

**SUPERCRITICAL-FLUID CARBON DIOXIDE (SCCO₂)
CLEANING OF NUCLEAR WEAPON COMPONENTS**

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ABSTRACT

Supercritical fluid carbon dioxide (SCCO₂) has been evaluated as a cleaning solvent for the cleaning of plutonium (Pu) metal parts. The results of the evaluation show that SCCO₂ is an effective alternative to halogenated solvents that are conventionally used for removing organic and inorganic contaminants from the surface of these parts. The cleaning process was demonstrated at the laboratory scale for steel and uranium substrates and has been found to be compatible with Pu.^{1,2,3} The efficacy of this cleaning method is found to be dependent on process conditions of pressure, temperature, fluid-flow rate, as well as cleaning time. Process parameters of P > 2500 psi, T > 40 °C, and moderate fluid flow rates, produced good cleaning results in less than 10 minutes using a simple flow-through process configuration. Within the parameter range studied, cleaning efficiency generally improved with increasing process pressure and flow rate. SCCO₂ cleaning is suitable for a variety of component cleaning tasks and is adaptable to precision cleaning requirements. The SCCO₂ cleaning process is currently being developed for deployment for weapons production at LANL.

KEYWORDS: plutonium, cleaning, de-greasing, supercritical fluid, carbon dioxide

INTRODUCTION

Plutonium metal, during the process of weapon component fabrication, undergoes various rolling, forming, and machining operations. To reduce surface deterioration during individual processing steps, the metal is protected by the application of various organic-based oils, used as lubricants and coolants. While these oils facilitate intermediate forming operations, the residual organic films they leave behind can interfere with subsequent processing and treatment operations and must be removed. In the past, the residual oils were removed by cleaning with halogenated hydrocarbon solvents such as 1,1,1-trichloroethane (TCA), which is no longer commercially available, and carbon tetrachloride (CCl₄), to remove the surface organic contaminants. Such

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halogenated hydrocarbons are heavily regulated due to environmental safety and occupational exposure concerns. While these types of solvents produce acceptable results, their use is by no means without complication. Improper or inadequate cleaning procedures can result in undesirable surface residues (e.g., the formation of halide compounds). Also, carbon- and halogen-based residues are quite often associated with stains and surface blemishes on component parts, and can significantly affect corrosion rates. Finally, while halogenated hydrocarbons are generally quite inert, incidents of vigorous chemical reactions resulting from their contact with plutonium and other reactive metals have been documented.⁴ A reliable and safe alternative to these conventional solvents is clearly desirable and perhaps necessary in the case of a reactive metal such as plutonium.

As an alternative to the use of conventional solvents, SCCO_2 is gaining wide popularity for large-scale precision cleaning and degreasing applications. Like halogenated hydrocarbon solvents, most organic compounds have very good solubility in supercritical CO_2 , but unlike halogenated solvents, CO_2 is an inert, non-toxic, and environmentally benign.

SUPERCritical FLUID CO_2

The temperature at which the vapor pressure above a pure liquid reaches one atmosphere is known as the normal boiling point. For water, the normal boiling point at one atmosphere is 100°C . Within an *open* container, the temperature of liquid water cannot be raised above 100°C since this would cause the vapor pressure of water to rise above one atmosphere, which would exceed the ambient pressure. If we place a quantity of liquid water in a *sealed* container, however, we can heat to higher temperatures, since there is no longer any limit on the vapor pressure we can attain (assuming that the container does not burst). As we uniformly heat the sealed container, the density of the liquid water decreases through thermal expansion. Simultaneously, the density of the water vapor increases as more molecules leave the liquid and enter the vapor phase. We can continue this heating process until the density of the liquid has been so reduced, and the density of the vapor phase has been so increased, that the two densities become equal. The temperature at which the liquid and vapor densities become equal is called the critical temperature. Since the temperature and density inside our sealed container is equal throughout, the laws of thermodynamics dictate that the pressure inside the container be equal throughout. This pressure is called the critical pressure. A liquid (or gas) which has been brought to conditions above its critical temperature and pressure is known as a supercritical fluid.

Figure 1 is a pressure-temperature-density surface of pure CO_2 . The critical conditions of temperature and pressure (31°C and 1072 psi), known as the critical point, are shown in the figure by the solid circle. It can be seen that relatively small changes in temperature or pressure near the critical point, result in large changes in density. It is this 'tunability' of density that is one of the most attractive attributes of supercritical fluids. The reason is that, to a first approximation, the ability of a fluid to solubilize other fluids is directly related to density: A higher fluid density results in higher solute solubilities.

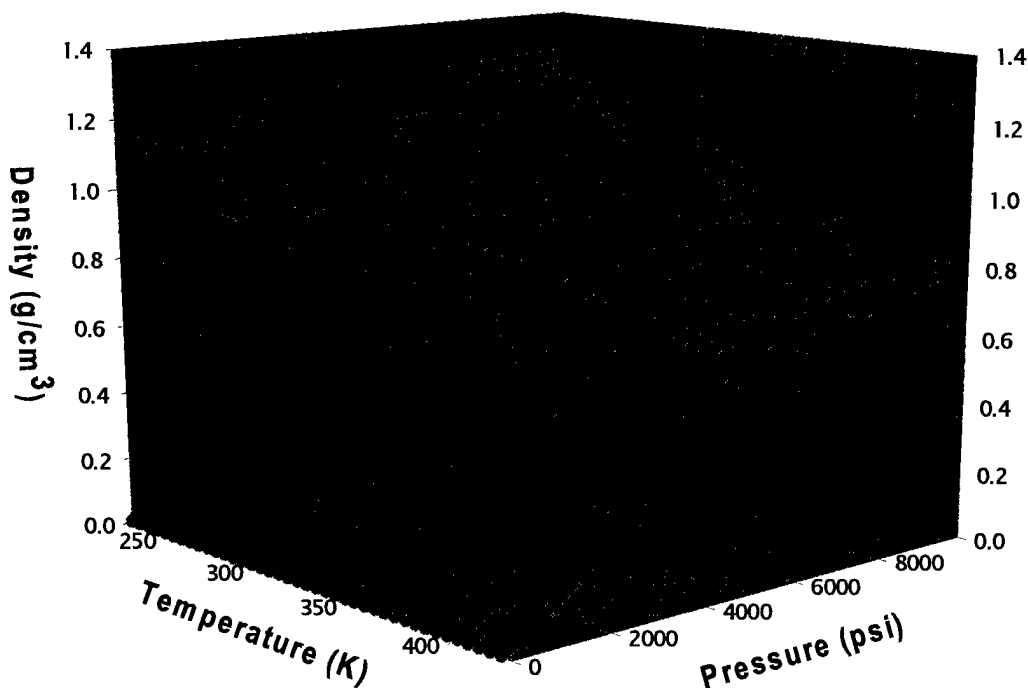


Figure 1. Pressure-temperature-density surface for pure CO₂.

Also, the gas-like properties of low viscosity and high diffusivity provide for efficient mass transfer and efficient contaminant removal. Finally, the absence of surface tension provides for excellent substrate wetting.

Supercritical CO₂, as a candidate for scale-up to an on-line production process, has several safety and economic advantages. CO₂ is non-toxic, non-flammable, and inexpensive (10 - 40 cents per pound). Its critical conditions of temperature and pressure are easily achievable using readily available process equipment. Also, there is already a well-established transportation infrastructure (virtually all restaurants serve carbonated drinks, which make use of compressed CO₂ gas cylinders).

The Department of Energy has made the decision to replace halogenated-hydrocarbon cleaning solvents with SCCO₂ for the cleaning of Pu components based on the following three issues: (1) Pu/CO₂ compatibility and the low level of post-cleaning residues, (2) environmental and occupational concerns, i.e., solvent exposure, cost, and recycle/disposal, and (3) process efficiency and efficacy. The first issue, Pu/CO₂ compatibility and cleaning process residues, is the most important when considering alternative cleaning solvents for this particular application. The weapons manufacturing complex has extensive experience, and familiarity, with traditional cleaning solvents such

as TCA. When changes to process operations were necessary, weapon designers and manufacturers have had in the past the ability to validate these changes by full-scale testing of assembled weapons. The Comprehensive Test Ban Treaty (CTBT) signed by President Clinton in 1996, however, prohibits such testing, so that materials compatibility and process alterations become important issues. The results of DOE-facility studies show that the evaporation of post-process SCCO₂ is extremely rapid and complete when compared to halogenated solvents. Further, any minute amounts of adsorbed CO₂ that remain after the cleaning process do not foster the additional corrosive potential observed for halogen residues. This rapid evaporation of SCCO₂ at ambient conditions precludes the need for a post-cleaning "drying" step since no solvent residue remains.

Secondly, since the SCCO₂ cleaning operation will be performed inside a pressurized, closed-loop system, post-process solvent recovery and recycle of the cleaning fluid will be an integral part of the operation. This mode of operation essentially eliminates cleaning fluid (and its vapor) exposures to personnel and associated process equipment which can be affected by conventional solvent vapors (or their radiolytic by-products). As solvent recovery and recycle are already integral parts of SCCO₂ cleaning, solvent usage and cost is minimized and process-generated waste is sharply reduced by eliminating solvent in the waste volume. A closed-loop system also minimizes evaporative losses and subsequent environmental impact resulting from solvent vapors escaping to the atmosphere.

Finally, comparative resource and process efficiencies can be realized by using SCCO₂ cleaning in place of conventional liquid-solvent cleaning because of the integration of the cleaning operation and cleaning-solvent recovery/recycle steps. Continuous recycle of cleaning solvent ensures the most effective fluid utilization and produces more consistent process results than sequential, dip-bath cleaning operations. Because solubility in supercritical fluids, in general, is a strong function of pressure near the critical point (see Figure 1), quasi-isothermal pressure/volume-cycling can be used to effectively dissolve and segregate the contaminants. Since the critical temperature of CO₂ is near ambient, minimal heating is required and the likelihood of thermally-activated degradation processes (such as oxidation) are diminished. Additionally, since supercritical fluids are normally volatile fluids under process conditions, spontaneous rarefaction and dissipation occur on re-pressurization ensuring low, process-related solvent residues in the after-process matrix.

DESCRIPTION OF THE SCCO₂ CLEANING SYSTEM

A cutaway, oblique angle drawing of the cleaning system and surrounding radiological enclosure is shown in Figure 2. The Pu component, after casting and machined, is passed into the cleaning process line from the right side of the radiological enclosure. The part is then attached to a component-handling assembly that is fixed to the bottom of the cleaning vessel lid. The component-handling assembly serves three purposes. First, it provides a level of protection for the Pu part as it is handled and transported within the

enclosure. Second, the assembly occupies some of the excess free volume inside the cleaning vessel, which directs the flow of the CO₂ across the metal surface, thereby optimizing cleaning efficiency. Lastly, this reduction in free volume minimizes the volume of pressurized fluid, reducing the possibility of rupturing the enclosure in the unlikely event of an uncontrolled pressure release.

The cleaning vessel lid and the component-handling assembly are attached to a vertical-lifting assembly, which are shown at the left of the drawing. The vertical lifting assembly is actuated by twin, linear-screw drives powered by a single ¼ hp DC servo motor. The vertical lifting assembly positions the 100 kg lid and component-handling assembly into and out of the cleaning vessel. The vertical lifting assembly also lowers the

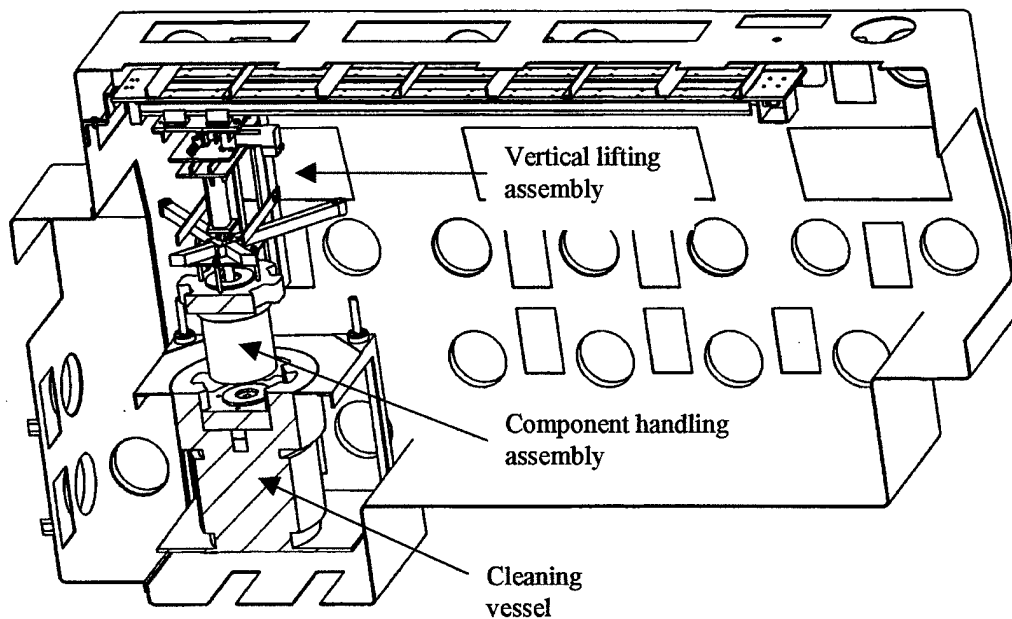


Figure 2. Cutaway, oblique view of the Pu component cleaning system and its radiological enclosure.

component-handling assembly onto the Pu component loading and unloading stations in the enclosure located inside the enclosure, to the right of the cleaning vessel. Horizontal positioning over the cleaning vessel is achieved by a linear track that is actuated by a single, linear screw-drive, powered by a ¼ hp DC servo motor. The horizontal linear track is attached to the top of the enclosure. All positioning is automatic and is controlled by programmable logic controllers.

The closed-loop cleaning process is depicted in Figure 3. The cleaning cycle begins with a liquid-CO₂ storage reservoir. The liquid is compressed above its critical pressure

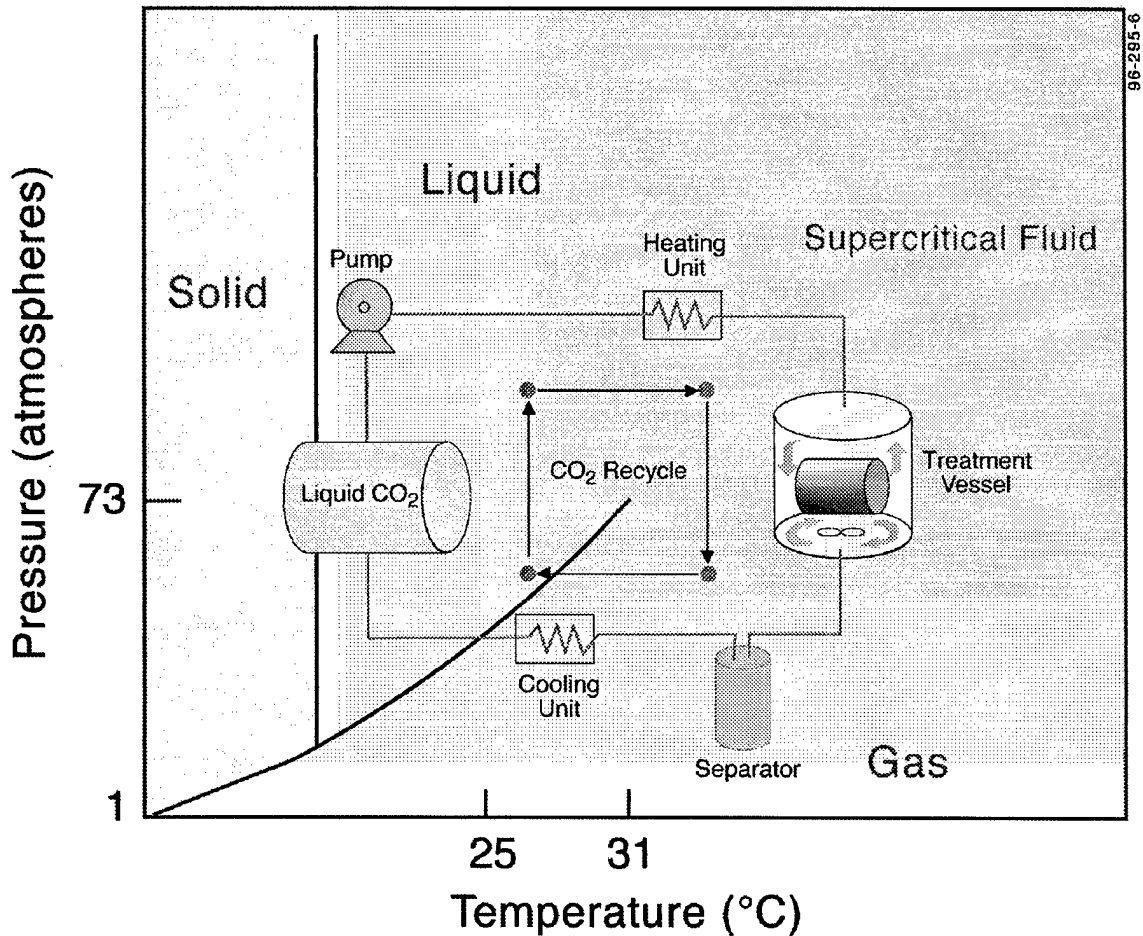


Figure 3. Pressure-temperature phase diagram of pure CO₂, with a superimposed flow diagram for a closed-loop supercritical fluid CO₂ cleaning system.

utilizing a pump, which then sends the pressurized liquid through a heating unit. The heating unit brings the temperature of the pressurized CO₂ to above the critical temperature, forming a supercritical fluid. The supercritical fluid enters the cleaning/treatment vessel and is brought into contact with the plutonium component. During this time any organics are removed from the component surface and solubilized into the CO₂. There is a constant flow of CO₂ through the cleaning vessel such that clean, dry CO₂ is continuously made available. On exiting the cleaning vessel, the supercritical fluid CO₂, containing the dissolved contaminants, is sent to a separation vessel, where the fluid is de-pressurized to below the critical pressure, reducing the CO₂

density to a gas-like value. The solubility of the entrained materials is greatly reduced in this low-density phase and is deposited in the bottom of the separator. The clean CO₂ gas exits the top of the separator, where it is chilled to liquefaction by a cooling unit before re-entering the storage vessel.

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