

Title: SUPERCRITICAL FLUID CARBON DIOXIDE CLEANING OF PLUTONIUM PARTS

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# **SUPERCRITICAL FLUID CARBON DIOXIDE CLEANING OF PLUTONIUM PARTS**

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## **ABSTRACT**

Supercritical fluid (SCF) carbon dioxide (CO<sub>2</sub>) is being evaluated for use as a cleaning solvent to replace 1,1,1-trichloroethane for the final cleaning of plutonium (Pu) parts. These parts must be free of organic residue to avoid corrosion in the stockpile. Thermodynamic and kinetic data for selected reactions of Pu metal are evaluated as a basis for assessing the risk of a violent exothermic reaction during the use of SCF CO<sub>2</sub> on Pu. The need for considering kinetic behavior of a reaction in assessing its thermal risk is demonstrated. Weight difference data and results of xray photoelectron spectroscopy to evaluate the surface after exposure to the supercritical fluid show that SCF CO<sub>2</sub> is an effective and compatible cleaning solvent.

## **1.0 INTRODUCTION**

The objective of this work is to develop a cleaning process which can be used to clean Pu parts. The Pu parts are repeatedly exposed to various organic substances during the fabrication and assembly of weapon components. These organic residues must be removed from the parts to avoid corrosion in the stockpile. Typically, these organic residues are removed in vapor degreasers using halogenated hydrocarbons such as 1,1,1-trichloroethane and carbon tetrachloride. With the current environmental issues and regulatory requirements, it has become necessary to avoid the use of these solvents.

An alternative cleaning medium is needed that is environmentally acceptable, non-hazardous, non-toxic, non-combustible, readily recyclable, low cost, compatible, and effective. Supercritical fluid carbon dioxide is a solvent which can meet these criteria. This work is focused on the evaluation of the compatibility and effectiveness of the SCF CO<sub>2</sub> cleaning process.

## **2.0 FUNDAMENTALS OF SUPERCRITICAL FLUID CARBON DIOXIDE**

A supercritical fluid is the compressed, dense gas phase above the critical temperature. Liquefaction of the gas cannot occur above the critical temperature regardless of the external pressure applied so a single gas phase is maintained. For CO<sub>2</sub>, the critical point is at 31°C and 74 bar (1088 psia). Figure 1 is the phase diagram for CO<sub>2</sub>, which

shows that liquid-like densities can be achieved and still remain in the gas phase. What makes CO<sub>2</sub> such a promising cleaning solvent is the fact that liquid-like densities can provide liquid-like solvent properties. There is the added benefit of the gas-like characteristics providing improved mass transport properties. Carbon dioxide is a good solvent for non-polar to slightly polar organic substances.

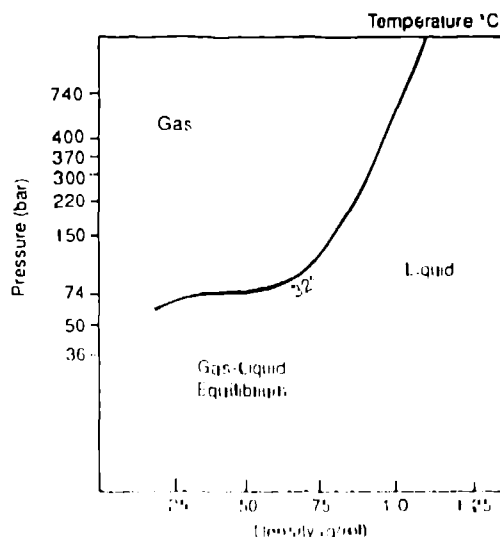


Fig. 1 Phase Diagram of CO<sub>2</sub>

### 3.0 COMPATIBILITY

The thermodynamics of the oxidation of plutonium in carbon dioxide suggest a compatibility issue. The suggestion is that since the oxidation of Pu metal is exothermic, the potential exists for a significantly large thermal excursion, and thus, poses a thermal hazard [1]. The thermodynamics do show an exothermic and potentially spontaneous reaction with a standard heat of reaction for the oxidation of Pu in CO<sub>2</sub> of -158.3 kcal/mol and a Gibbs Free energy of -144.2 kcal/mol. The question is raised regarding the thermodynamics of the reaction at supercritical conditions and any resulting increased hazard. At constant temperature, the free energy for a reaction at non-standard conditions is defined by the standard state free energy,  $\Delta G^\circ$ , and by the equilibrium constant,  $K$ , as follows:  $\Delta G = \Delta G^\circ + RT \ln K$ . Since  $K = 1/P(\text{CO}_2)$  and  $\Delta G^\circ$  is constant at -144.2 kcal/mol over a limited temperature range, the  $\Delta G$  derived at the critical point ( $T_c = 31.2^\circ\text{C}$ ,  $P_c = 72.9 \text{ atm}$ ) is -146.8 kcal/mol. Using Gibbs equation,  $\Delta H = \Delta G + T\Delta S$ , the heat of reaction at supercritical conditions can be calculated. Calculation of the enthalpy change at a non-standard pressure depends on the availability of entropy data at the condition of interest. The entropies of solids are insensitive to pressure change over the range of interest. However, the entropy of CO<sub>2</sub> is decreased by increasing the pressure and changes from 51.1 cal/K mol at one atm to 34.7 cal/K mol at 72.9 atm [4]. Consequently, the

TAS term is -10.4 kcal/mol and  $\Delta H$  is -156.9 kcal/mol at the critical pressure. Since the operating conditions for SCF  $\text{CO}_2$  are expected to be near 40°C and 200 atm [3], consideration should be given to the thermodynamic behavior at substantially higher pressures. At these conditions,  $\Delta G$  is -147.6 kcal/mole and  $S$  for  $\text{CO}_2$  is 34.8 cal/K mol. The resulting  $\Delta H$  value is -157.2 kcal/mol. The heat produced by the reaction at the critical point and at operating conditions is slightly less than at standard conditions; therefore, the thermal hazard is not increased.

The fact that the oxidation of Pu in  $\text{CO}_2$  is a thermodynamically favorable reaction does not assess the risk associated with the reaction. The rate of the reaction is required for a valid assessment. A hazardous situation occurs only when the rate of reaction is such that unacceptable temperature excursions are encountered. Previous studies have shown that the rate of oxidation of Pu in  $\text{CO}_2$  at temperatures in which the cleaning system will operate are very slow and negate the possibility of a thermal excursion. There is no kinetic data for the oxidation of Pu by  $\text{CO}_2$  at supercritical conditions. The expectation is that the kinetics will be similar at supercritical conditions to the known kinetics at subcritical conditions. This is consistent with results of studies performed by the authors in which freshly burnished Pu coupons were exposed to high density  $\text{CO}_2$  (0.8 - 0.9 g/cc) at 3000 - 4500 psi and temperatures from 40° to 100° C for one hour. There was no detectable oxidation, no visible change to the surface, and no mass change.

#### **4.0 CLEANING STUDIES**

Experiments were performed in which Pu coupons were freshly burnished and contaminated with a known quantity of Nye watch oil. The coupons were then placed in the cleaning apparatus and exposed to flowing  $\text{CO}_2$  at densities ranging from 0.7 to 0.9 g/cc, pressures ranging from 1653 to 4069 psi, and the temperature at 40°C. A sampling of these results is given in Figure 2. By weight difference, all but one test showed that the oil put onto the coupon was removed by the SCF  $\text{CO}_2$  process. Although weight difference only provides information to 0.1 milligram levels, this data was adequate for illustrating the cleaning potential. In Figure 2 each pair of run numbers indicates the amount of oil applied and the amount of oil removed. Run #1 indicated that more oil was removed than was applied. This run raised the question of the possibility of removing metal as well. The supercritical fluid would not solubilize the Pu, but there could be a question about the interaction of water,  $\text{CO}_2$ , and Pu. Therefore, a test was performed with 0.023  $\mu$  of water added to the supercritical fluid while exposing the fluid to a Pu coupon. After static exposure for an hour at 40°C and 3000 psi  $\text{CO}_2$ , the coupon mass increased by 0.0001  $\mu$ . This test indicated that there is very little interaction of the Pu with water at these conditions.

#### **5.0 SURFACE STUDIES**

Surface evaluations were performed with X-ray Photoelectron Spectroscopy (XPS). Two plutonium coupons were treated identically by scraping the surface to expose

clean metal and then air oxidized for 15 minutes. One coupon was immediately evaluated by XPS for a reference while the other was cleaned in CO<sub>2</sub> and then

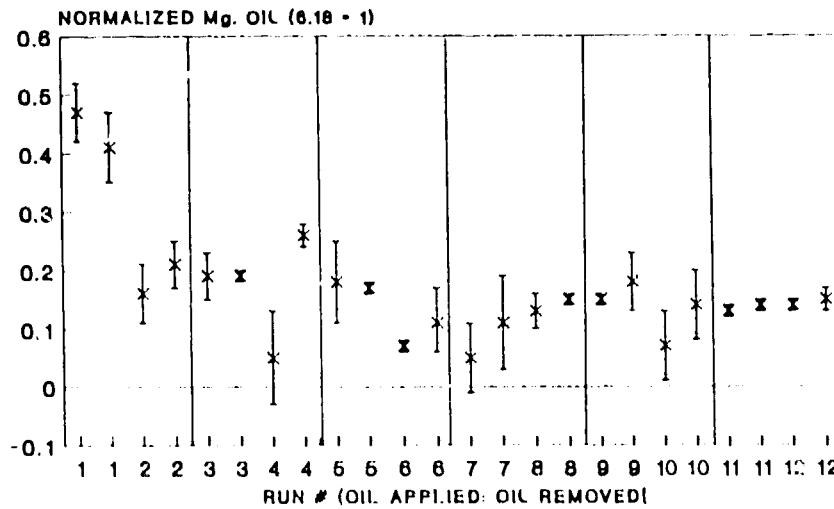


Fig. 2 Removal of Oil from Pu with SCF CO<sub>2</sub>

evaluated by XPS. Figure 3 is a spectrum showing that of the cleaned coupon (lower, dotted line) compared to the uncleaned coupons (upper, solid line). The cleaned coupon contains no silicon peak and the adventitious carbon seen at 286 eV is greatly reduced.

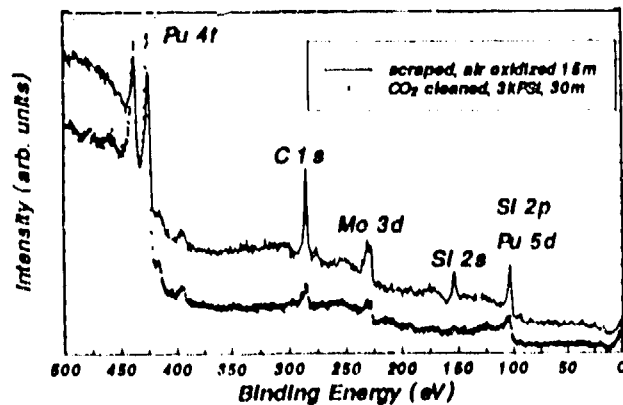


Fig. 3 XPS of Pu Surface

Figure 4 is an expanded view of the adventitious carbon envelope illustrating the marked decrease in the adventitious hydrocarbon. The carbon area just above 289 eV is attributed to carbon dioxide and derivative compounds. The adventitious carbon

peak at 286 eV is commonly a stable peak which is frequently used as a reference peak in XPS. Often this carbon must be sputtered off to remove it from the XPS spectrum. The reduction of adventitious carbon is a preliminary indication that the removal of simple hydrocarbon from plutonium surfaces is easily accomplished in supercritical fluid carbon dioxide.

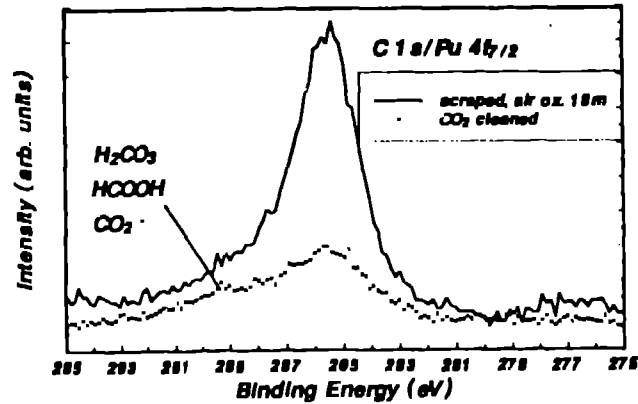


Fig. 4 XPS of Pu Surface: Expanded Carbon Envelope

Figure 5 is an expanded view of the oxygen envelope from 528 to 538 eV. The uncleaned coupon exhibits a significant quantity of hydrated hydroxide species. The cleaned coupon shows that most of the hydroxyl species are removed. This result assists in the explanation of the unexpected small interactions with water in previous tests in which water was intentionally added to the  $\text{CO}_2$  while cleaning.

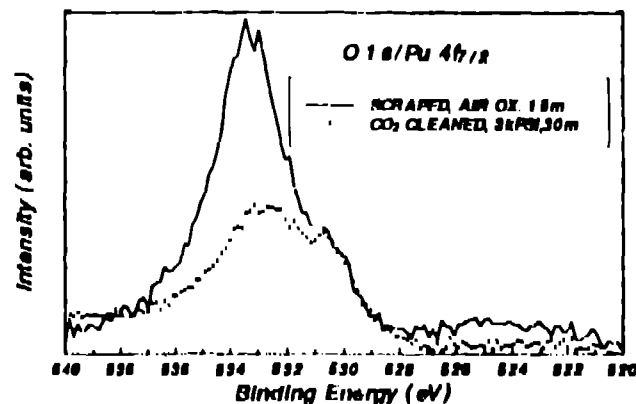


Fig. 5 XPS of Pu Surface: Expanded Oxygen Envelope

Figure 6 shows that the overlayer matrix is greatly reduced in the cleaned coupon indicating a marked decrease in the adsorbed species and general surface cleaning.

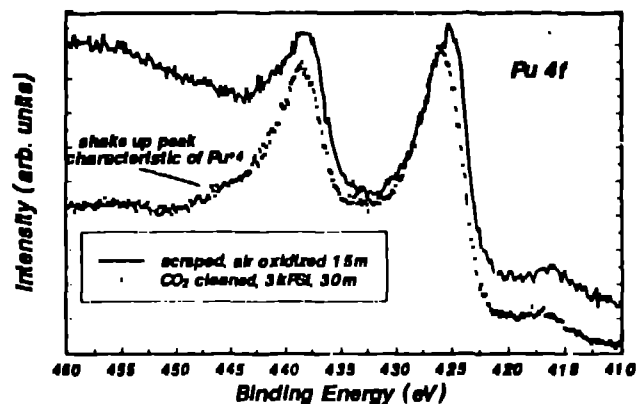


Fig. 6 XPS of Pu Surface

## 6.0 SUMMARY

Although the thermodynamics of the oxidation of plutonium in supercritical fluid carbon dioxide indicates an exothermic and spontaneous reaction, the kinetics are so slow that the reaction does not occur within the exposure times. Tests using weight difference and visual observation as well as XPS data confirm that plutonium is compatible with the supercritical fluid carbon dioxide. The XPS data also provide a preliminary indication that the removal of hydrocarbon from the plutonium should not be difficult. All indications are that the supercritical fluid carbon dioxide is an effective cleaning solvent for plutonium surfaces.

## REFERENCES

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2. Thermodynamic Functions of Gases, Vol 1, Butterworth, London, 1956.
3. K. M. Motyl, USDOE Report REP 4150, Rockwell International, Rocky Flats Plant, Golden, CO, 1988

NUCLEAR MATERIALS TECHNOLOGY DIVISION

SUPERCRITICAL FLUID CARBON DIOXIDE  
CLEANING OF PLUTONIUM

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2ND INTERNATIONAL CONGRESS  
ENVIRONMENTALLY CONSCIOUS MANUFACTURING  
SEPTEMBER, 1993

LOS ALAMOS NATIONAL LABORATORY



OBJECTIVE

DEVELOP A CLEANING PROCESS TO CLEAN PLUTONIUM PARTS

AVOID THE USE OF HALOGENATED HYDROCARBONS

FIND A SOLVENT THAT IS

ENVIRONMENTALLY ACCEPTABLE

NON-HAZARDOUS

NON-TOXIC

NON-COMBUSTIBLE

READILY AVAILABLE

RECYCLABLE

LOW COST

NOT REGULATED

COMPATIBLE

EFFECTIVE

PURPOSE FOR CLEANING

EXPOSURE TO ORGANIC SUBSTANCES DURING FABRICATION

CLEANLINESS CRITERION = 5 - 10  $\mu\text{g}/\text{cm}^2$

AVOID CORROSION IN STOCKPILE

SUPERCRITICAL FLUID FUNDAMENTALS

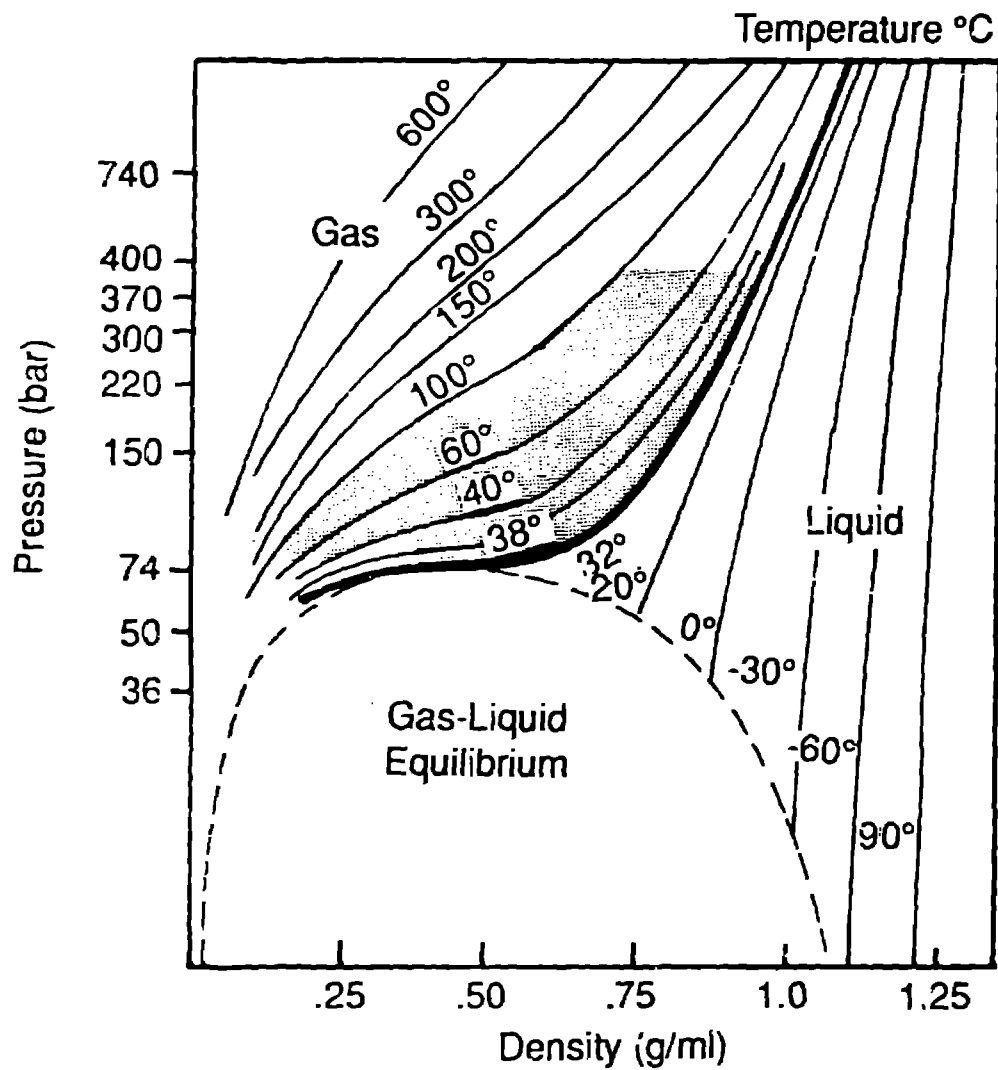
LIQUEFACTION OCCURS WHEN A GAS IS SUFFICIENTLY COMPRESSED BELOW THE  $T_c$

ABOVE  $T_c$  LIQUEFACTION DOES NOT OCCUR

SUPERCRITICAL FLUID IS THE COMPRESSED GAS PHASE ABOVE THE  $T_c$

CRITICAL POINT CARBON DIOXIDE: 31 C, 74 BAR

### PHASE DIAGRAM OF CARBON DIOXIDE



SUPERCRITICAL FLUID CO<sub>2</sub> AS A CLEANING SOLVENT  
(GENERAL)

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

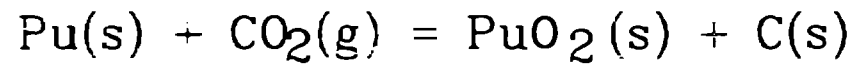
SUPERCRITICAL FLUID CO<sub>2</sub> AS A CLEANING SOLVENT  
(SPECIFICALLY FOR CLEANING PLUTONIUM PARTS)

GOOD SOLVENT FOR CONTAMINANTS OF INTEREST

LEAVES NO UNDESIRABLE RESIDUE

GAS PHASE SEPARATION OF SOLVENT MINIMIZES MIXED WASTE  
GENERATION SIGNIFICANTLY

THERMODYNAMICS



$$\Delta H_{298}^{\circ} = -158.3 \text{ kcal/mole}$$

$$\Delta G_{298}^{\circ} = -144.2 \text{ kcal/mole}$$

OPERATING CONDITIONS (40 C, 200 ATM)

$$\Delta H_{313} = -157.2 \text{ kcal/mole}$$

$$\Delta G_{313} = -147.6 \text{ kcal/mole}$$

KINETICS AND THERMODYNAMICS

	$\Delta H^{\circ}_{298}$ kcal/mole	$\Delta G^{\circ}_{298}$ kcal/mole
$\text{Pu(s)} - \text{O}_2(\text{g}) = \text{PuO}_2(\text{s})$	-252.4	-238.5
$\text{Pu(s)} - \text{H}_2(\text{g}) = \text{PuH}_2(\text{s})$	-39.2	-31.1

ESTIMATED RATE OF OXIDATION AT 0.67 ATM, 25 C =  
30 nmol O<sub>2</sub> /cm<sup>2</sup> hr

KINETIC RESULTS FOR HYDRIDING AT 1 ATM, 25 C =  
60 mmol H<sub>2</sub> /cm<sup>2</sup> hr



SUPERCRITICAL FLUID CARBON DIOXIDE AND PLUTONIUM  
COMPATIBILITY

FRESHLY BURNISHED PLUTONIUM COUPONS

3 cm<sup>2</sup> area

P = 3000 psig

T = 35 - 40 C

d = 0.8 - 0.9 g/cc

P = 4500 psig

T = 100 C

d = 0.75 g/cc

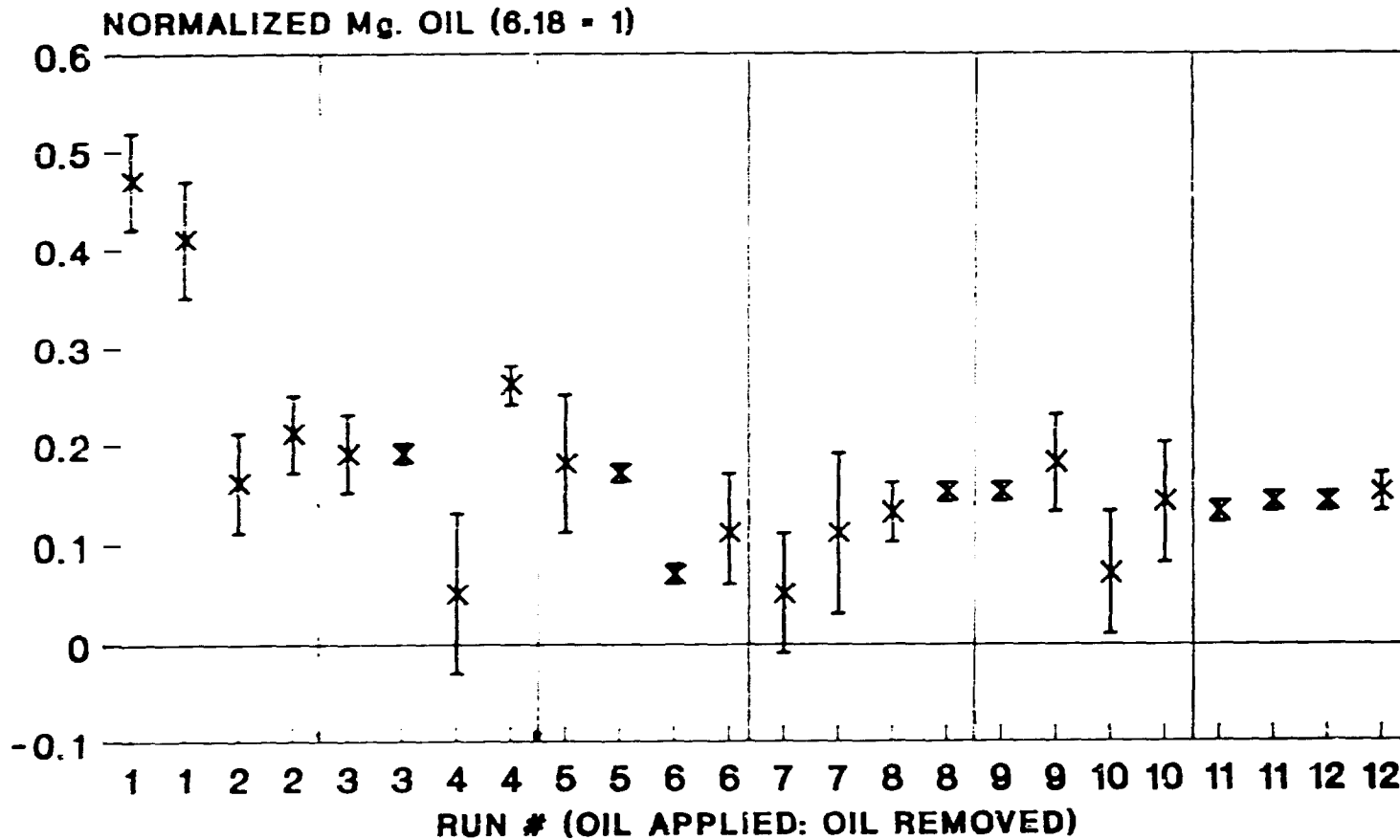
NO VISUAL CHANGES TO SURFACE

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



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

WATER TEST

- TEST CONDITIONS:  
0.023 g H<sub>2</sub>O; 1 HR; STATIC; 40 C; 3000 PSI
- OBSERVATIONS:  
COUPON TURNED BLUE & GAINED 0.0004 g
- CONCLUSIONS:  
NO LOSS OF METAL  
VERY LITTLE WATER INTERACTED

SUPERCRITICAL FLUID CARBON DIOXIDE CLEANING HAS BEEN SHOWN TO BE EFFECTIVE AND WILL BE IMPLEMENTED TO REPLACE 1,1,1-TRICHLOROETHANE FOR CLEANING PLUTONIUM PARTS.

THIS CLEANING PROCESS COULD BE USED FOR OTHER REACTIVE METALS OR ITEMS WITH COMPLEX GEOMETRIES.

CURRENT DIRECTION

1. FULL-SCALE CLEANING FACILITY
2. MIXED WASTE REMEDIATION