SUPERCritical FLUID CARBON DIOXIDE 
CLEANING OF PLUTONIUM PARTS 

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ABSTRACT

Supercritical fluid carbon dioxide is under investigation in this work for use as a cleaning solvent for the final cleaning of plutonium parts. These parts must be free of organic residue to avoid corrosion in the stockpile. Initial studies on stainless steel and full-scale mock-up parts indicate that the oils of interest are easily and adequately cleaned from the metal surfaces with supercritical fluid carbon dioxide. Results from compatibility studies show that undesirable oxidation or other surface reactions are not occurring during exposure of plutonium to the supercritical fluid. Cleaning studies indicate that the oils of interest are removed from the plutonium surface under relatively mild conditions. These studies indicate that supercritical fluid carbon dioxide is a very promising cleaning medium for this application.

INTRODUCTION

Our aim in this work is to develop a cleaning process that can be used to clean plutonium parts. The plutonium parts are repeatedly exposed to various organic substances during the fabrication and assembly of weapons components. The plutonium is machined and requires organic based coolants, lubricants, and oils. These organic residues must be removed from the parts to avoid corrosion in the stockpile. In light of the President's recent initiative toward limiting production of new weapons and, consequently, the long-term storage of these, it has become essential that these parts are free from any organic residue.

Typically, these organic residues are removed in vapor degreasers using halogenated hydrocarbons like 1,1,1-trichloroethane and carbon tetrachloride. Large amounts of mixed waste are generated and a significant quantity of these volatile organic compounds are released to the atmosphere. With the current environmental issues and regulatory requirements, it has become prudent to avoid the use of halogenated hydrocarbons. Additionally, it is suspected that these solvents leave a residue on the cleaned parts that can lead to undesirable corrosion reactions.

An alternative cleaning medium is needed that is environmentally acceptable, nonhazardous, nontoxic, noncombustible, readily recyclable, low cost, not regulated, compatible, and effective. Supercritical Fluid Carbon Dioxide (SCF CO₂) is, in fact, a cleaning solvent that meets these criteria. Work on this project is focused on the evaluation of the compatibility and effectiveness of the SCF CO₂ cleaning process.
EXPERIMENTAL RESULTS

Preliminary tests

The preliminary work was accomplished by Motyl in the early 1980's. Stainless steel coupons were contaminated with Texaco Regal R&O 32 Oil (a commonly used machining oil) and cleaned in SCF CO₂ under conditions of pressure ranging from 1260 to 4000 psig, temperature ranging from 33 to 50°C, densities ranging from 0.65 to 0.92 g/cc, cleaning times of 10 to 30 minutes, and at different flowrates. Auger electron spectroscopy (AES) showed a measurable but acceptably small residue. It was found that this oil removal showed little pressure, temperature, density, or flowrate dependency. Further studies using steel wool to simulate plutonium machining turnings proved that the cleaning process was adequate; although, a strong density and flowrate dependency was seen for the removal of the same oil.

The studies continued using uranium. The uranium coupons were cleaned at 2029 psig and 34°C. The oil was removed easily and there were no observable changes in appearance after the cleaning process. AES suggested the possibility of CO₂ chemisorbed to the UOX surface.

A preliminary compatibility test was done on plutonium in a static test at 1500 psig and 50°C. AES of the plutonium surface after carbon dioxide cleaning showed no difference in the oxide layer before and after cleaning which suggests compatibility of plutonium in supercritical fluid carbon dioxide.

Subsequent tests

In recent subsequent studies full-scale mock-up parts were used to evaluate the cleaning of an appropriate shape. A rinse analysis was used to evaluate the cleaning efficacy of the process using hexane and gas chromatography. A cleaning criterion has been calculated and established at about 5 - 10 μg/cm². These stainless steel hemisphere were contaminated with the R&O oil and cleaned with SCF CO₂ varying the operating conditions of pressure, temperature, density, flow rate, and process times. In all cases the residue levels were far below the lowest required limit of 5 μg/cm². In fact, this oil was removed so easily, it was not possible to optimize on any process parameters.

Nye Watch Oil is an oil commonly used in the gauging and contouring process for the finished parts. It was anticipated that this oil might be slightly more difficult to remove owing to a polar ester component in the formulation of the oil. Removing this oil from the mock-up part did require densities above 0.71 g/cc (1400 psig and 35°C) as shown in Figure 4. This information provided the lower limits for operating parameters since it is reasonable to assume that this oil is a typical contaminating oil.
Cleaning studies were then undertaken to evaluate the process for removal of Nye Watch Oil. At this time an analytical method has not been approved for the plutonium area within which we are working. Therefore, the evaluation of oil removal was done by weight differential. While this method is adequate to determine cleanliness to the mg level, it is not sufficient to meet the µg requirements. Fourier Transform Infrared (FTIR) techniques are being developed at LANL for use as an analytical rinse method as well as a surface analysis method for determining cleanliness levels for plutonium and should be implemented in the near future. At present, however, mg level detection provides valuable cleaning information.

Figure 5 represents the results of the first plutonium cleaning tests. The tests were run at CO₂ densities ranging from 0.7 to 0.9 g/cc, pressures ranging from 1653 to 4069 psig, and the temperature was held at 40°C. In all but one case the oil put onto the coupon was completely removed by the SCF CO₂ process, within the limits of detection. Additionally, there has been no observable deleterious effects to the surfaces of these coupons. There was some indication in these tests that the plutonium coupons with observable oxide layers before contamination with oil and cleaning were consistently less clean after the SCF CO₂ process than freshly polished plutonium surfaces. Since, in actuality, it is oxidized surfaces that will be cleaned, this observation merits further investigation. However, it is also noted that even the oxidized surfaces yielded virtually completely cleaned surfaces after SCF CO₂ cleaning.

Plutonium studies

Having determined that the oils in question were easily removed from stainless steel and from the appropriate shapes, it followed that the focus should turn to plutonium. A lab-scale cleaning facility was built at Los Alamos National Laboratory (LANL) and plutonium coupon tests were initiated.

The compatibility of plutonium in supercritical fluid carbon dioxide remained questionable since the thermodynamics of the oxidation of plutonium in carbon dioxide indicate a favorable reaction. It is anticipated that the kinetics of the process are such that the reaction would not occur under normal operating conditions; however, the kinetics at supercritical conditions have not been evaluated. Although rate data are not available for oxidation of plutonium by carbon dioxide, kinetic experiments reported for the reaction of Pu-Zr alloys with CO₂ at elevated temperatures assist in predicting the kinetic behavior of Pu in SCF CO₂. This predicted kinetic behavior is consistent with results from recent compatibility tests. Freshly burnished gram-sized samples of delta-phase plutonium foil were exposed to high density (0.8 - 0.9 g/cc) flowing CO₂ at temperatures up to 100°C and pressures up to 4500 psig. After one-hour exposures, sample masses were unchanged and there were no observable changes of the surface.

Fig. 4: Dependence of oil removal on density of CO₂

A test was performed in which a hemisheef was fitted with small coupons on both the convex and concave surfaces. The part with the coupons was contaminated with Nye Watch Oil and cleaned in SCF CO₂. The coupons were then removed and evaluated for residue by X-ray Photoelectron Spectroscopy (XPS). Although all the coupons were more than adequately cleaned, it was discovered that the coupons residing at the pole of the hemishell had a substantially higher carbon layer than all the other coupons. This indicates that in some configurations the potential exists for nonuniform cleaning and this requires further investigation.

Figure 5: Removal of oil from Pu with SCF CO₂
CONCLUSIONS

The successful removal of contaminating oils from full-sized mock-up (stainless steel) parts and plutonium coupons in SCF CO₂ indicates a promising alternative cleaning technology for the final cleaning of machined plutonium parts. Observations such as the slightly less effective cleaning of oxide surfaces and the potential for nonuniform cleaning in certain configurations provide areas for further evaluation. However, all results thus far indicate that the SCF CO₂ cleaning process is an excellent method for this purpose.

This technology is particularly attractive for this application for many reasons including waste minimization and hazardous solvent elimination. The cleaning of plutonium parts is a unique application. Most cleaning applications do not involve cleaning plutonium or other reactive metals. However, this cleaning technology can be applied to cleaning complex geometries or in processes where conventional methods such as aqueous cleaning are not feasible.

REFERENCES


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SUPERCritical FLUID CARBON DIOXIDE CLeANING
OF PLUTONIUM PARTS

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TECHNOLOGY NEED: PURPOSE OF CLEANING

- EXPOSURE TO ORGANIC SUBSTANCES DURING FABRICATION
- AVOID CORROSION IN STOCKPILE
- PRESIDENT'S RECENT INITIATIVE REQUIRES LONG TERM STORAGE
TECHNOLOGY NEED: REPLACE CURRENT CLEANING PROCESS

- VAPOR DEGREASERS USING HALOGENATED HYDROCARBONS
- LARGE AMOUNTS OF MIXED WASTE ARE GENERATED
- AVOID USING HALOGENATED HYDROCARBONS
- THESE SOLVENTS CAN LEAVE RESIDUES
MISSION: FIND AN ALTERNATIVE CLEANING SOLVENT

ENVIRONMENTALLY ACCEPTABLE
NONHAZARDOUS
NONTOXIC
NONCOMBUSTIBLE
RECYCLABLE
LOW COST
NOT REGULATED
COMPATIBLE
EFFECTIVE
SUPERCRITICAL FLUID FUNDAMENTALS

- COMPRESSED GAS PHASE ABOVE CRITICAL TEMPERATURE

- LIQUEFACTION CAN OCCUR BELOW Tc

- ABOVE Tc NO LIQUEFACTION OCCURS

- \( C_p (\text{CO}_2) \): 31°C, 74 BAR
CONSTANT-DENSITY CURVES FOR CO₂ AS FUNCTION OF PRESSURE AND TEMPERATURE
SUPERCritical FLUID CO\textsubscript{2} AS A CLEANING SOLVENT

- LIQUID–LIKE DENSITIES AND LIQUID–LIKE SOLVENT PROPERTIES
- GOOD FOR NON–POLAR & SLIGHTLY POLAR COMPOUNDS
- GAS–LIKE CHARACTERISTICS
  IMPROVED MASS TRANSPORT OVER LIQUIDS
  NO SURFACE TENSION
SUPERCRITICAL FLUID CARBON DIOXIDE CLEANING
OF PLUTONIUM PARTS
WASTE MINIMIZATION

Organic residue + Hazardous Solvent \(\rightarrow\) Mixed Waste

Organic residue + Non-hazardous Solvent \(\rightarrow\) Residue
\(\rightarrow\) Non-hazardous Solvent
\(\rightarrow\) Organic residue waste
Schematic view of a closed-loop SCF cleaning system

- Glove Box
- Temperature
- Pressure
- Flow
- Heated Cleaning Chamber
- Preheater
- CO₂ Supply
- Pump
- Residue Collection Vessel
- Heated Expansion Valve
- CO₂ Collector
- Mechanical or Thermal Compression

The diagram illustrates the components and flow of a closed-loop supercritical fluid (SCF) cleaning system, including the glove box, pressure, flow, and temperature control, along with the CO₂ supply, pump, residue collection vessel, and CO₂ collector.
PRELIMINARY STUDY

- **SS COUPONS**
  -- $P = 1260 - 4000$ psig
  -- $T = 33^\circ - 50^\circ$ C
  -- $d = 0.65 - 0.92$ g/cc
  -- AES showed measurable but small residue
  -- Little $P, T, d$ dependence to remove oil

- **STEEL WOOL**
  -- Strong density & flowrate dependency
PRELIMINARY STUDY

- **URANIUM**
  -- P = 2029 psig
  -- T = 34° C
  -- No observable change in appearance
  -- AES suggested CO₂ chemisorbing to UO₂

- **PLUTONIUM (STATIC TEST)**
  -- P = 1500 psig
  -- T = 50° C
  -- AES showed no difference in oxide layer
  -- Suggested compatibility
SCF CLEANING OF MOCK (STAINLESS STEEL) PARTS

DEPENDENCE OF NYE WATCH OIL REMOVAL ON DENSITY OF CO₂

% Nye Watch oil removed

Density of carbon dioxide

0.59 0.67 0.71 0.73
SCF CO₂ AND PLUTONIUM COMPATIBILITY

FRESHLY BURNISHED PLUTONIUM COUPONS

3 cm² area

P = 3000 psig
P = 4500 psig

T = 35° - 40° C
T = 100° C

d = 0.8 - 0.9 g/cc
d = 0.75 g/cc

NO VISUAL CHANGES TO SURFACE
NO CHANGE IN MASS OF COUPONS
REMOVAL OF OIL FROM Pu WITH SCF CO2

CO2 Densities 0.7 to 0.9 g/cc
Contaminant: Nye Watch Oil

NORMALIZED Mg. OIL (6.18 = 1)

Run Time=30 min.  Flow=0.02 lpm
Temp.=40 C  Pressure=1653-4069 psig
CONCLUSIONS

- The contaminating oils are readily removed by SCF CO$_2$ from metal surfaces – including Pu
- Evaluate process for other potential residues
- Evaluate process on oxide surfaces
- Implement the improved analytical techniques to determine efficacy down to $\mu$g levels on Pu
- SCF CO$_2$ remains a promising substitute solvent for trichloroethane and carbon tetrachloride in the final cleaning process for plutonium parts.