-30	Apr V-31	June V-30	Aug V-31
Sample date and tank number					
Untreated oil sample	31 $\pm$ 1	60 $\pm$ 8	46 $\pm$ 3	102 $\pm$ 10	160 $\pm$ 15
Filtered (0.8 μ m)	3.6 $\pm$ 0.5	31 $\pm$ 1	12 $\pm$ 1	70 $\pm$ 6	47 $\pm$ 4
Filtered (0.1 μ m)	3.0 $\pm$ 0.5	40 $\pm$ 3	11 $\pm$ 1	66 $\pm$ 4	51 $\pm$ 5
Filtered (0.01 μ m)	2.4 $\pm$ 0.4	32 $\pm$ 2	8.4 $\pm$ 0.5	68 $\pm$ 5	59 $\pm$ 4
Filtered through 0.01- μ m Millipore and Whatman 1PS phase separating paper	—	—	—	—	—
Stored over calcium sulfate, Filtered (0.01 μ m)	0.2 $\pm$ 0.2	0.1 $\pm$ 0.2	0.1 $\pm$ 0.1	0.6 $\pm$ 0.2	—

TABLE 3. Characterization of Lathe Coolant Oil

Description	Results of Analyses									
	Sept V-30	Sept V-31	Oct V-30	Oct V-31	Jan V-30	Jan V-31	Apr V-30	Apr V-31	June V-30	Aug V-31
Sample date and tank number										
Nonfilterable plutonium (wt %) ^a	16	19	45	43	2	8	52	18	65	29
Carbon tetrachloride (vol %) ^b	45	37	45	63	54	55	59	68	69	70
pH	2.6	3.0	2.9	2.9	3.0	3.0	3.4	2.7	6.2	2.2
Chloride (10^{-3} M)	8.2	2.3	3.3	8.4	2.2	4.1	4.8	6.3	6.0	2.8

a. Concentration of plutonium after filtering divided by amount in original sample (approximately) multiplied by 100.

b. Besides carbon tetrachloride, traces (<1 vol %) of other halogenated hydrocarbons were detected—trichloroethylene, perchloroethylene, 1,1,1-trichloroethane, and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113).

of soluble plutonium could have been caused by adsorption of plutonium onto the polyethylene bottle and/or precipitation of the plutonium.

No method for determining water concentrations below 1000 ppm was available at this point, but

later analyses showed the mixtures of oil and carbon tetrachloride contained an average of 33 microliters per liter of water (see Appendix 2).

Nonfilterable plutonium remaining in the oil [approximately 0.005 mM (millimolar) Pu] was

presumed to be present as hydrated chloro species since the mixture usually contained about 0.002 mM water and about 0.14 mM chloride. Another potential ligand or complexing agent for plutonium in the oil mixtures is the ~3 wt % antioxidant agent (2,6-Di-*tert*.-butyl-4-methylphenol) present in the oil.

Experiments were performed with plutonium metal coupons stored in batches of synthetic oil and carbon tetrachloride mixtures. These mixtures contained various amounts of the antioxidant agent. Results showed increasing levels of nonfilterable plutonium with increasing concentrations of antioxidant (Table 4). The data suggest only the possibility of a soluble 2,6-Di-*tert*.-butyl-4-methylphenol plutonium complex being formed in the mixtures of oil and carbon tetrachloride.

Attempts to characterize the actual plutonium species in the oil mixture by separation-mass spectroscopy techniques failed. The particulate plutonium removed by filtration averaged 1 mg/l and was identified by X-ray diffraction techniques as plutonium dioxide. No evidence for plutonium metal or other plutonium compounds was observed.

Removal of Plutonium from Lathe Coolant

The particulate plutonium in the untreated lathe coolant was not entirely removed by filtering through 3- μ m production filters as shown in Table 2. Filtering with <0.8- μ m Millipore filters, however, appears to remove almost all of the plutonium particles.

Soluble plutonium was found to be removable (<0.01 mg/l) by adsorption on alumina, calcium sulfate, calcium oxide, charcoal, Fuller's earth, JM Chromosorb, and molecular sieves, or by contact with 7M HNO₃-0.1M HF. Only alumina, Chromosorb, and Fuller's earth had fast enough adsorption rates to remove plutonium in a column at 10-ml/hr flow rates. Results indicate the other reagents, shown in Table 5, were not entirely effective. Treatment of the June V-30 oil sample with dehydrating agents (DMP and TEOF) reduces the amount of soluble plutonium somewhat, indicating possibly that removal of water causes some precipitation of the plutonium.

TABLE 4. Effect of Antioxidant Agent on the Growth of Soluble Plutonium in Mixture of Oil and Carbon Tetrachloride

Antioxidant Agent ^a (mg/l)	Soluble Plutonium ^b (mg/l)	
	15 days storage	66 days storage
0	11	18
100	—	42
1,000	35	63
10,000	—	85

a. 2,6-Di-*tert*.-butyl-4-methylphenol.

b. Average of triplicate analysis.

The use of alumina, JM Chromosorb, and Fuller's earth in a routine process probably would generate excessive waste, especially since regeneration of the reagents appeared unlikely. The most compatible reagents for a plutonium recovery facility were charcoal for adsorption and nitric acid plus hydrofluoric acid, which were used for washing. The charcoal could be incinerated, and the acids could be disposed of in the plutonium waste stream. The acid scrub would not permit reuse of the oil, but charcoal would. Plutonium adsorption kinetics would have to be studied further, however, before charcoal adsorption could be considered in a plutonium removal process. (Other types of charcoals and smaller particle size charcoal also should be studied.)

Recovery of Oil and Carbon Tetrachloride

To determine the feasibility of recovering and recycling used oil for lathe coolant, various oil samples were subjected to conventional (weight loss), plutonium-metal corrosion tests. The results of plutonium corrosion in new Texaco 643 oil and two, used mixtures of oil and carbon tetrachloride are shown in Table 6.

Plutonium corrosion relative to new oil was increased when water and carbon tetrachloride were present, especially when present together.

TABLE 5. Removal of Soluble Plutonium from Mixture of Oil and Carbon Tetrachloride Using Various Reagents

Reagent ^a	Soluble Plutonium Removed in Column ^b (wt %)	Soluble Plutonium Removed after Static Storage ^c (wt %)		
		1 day	2 days	6 days
Alumina	99.5	85	99.1	99.8
JM Chromosorb	99.5	98	99.6	—
Fuller's Earth	99.5	97	>99.9	—
Molecular Sieve	48	>99.9	—	—
Calcium Sulfate	34	97	98	99.1
Calcium Oxide	—	99	99.5	—
Charcoal	50	99	—	—
Coconut Charcoal	46	80	90	98
Silica Gel	—	47	73	92
Cellex N-1	90	88	—	—
Powdered Calcium Sulfate	70	69	—	—
Sodium Hydroxide	—	21	32	48
Sucrose	8	43	—	—
Sodium Carbonate	—	23	—	—
Corn Starch	61	21	—	—
Polyethylene	—	0	4	20
Teflon	—	0	1	18
Polystyrene	—	9	11	—
DMP (2,2-dimethoxypropane)	—	17	24	49
TEOF (triethylorthoformate)	—	0	15	43
10M Sodium Hydroxide	—	81 ^d	—	—
7M Nitric Acid and 0.1M Hydrofluoric Acid	—	97 ^d	—	—

a. See Table 1 for reagent description.

b. Passed 14 ml of June V-30 mixture of oil and carbon tetrachloride through 3.2-cm-long, 1.4-cm-diameter column of reagent at 10 ml/hr flow rate.

c. Stored 15 ml of reagent covered with June V-30 mixture of oil and carbon tetrachloride in sealed vials or stored 5-ml mixture of oil and carbon tetrachloride and 2 ml dehydrating agent or equal volumes of aqueous solutions and mixture of oil and carbon tetrachloride.

d. Contacted for 5 minutes.

New oil with carbon tetrachloride added and then removed by distillation (to <0.1 percent) showed no more corrosion than new oil. Used mixtures of oil and carbon tetrachloride were much more corrosive than new oil, but plutonium corrosion decreased when the carbon tetrachloride was removed (to <0.1 percent), and reduced further after contact with charcoal.

Corrosion results showed that used oil with the carbon tetrachloride removed (to <0.1 percent) was not as good as new oil. Treatment with charcoal appears to reduce the corrosive behavior of recycled oil. Plutonium corrosion in oil bottoms containing <3 percent carbon tetrachloride (resulting from distillation of several spent lathe-coolant mixtures; see Appendix 2) was about the same as

TABLE 6. Results of Plutonium Corrosion Tests with Lathe Coolant Oil

Description of Lathe Coolant	Plutonium Corrosion (mg/dm ² · day) ^a After		
	2 weeks	4 weeks	8 weeks
None (air)	14	10	5
New oil	17	10	6
New oil + 0.02 vol % H ₂ O	—	15	—
New oil + 0.1 vol % H ₂ O	58	21	15
New oil + 1 vol % H ₂ O	56	10	9
New oil + 0.1 vol % CCl ₄	25	12	8
New oil + 1 vol % CCl ₄	27	21	11
New oil + 0.1 vol % H ₂ O + 0.1 vol % CCl ₄	—	73	—
New oil with CCl ₄ added, then removed (<0.1 vol %)	—	9	—
June V-30 oil-CCl ₄	—	32	—
June V-30 CCl ₄ (<0.1 vol %) removed	—	17	—
June V-30 CCl ₄ (<0.1 vol %) charcoal treated ^b	—	14	—
June V-30 CCl ₄ (<0.1 vol %) charcoal, CaSO ₄ treated ^b	—	14	—
Jan V-30 oil-CCl ₄	27	19	12
Jan V-30, CCl ₄ (<0.1 vol %) removed	23	13	11
Jan V-30, CCl ₄ (<0.1 vol %) removed, AO added ^c	23	15	8

a. Milligrams per square decimeter per day. All values have an estimated accuracy of ±15 percent.

b. Oil stored over reagent for two weeks.

c. AO = antioxidant (1000 mg/l).

TABLE 7. Characterization Results of Reclaimed Carbon Tetrachloride

Sample	Oil Content (g/l)	Water Content (μl/l)	Plutonium (mg/l)	Plutonium Corrosion Rate ^a (mg/dm ² · day) ^b
1	0.162	56	1.5×10^{-6}	77
2	—	53	1.4×10^{-6}	74
3	0.308	58	1.0×10^{-6}	75
4	0.096	56	3.0×10^{-6}	64
5	0.041	50	1.8×10^{-6}	78
6	—	53	1.3×10^{-6}	70
new CCl ₄	0.004	59	1.2×10^{-6}	70

a. Average of 7 and 14 day determinations; estimated accuracy ±15%.

b. Milligrams per square decimeter per day.

the reclaimed carbon tetrachloride, but a small amount (0.04 to 0.30 g/l) of oil was found. The oil contamination probably could be prevented by installing a trap between the distillation flask and the condenser.

Water concentrations in the reclaimed carbon tetrachloride were no greater than reagent-grade carbon tetrachloride (59 μl/l H₂O) stored under the same conditions as the recovered carbon tetrachloride samples. Although the water concentration (0 to 150 ppm) was reported as varying linearly with relative humidity (0 to 100 percent),¹ the water analyses obtained in this study were performed under low humidity conditions and the reagent-grade carbon tetrachloride was used as a control.

The samples of reclaimed carbon tetrachloride contained $<3 \times 10^{-6}$ mg/l plutonium (low enough to be recycled in plutonium handling areas) and were no more corrosive toward plutonium metal than new reagent-grade carbon tetrachloride. Increased levels of water in the carbon tetrachloride would increase plutonium corrosion; consequently, the relative humidity of air in contact with the carbon tetrachloride should be controlled.

in the new oil. The main difference in the recovered oil shown in Table 6 versus Appendix 2 is that the former had been stored for over three months whereas the latter was less than one month old.

Using a simple laboratory-scale distillation technique, carbon tetrachloride was recovered from spent lathe-coolant mixtures to evaluate product purity. The oil mixtures were obtained directly from the machining areas since oil in Waste Tanks V-30 and V-31 (see Table 3) contained other solvents. Characterization results of the reclaimed carbon tetrachloride are shown in Table 7.

No miscellaneous solvent contamination was detected by infrared spectroscopy techniques in

CONCLUSIONS

A research program was completed to determine the nature of plutonium in spent lathe-coolant oil and to develop methods for removing plutonium and for recycling the oil and carbon tetrachloride. The plutonium-contaminated lathe-coolant oil, with its carbon tetrachloride diluent, is generated in plutonium machining areas at Rocky Flats.

Studies showed that the mixtures of spent oil and carbon tetrachloride contained both particulate plutonium (identified as plutonium dioxide) and plutonium species that were soluble in water or in mixtures of oil and carbon tetrachloride (perhaps chloride and/or 2,6-Di-*tert.*-butyl-4-methylphenol soluble complexes). The particulate plutonium was removed by filtration; the soluble plutonium was removed by adsorption on various reagents. Charcoal appeared to be the most desirable adsorbent for removing soluble plutonium; however, additional studies are needed.

Laboratory-scale tests showed the lathe-coolant mixture could be separated by distillation of the carbon tetrachloride, provided the lathe coolant was free of other low-boiling solvents. The carbon tetrachloride and oil bottoms appeared acceptable for reuse. Recycling of the oil bottoms was dependent on the concentration of residual carbon tetrachloride in the oil and perhaps on deterioration of the oil with usage. Incineration of the oil bottoms should be evaluated as a step replacing the solidification-retrievable storage practice. The carbon tetrachloride recovery process will be evaluated on a large scale to further evaluate product acceptance and the economic feasibility of this process.

REFERENCES

1. J. L. Holst and D. K. Strangfeld. *The Determination of Trace Residues on Metal Surfaces*. RFP-419. The Dow Chemical Company, Rocky Flats Division, Golden, Colorado. November 16, 1964.

APPENDIX 1

Characterization of Lathe Coolant Oil

Sample Date and Tank Number	Pu $\times 10^{-5}$ (g/l)	Cl $\times 10^{-2}$ (M)	pH	Percent C=O ^a	Observed Degradation ^b
Sept V-30	886	0.8	2.6	0.09	Major (1,2,3)
(c)	152	1.1	4.1	0.16	Minor (1,2)
Sept V-31	116	0.2	3.0	0.08	Major (1,2,3)
(c)	50	0.9	3.9	0.13	Minor (1,2)
Oct V-30	157	0.3	2.9	0.04	Major (1,3)
(d)	4	0.6	3.3	0.10	Minor (1,2)
Oct V-31	143	0.8	2.9	0.10	Major (1,2,3,4)
(d)	35	0.3	4.2	0.17	Minor (1,2)
Jan V-30	57	0.2	3.0	0.04	Minor (1,3)
(e)	4	0.6	4.5	0.11	Minor (1,2)
Jan V-31	31	0.4	3.0	0.06	Major (1,3)
(e)	22	3.4	5.6	0.12	Minor (1,2)
Apr V-30	60	0.5	3.4	0.02	Minor (1,3)
(f)	16	0.8	4.9	0.09	Minor (1,2)
Apr V-31	46	0.6	2.7	0.04	Major (1,3)
(f)	40	0.2	5.8	0.10	Minor (1,2)

a. Carbonyl stretching band. Relative oxidation measured as volume percent dibutyl sebacate in 643 oil. Unused 643 oils fresh from supplier's 55-gallon drums generally have oxidation levels in the <0.010 to 0.030 percent range. Measurements made on samples after removal of volatiles.

b. Observed degradation is determined by relative changes in the infrared spectra of 0.1-mm films of the sample oils (after volatilization of halogenated hydrocarbons) over the 1250- to 670-cm⁻¹ region against the spectrum of a fresh 643 oil. Observed changes in the spectrum include:

- (1) Subtle changes in absorbance bands, and an increase in the overall absorbance from 1300 to 670 cm⁻¹, because of normal degradation through use (e.g., chain cleavage, dehydrogenation, oxidation, nitration).
- (2) Gross changes near 1700 cm⁻¹ and 1100 to 900 cm⁻¹ caused by radiolytic degradation, oxidation, and polymerization of the oil skeletal chain.
- (3) Increase in the 1020 cm⁻¹ absorbance resulting from the presence of siliceous matter (dissolved or suspended).
- (4) Anomalous bands attributed to impurities such as silicone oils.

c. Stored oil and carbon tetrachloride in sealed polyethylene bottles for 10 months, then resampled.

d. Stored 9 months.

e. Stored 6 months.

f. Stored 3 months.

APPENDIX 2

Characterization of Spent Lathe Coolant and Reclaimed Products

Description	Carbon Tetrachloride (vol %)	Oil (g/l)	Water (μ l/l)	Plutonium (mg/l)	Chlorine ($10^{-3} M$)	pH	Oxidation (%)	Degradation	Plutonium Corrosion (mg/dm ² · day)* After	
									1 Week	2 Weeks
Oil-CCl ₄	33.2	—	23	1.8	1.0	3.4	0.02	Minor	81	63
Oil Bottoms	0.7	—	42	—	2.3	2.4	0.03	Major	—	—
CCl ₄ #1	—	0.16	56	1.5×10^{-6}	1.3	8.2	—	—	91	64
Oil-CCl ₄	1.4	—	43	1.8	0.8	5.3	0.01	—	85	49
Oil Bottoms	3.0	—	34	—	1.0	2.9	<0.01	Minor	64	36
CCl ₄ #2	—	—	53	1.4×10^{-6}	<0.1	6.9	—	—	93	53
Oil-CCl ₄	—	—	—	3.3	—	—	—	—	88	50
Oil Bottoms	2.4	—	71	—	1.3	2.8	<0.01	Minor	59	42
CCl ₄ #3	—	0.31	58	1.0×10^{-6}	1.1	4.4	—	—	91	58
Oil-CCl ₄	21.3	—	35	2.5	2.0	3.1	<0.01	Trace	88	58
Oil Bottoms	4.6	—	35	—	0.9	3.0	<0.01	Minor	78	35
CCl ₄ #4	—	0.10	56	3.0×10^{-6}	0.5	3.1	—	—	82	45
Oil-CCl ₄	—	—	—	—	—	—	—	—	75	47
Oil Bottoms	0.7	—	40	—	1.8	2.7	0.02	Major	48	38
CCl ₄ #5	—	0.04	50	1.8×10^{-6}	0.6	5.0	—	—	97	59
Oil-CCl ₄	20.7	—	32	3.3	0.8	3.2	<0.01	None	79	51
Oil Bottoms	3.4	—	32	—	1.7	2.6	<0.01	Minor	—	—
CCl ₄ #6	—	—	53	1.3×10^{-6}	—	—	—	—	87	55
New Oil	< 0.1	—	43	—	<0.1	7.5	0.05	None	51	39
New Reagent } CCl ₄	—	<0.04	59	—	<0.1	3.5	—	—	85	55
Production } CCl ₄	—	—	—	—	—	—	—	—	69	59
Air	—	—	—	—	—	—	—	—	28	21

*Milligram per square decimeter per day.