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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 CO_2) is, in fact, a cleaning solvent that meets these criteria. Work on this project is focussed on the evaluation of the compatibility and effectiveness of the SCF CO_2 cleaning process.

BACKGROUND

A supercritical fluid is the compressed, dense gas phase above the critical temperature. Liquefaction of a gas can occur upon compression below the critical temperature but above the critical temperature the gas cannot liquefy regardless of the applied pressure and a single gas phase is maintained. The critical point for carbon dioxide is 31°C and 74 bar (1088 psi) which means that the supercritical fluid can be attained under relatively mild conditions.

The phase diagram of CO_2 (Figure 1) shows the supercritical region above 74 bar and the 32° isotherm. It can be seen that very liquid-like densities can be achieved and still remain in the gas phase.

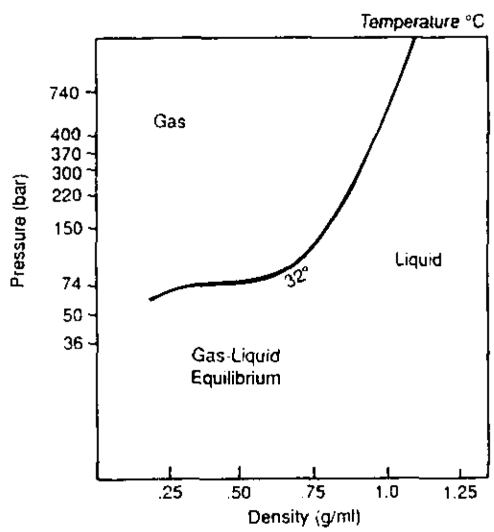

Fig. 1: Phase diagram of CO_2

The constant density curves for CO_2 (Figure 2) as a function of temperature and pressure illustrate that small changes in pressure can result in significant changes in the density of the CO_2. And, since the solubility of a substance in CO_2 is dependent upon density, one can fine-tune the system using pressure changes to obtain the required solubilities.

What makes SCF CO_2 such a promising cleaning medium is that these liquid-like densities can be achieved resulting in very liquid-like solvent properties. It is a very good solvent for non-polar to slightly polar organic substances. There is the added benefit of its gas-like characteristics which means improved mass transport characteristics such as improved diffusivities and lower viscosities than liquids.

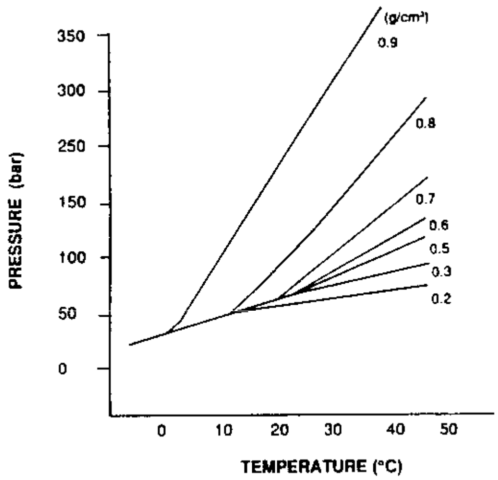

Fig. 2: Constant density curves for CO_2

The benefit of no surface tension is especially useful when cleaning complex geometries. Since it acts like a gas, it expands to fill the entire volume of a chamber, thus exposing all of the surface area of the complex geometry to the cleaning medium.

A SCF CO_2 cleaning process is especially attractive with respect to waste minimization. Typically, the organic residue is removed with a hazardous solvent. Although most of the solvent escapes to the atmosphere, a significant quantity contributes to the overall volume of waste, forming a mixed waste. A mixed waste is one containing both a radioactive component and a hazardous one, and the disposition of this waste is difficult. The proposed plan to use a nonhazardous solvent to remove the residue circumvents the formation of a mixed waste. The supercritical fluid can be expanded to the gas phase and recycled leaving only the organic residue and avoids the addition of the solvent to the waste volume.

The schematic given in Figure 3 depicts a simplistic version of the proposed system. The CO_2 is pumped, compressed and sent through the cleaning chamber which resides in a glovebox. The glovebox is necessary, of course, when working with plutonium. It then goes through an expansion process where the oil is dropped out and the gas is recycled. This may be more energy intensive than using a low boiling solvent in a vapor degreaser, but the cost difference should be negligible outside the capital expense of the initial system.

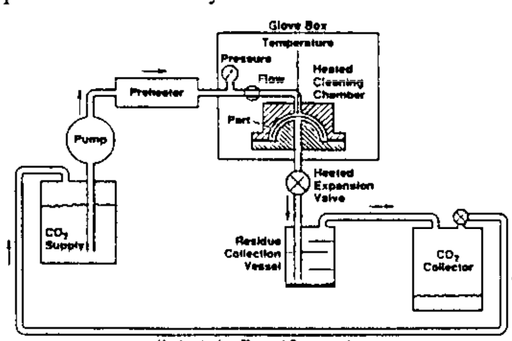

Fig. 3: Schematic of SCF cleaning system

EXPERIMENTAL RESULTS

Preliminary tests

The preliminary work was accomplished by Motyl[1] 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 CO_2 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 CO_2 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[2] 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 $\mu g/cm^2$. These stainless steel hemishells were contaminated with the R&O oil and cleaned with SCF CO_2 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 $\mu g/cm^2$. 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.

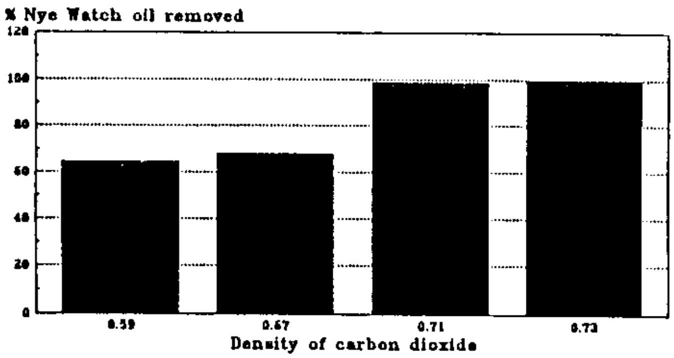

Fig. 4: Dependence of oil removal on density of CO_2

A test was performed in which a hemishell 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 CO_2. 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.

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 CO_2 at elevated temperatures[3,4] assist in predicting the kinetic behavior of Pu in SCF CO_2. 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 CO_2 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.

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 CO_2 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 CO_2 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 CO_2 process than freshly polished plutonium surfaces. Since, in actuality, it is oxided surfaces that will be cleaned, this observation merits further investigation. However, it is also noted that even the oxided surfaces yielded virtually completely cleaned surfaces after SCF CO_2 cleaning.

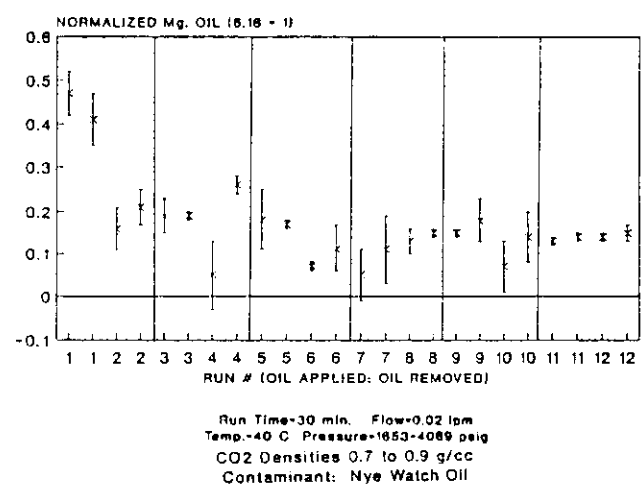

Fig. 5: Removal of oil from Pu with SCF CO_2

CONCLUSIONS

The successful removal of contaminating oils from full-sized mock-up (stainless steel) parts and plutonium coupons in SCF CO_2 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 CO_2 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

[1] K. M. Motyl, USDOE Report, RFP-4150, Rockwell International, Rocky Flats Plant, Golden, CO, 1988.

[2] S. J. Hale, D. R. Horrell, G. S. Fenner, J. M. Haschke, J. P. Baiardo, RFP Report PPC-91-017, EG&G Rocky Flats, Inc., Golden CO, 1991.

[3] J. T. Waber, "Corrosion and Oxidation" in Plutonium Handbook, O. J. Wick, ed., Vol. 2, Chapter 6, American Nuclear Society, LaGrange Park, IL, 1980.

[4] J. M. Haschke and S. J. Hale, LANL Formal Report, in publication, Los Alamos National Laboratory, Los Alamos, NM, 1991.

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on Solvent Substitution
Phoenix, Arizona

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SSUB01

TECHNOLOGY NEED: PURPOSE OF CLEANING

- EXPOSURE TO ORGANIC SUBSTANCES DURING FABRICATION
- AVOID CORROSION IN STOCKPILE
- PRESIDENT'S RECENT INITIATIVE REQUIRES LONG TERM STORAGE

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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

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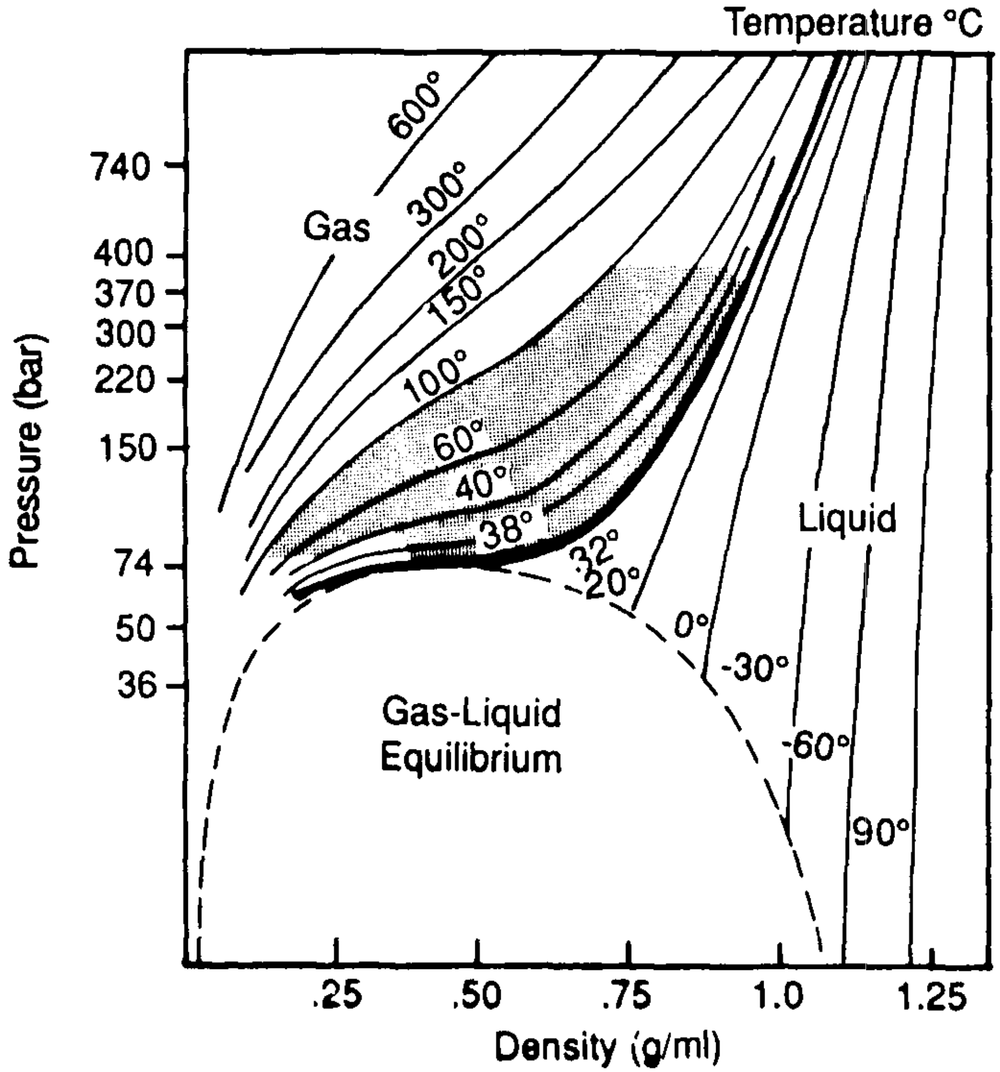
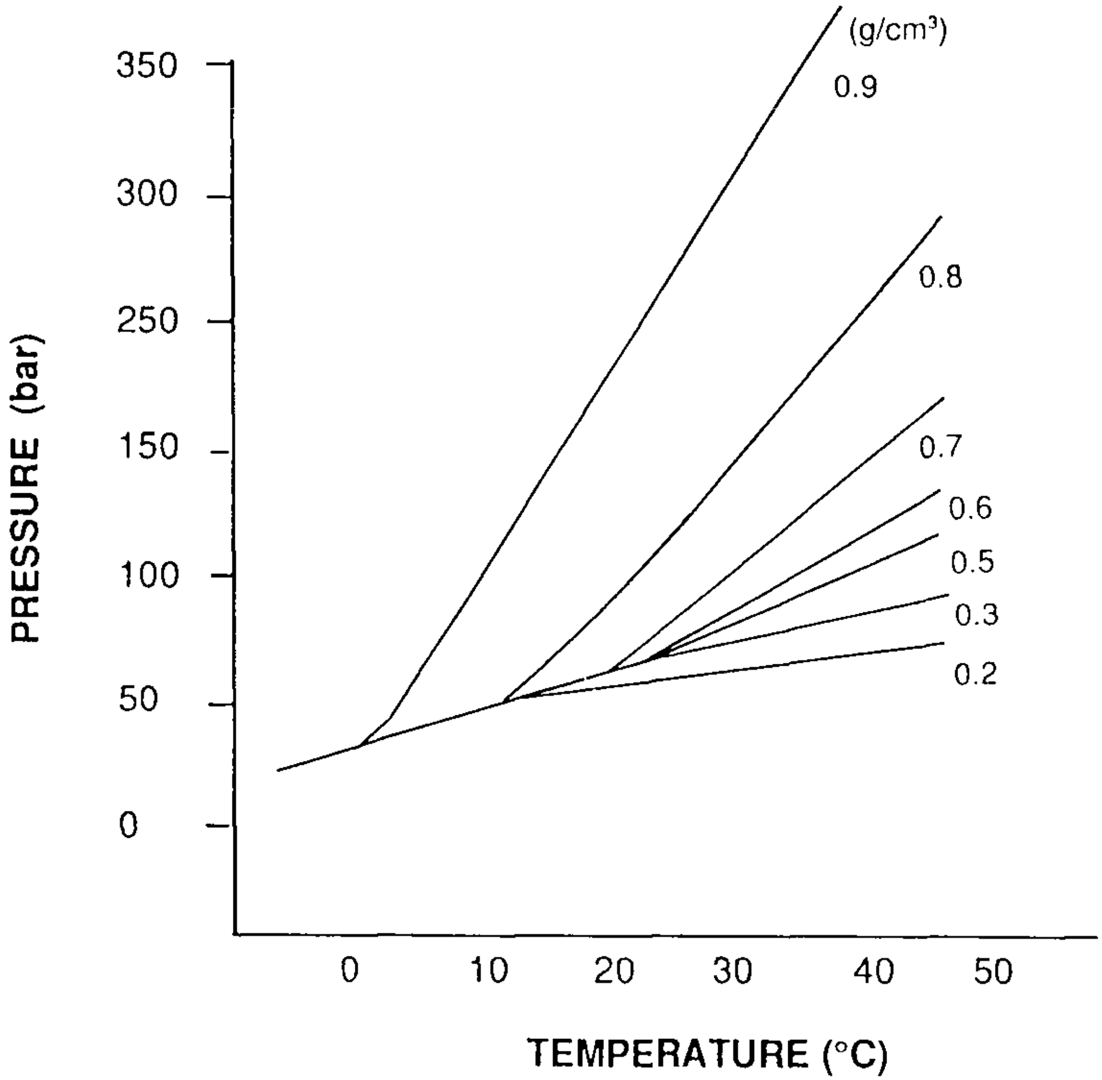
SUPERCRITICAL FLUID FUNDAMENTALS

- COMPRESSED GAS PHASE ABOVE CRITICAL TEMPERATURE
- LIQUEFACTION CAN OCCUR BELOW Tc
- ABOVE Tc NO LIQUEFACTION OCCURS
- Cp (CO_2): 31°C, 74 BAR

PHASE DIAGRAM OF CO_2



CONSTANT-DENSITY CURVES FOR CO_2 AS FUNCTION OF PRESSURE AND TEMPERATURE



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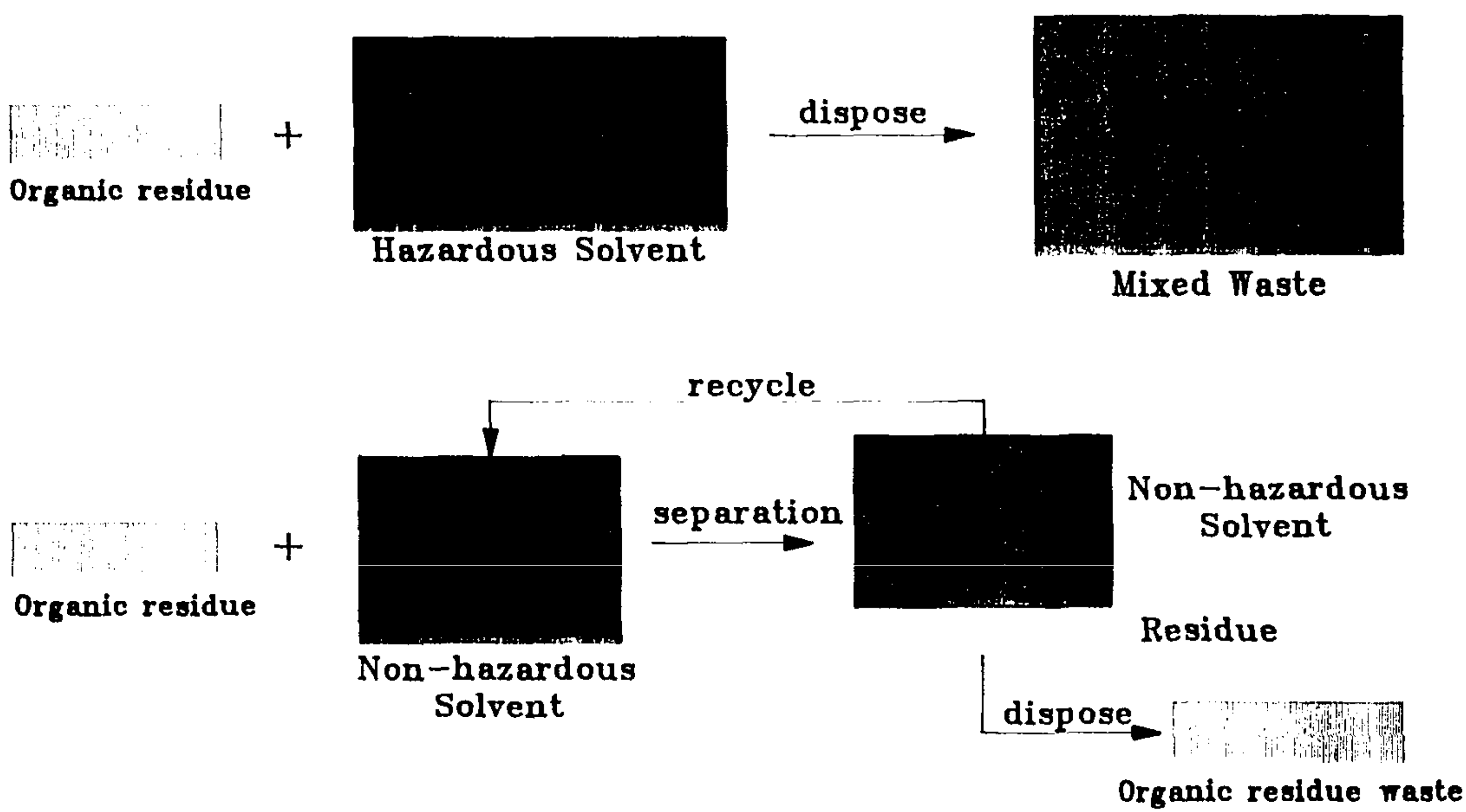
SUPERCRITICAL FLUID CO_2 AS A CLEANING SOLVENT

- 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



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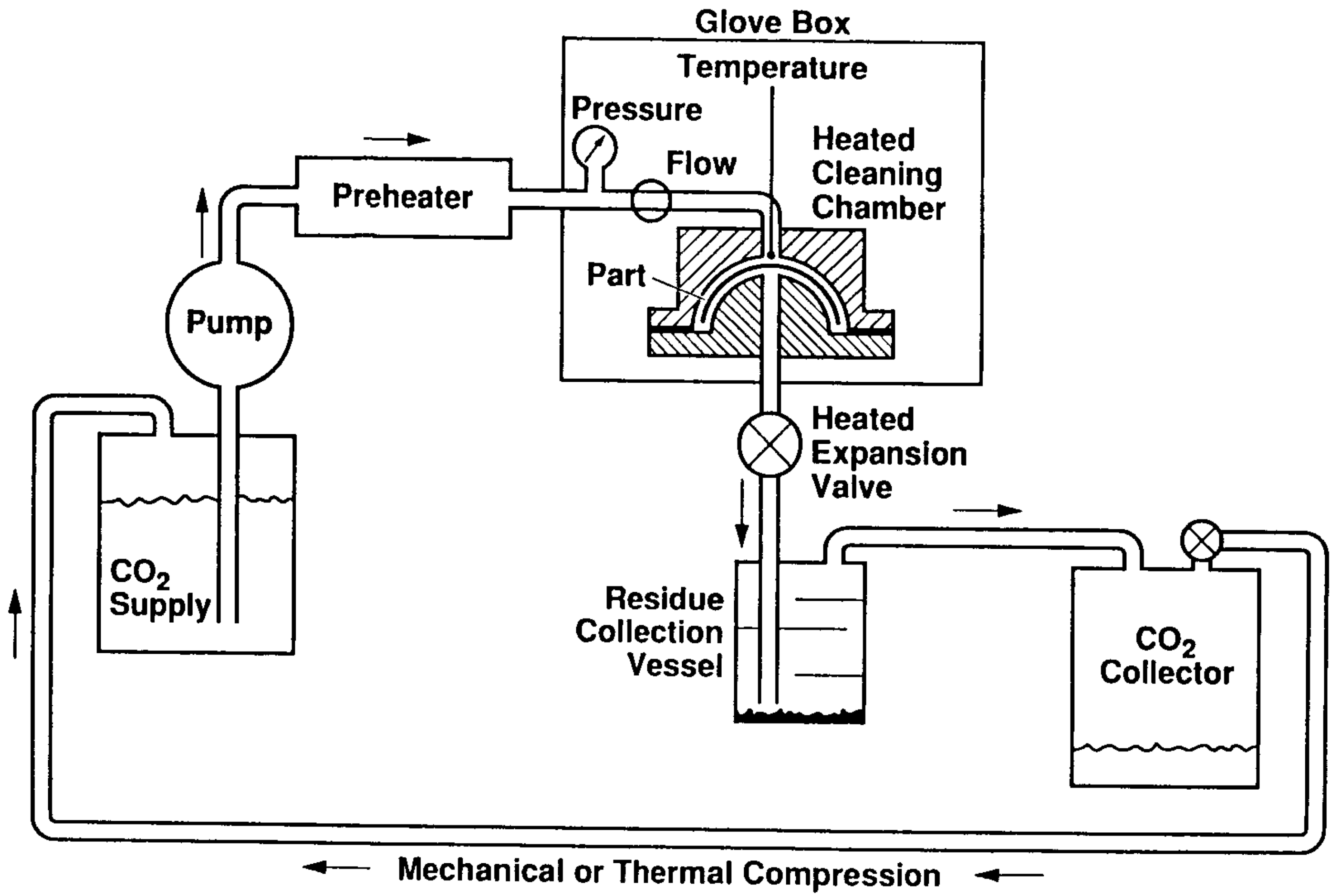
Schematic view of a closed-loop SCF cleaning system



PRELIMINARY STUDY

- SS COUPONS
  --P = 1260 – 4000 psig
  --T = 33° – 50° 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

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PRELIMINARY STUDY

- URANIUM
  --P = 2029 psig
  --T = 34° C
  --No observable change in appearance
  --AES suggested CO_2 chemisorbing to UOx

- PLUTONIUM (STATIC TEST)
  --P = 1500 psig
  --T = 50° C
  --AES showed no difference in oxide layer
  --Suggested compatibility

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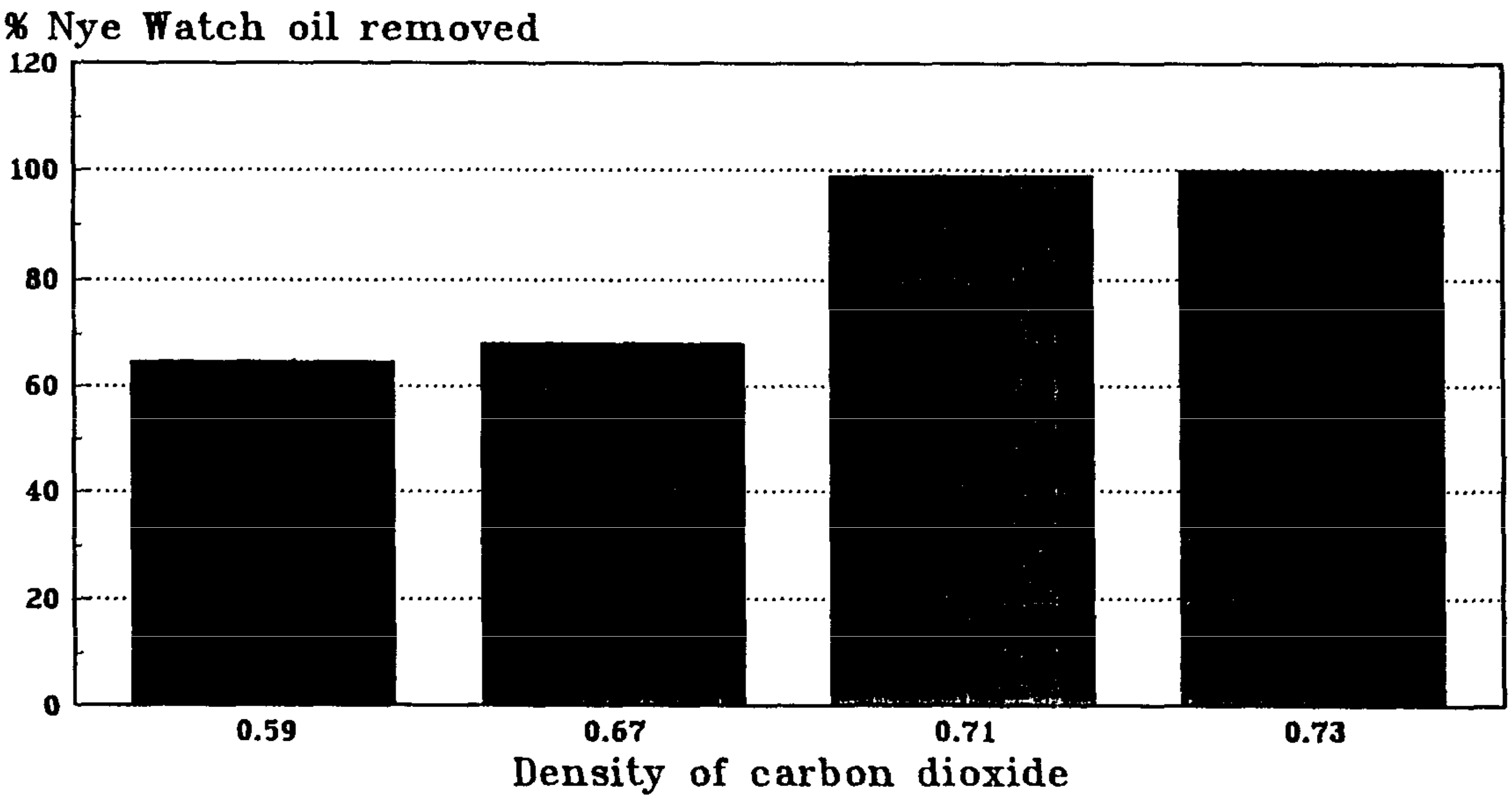
SCF CLEANING OF MOCK (STAINLESS STEEL) PARTS

DEPENDENCE OF NYE WATCH OIL REMOVAL ON DENSITY OF CO_2



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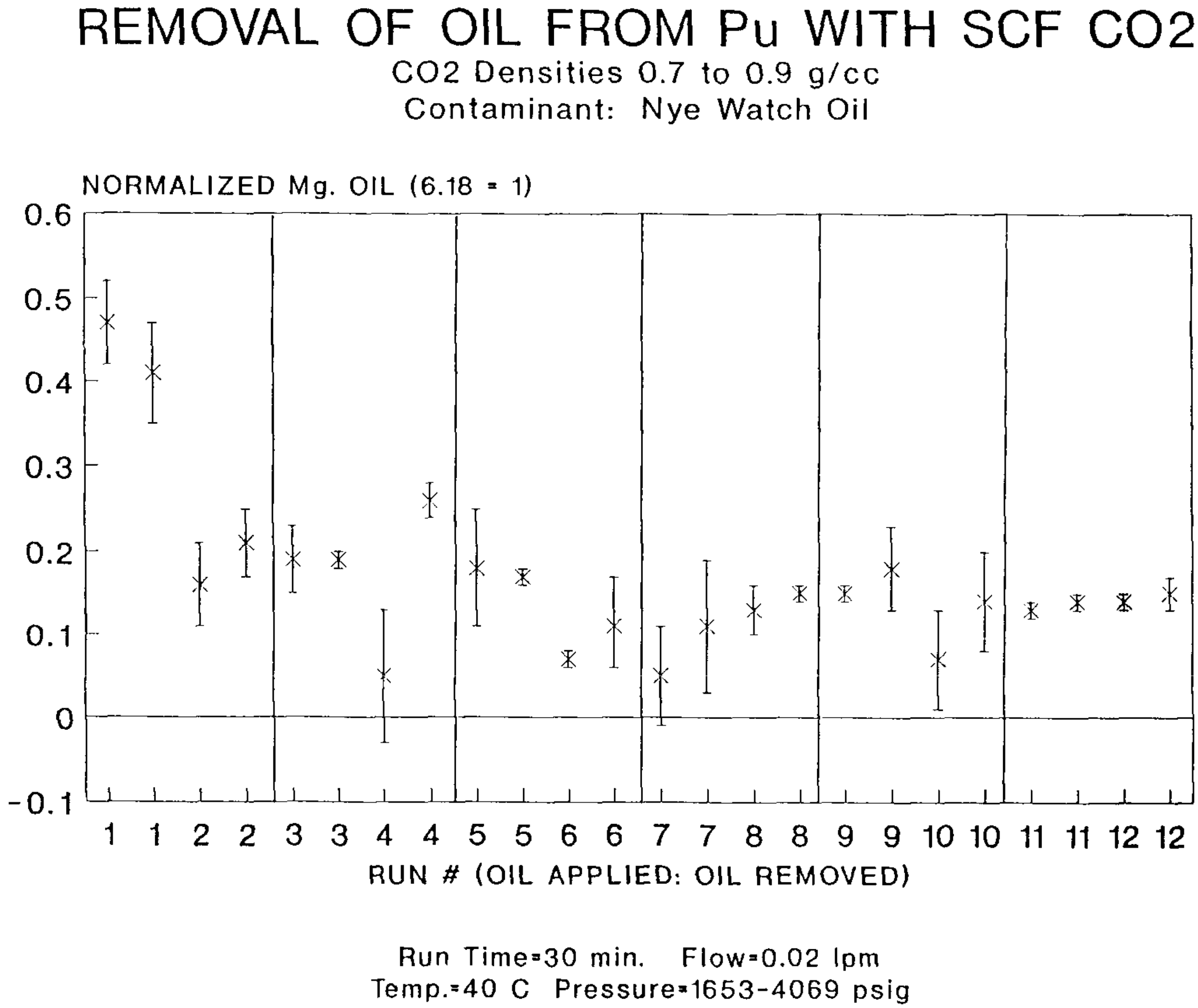
SCF CO_2 AND PLUTONIUM COMPATIBILITY

FRESHLY BURNISHED PLUTONIUM COUPONS
3 cm^2 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)
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
1 1 2 2 3 3 4 4 5 5 6 6 7 7 8 8 9 9 10 10 11 11 12 12
RUN # (OIL APPLIED: OIL REMOVED)
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 μg levels on Pu
- SCF CO_2 remains a promising substitute solvent for trichloroethane and carbon tetrachloride in the final cleaning process for plutonium parts.