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SUPERCRITICAL CARBON DIOXIDE PRECISION CLEANING FOR SOLVENT AND WASTE REDUCTION

W. DALE SPALL
LOS ALAMOS NATIONAL LABORATORY
LOS ALAMOS, NM 87545

Murphy's Law of Cleaning: ***You can't get the part cleaner than the dishwater, but is it possible to get both the part and the dishwater dirty.***

Supercritical carbon dioxide as a cleaning solvent offers many advantages for the cleaning of selected materials. This paper discusses the applicability of supercritical carbon dioxide to precision cleaning of a wide variety of parts. The economics involved and a description of the work in progress is included.

INTRODUCTION

Ascetics, performance, improved work life, product specifications, and marketing strategies are among the many reasons to clean an object. Currently, cleaning technologies can be divided into two broad categories, aqueous and non-aqueous based. These technologies face an upheaval brought on by imposition of the Montreal Protocol, which restricts or prevents the use of chlorofluorocarbons (CFCs) for all uses, from refrigerants to dry cleaning. Some 20% of the total CFC production worldwide is used in cleaning, generally during the manufacturing process. The loss of CFCs as cleaning solvents has led to a reevaluation of the entire cleaning process from an environmental point of view. A sense of urgency is associated with search for solvent replacement because CFCs and many other solvents will be phased out in the next few years. The problem facing industry is to find acceptable replacement cleaning strategies quickly.

Any discussion of cleaning should begin with a definition of what is being cleaned and what level of cleanliness is expected. In other words, how clean is clean? The answer is often couched in terms of specifications pertaining to the amount of soil remaining on the part after cleaning. Specifications such as this lead to many parts being overcleaned, while others are undercleaned. The rigidity of specifications often rests on habitual practices rather than actual needs. Specifications should consider how clean a part needs to be to meet speicific requirements on the whole. This should lead to more cleaning for some parts, but to less cleaning for most parts.

Because the entire cleaning process is now at question, manufacturing engineers should seize this opportunity to change the specifications of the cleaning process. The throughput rate of the process, acceptable surface contamination levels, and types of contaminants to be removed should be reevaluated. The overall cleaning process, which includes solvent preparation, waste disposal, drying time, rinse operations, pre- and post- treatment times, worker safety, and ease of operation, as well as total time spent in the process, must be reassessed. The need to clean is directly related to cost of a part or assembly. Increased cleaning during the manufacture process will always drive unit cost up. By the same token, increased cleaning can lead to a higher-quality part while reducing worker risk, improving throughput, and generating less waste material in the production line.

The simplified scale in Fig. 1 is a reasonable estimate of cleanliness levels. Many cleaning specifications are based on the level of specific or characteristic compounds (e.g.,

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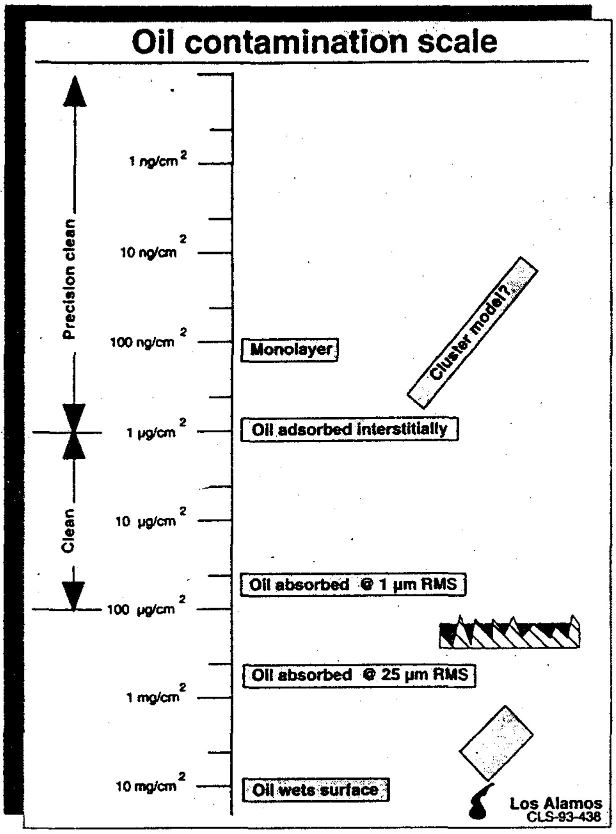


Fig. 1. How clean is clean? Above, is a schematic representation of the levels of contamination and the desired degree of cleanliness of parts.

inorganic or organic) remaining. It is generally assumed that contaminants are uniformly spread across a part's surface, which is obviously not true at the molecular or near-molecular level. Contamination concentrates in pockets on the surface, in surface irregularities, and in the least accessible locations. This clustering of contaminants presents special difficulties to solvent cleaning at low contaminant levels because the contaminated surface area is smaller than if it were spread uniformly across a perfectly smooth surface. The greater the interaction between contaminant and surface, the more difficult it will be to remove the contaminant. For this paper, precision cleaning is defined as cleaning a part's surface to less than 10 micrograms of contaminant per square centimeter, although the goal for most precision-cleaning levels is less than 1 microgram per square centimeter.

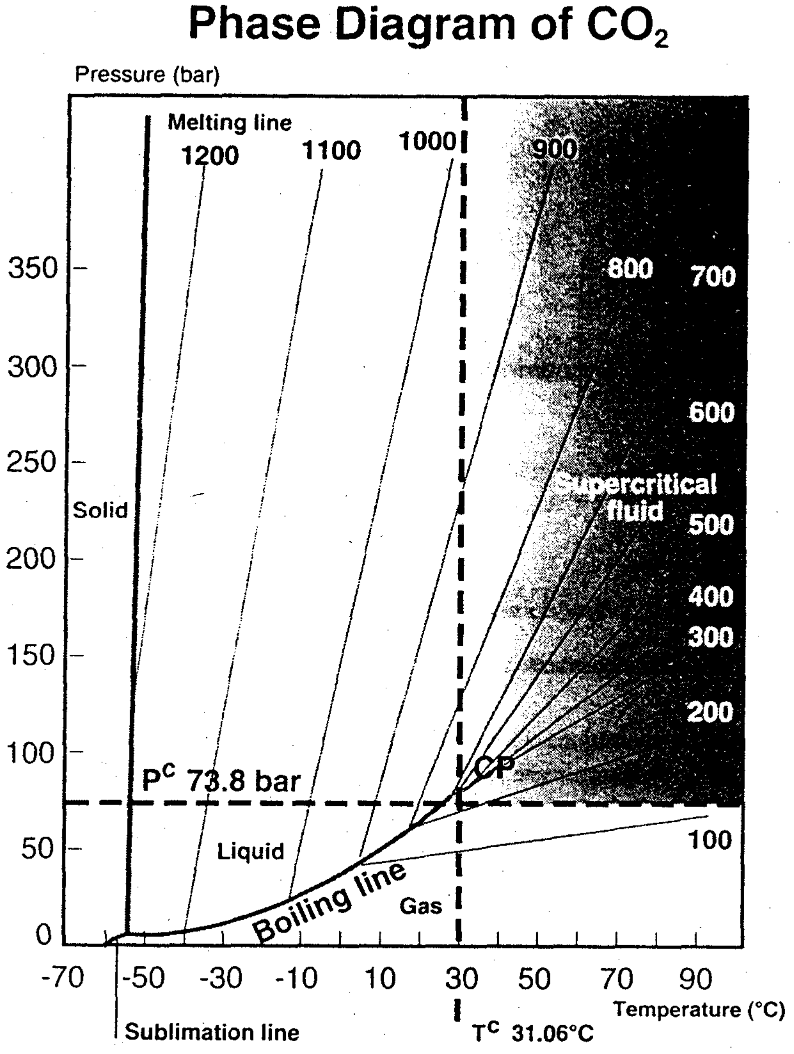
The 10-microgram level of cleanliness is either very desirable or required by the function of parts such as electronic assemblies, optical and laser components, electromechanical elements, hydraulic items, computer parts, ceramics, plastics, and many cast or machined metals. A large number of potential contaminants must be removed from these parts. Table 1 lists common substrates and contaminants. Some contaminants are amenable to solvent cleaning; others require a different approach. Supercritical carbon dioxide cleaning can remove many of these common contaminants.

SUPERCRITICAL FLUIDS CLEANING

To appreciate the unique properties of supercritical fluids, particularly supercritical carbon dioxide, that make them ideal solvents for many cleaning applications, we must define what a supercritical fluid is. All elements and compounds can be described in terms of a phase diagram, which is a representation of the states of the material as a function of temperature and pressure or of other properties of the material. The phase diagram of carbon dioxide is

TABLE 1
Common Contaminants and Substrates Encountered in Precision Cleaning

Substrates	
Pure Metals	aluminium beryllium magnesium copper gold iron nickel silver tantalum titanium
Alloys	carbon steels stainless steels brass chrome alloys monel inconel hastelloy aluminium alloys
Elastomers	viton neoprene buna rubbers silicon rubbers
Polymers	polyimide polyester nylon ethylene propylene polyethylene (UHMW, LD, HD) teflon polystyrene
Ceramics	
Contaminants	machining oils (lubricants, cutting fluids, engine oils) hydraulic fluids damping fluids fingerprints body oils lanolin grease waxes adhesives sealants fluxes particulates (fibers, machining fines, dust, cotton fibers)



PT diagram of CO_2 with the density as third dimension. Densities given from 100 to 1200 g/liter.

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Fig. 2. Temperature-pressure phase diagram for carbon dioxide.

shown in Fig. 2. A few salient points on the phase diagram have special significance. The lines depict phase changes of the material (e.g., from liquid to gas). The critical point (designated CP in the diagram) is defined by both a pressure and a temperature. Any fluid above the critical temperature cannot be turned into a liquid no matter how much pressure applied. For CO_2, this point occurs at 31.1 degrees centrigrade and 74.8 atmospheres (atm) of pressure. The region above the critical point is called the supercritical fluid region; this region exhibits some properties of a gas and some of a liquid.

Supercritical fluids have low viscosities and nearly zero surface tension. Diffusion coefficients of substances in the fluid are between those of liquids and those of gases. These properties make supercritical fluids ideal for cleaning parts having porous, intricate, or rough surfaces or confined work areas because the solvent can penetrate into these regions to remove contaminants.

A large increase in the solubility of compounds generally results when going from the gas to the supercritical state. Most materials are nearly insoluble in the gas phase, but many have quite high solubilities in the supercritical state. This enhanced solubility of organic compounds in the supercritical state forms the basis for using supercritical fluids as cleaning solvents. The low viscosity, low surface tension, and high diffusion rates mean that supercritical fluids can readily penetrate into small regions to remove contaminants. As a result, the removal process is more rapid than when using liquid solvents.

Although this sounds as if supercritical fluids are an absolute solution to the cleaning problem, many substances (e.g., ionic solids) are insoluble in supercritical fluids with low polarities such as carbon dioxide. Many of the more polar supercritical fluids such as water, which would be capable of dissolving polar and ionic compounds, are very reactive and cause deterioration of the materials to be cleaned. Volatile compounds (having high vapor pressures) are generally quite soluble in CO_2, but separating them from gaseous CO_2 is difficult. Supercritical carbon dioxide is best applied to the removal of organic compounds with mid-to-low volatilities. This class of compound often occurs as common contaminants encountered in precision cleaning.

Supercritical fluids cleaning or extraction apparatus is conceptually simple, as shown in Fig. 3. A source of CO_2 such as standard gas cylinders provides the fluid for the pump used to elevate the CO_2 to pressures above the critical pressure. At this point, the physical state is usually liquid in the extraction vessel. The temperature is raised to the desired point above the critical temperature, and extraction begins. The supercritical CO_2 flows through the cell and reaches the throttle valve. The fluid is then expanded into a volume so the physical state is that of a gas. The extracted compounds are collected in the separator, and the gaseous CO_2 is passed back into the flow stream to be used again in the cleaning process.

Although many compounds can easily attain their critical points, making them potential supercritical fluids, these substances are generally flammable or toxic. Carbon dioxide is the most frequently used supercritical fluid, primarily because of its low-cost, non-toxic, envi-

Generalized equipment schematic

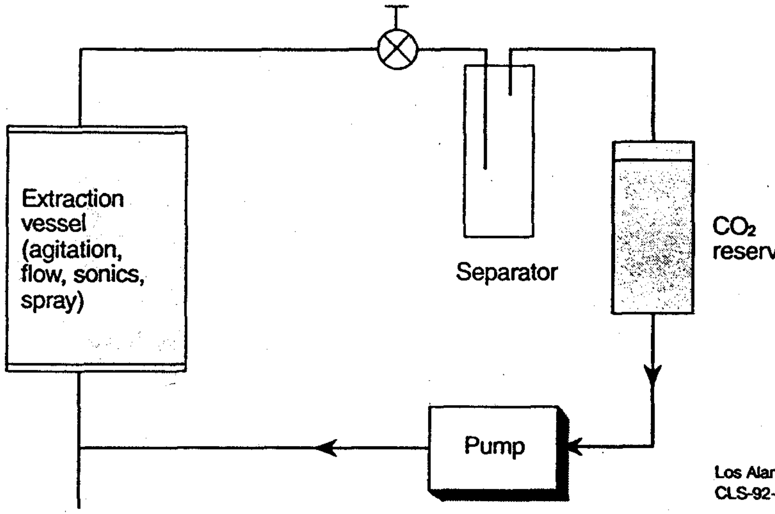

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Fig. 3. Generalized equipment schematic for supercritical fluids extraction.

ronmentally benign nature, as well as its relatively low critical temperature (88 degrees Fahrenheit) and pressure (1100 pounds per square inch). These low critical parameters make the use of CO_2 relatively efficient in terms of energy use during operation, although not as efficient as operations conducted at room temperature. The elevated pressure needed for attaining the supercritical state adds cost to the cleaning vessel and makes batch-mode operation necessary. Many increased costs are offset by the low cost of CO_2 (about \$0.03 per pound) and the simplicity of the overall cleaning operation.

Operational costs for CO_2 tend to be lower than for other cleaning processes. With CO_2, the solvent is removed by releasing the pressure in the extraction chamber. The solvent in the chamber is lost, but in today's commercial units, this loss of solvent amounts to approximately 20 pounds of CO_2 per 8-hour operating day, making the cost of solvent loss during operations about \$1 per day. For alternate cleaning ystems, it is often necessary to rinse a part in a separate unit, then dry the part in yet another unit. Any rinsing needed with CO_2 is performed in the chamber used for cleaning; no drying is needed because the solvent dissipates upon pressure release. These factors make supercritical CO_2 cleaning a viable alternative for many cleaning applications.

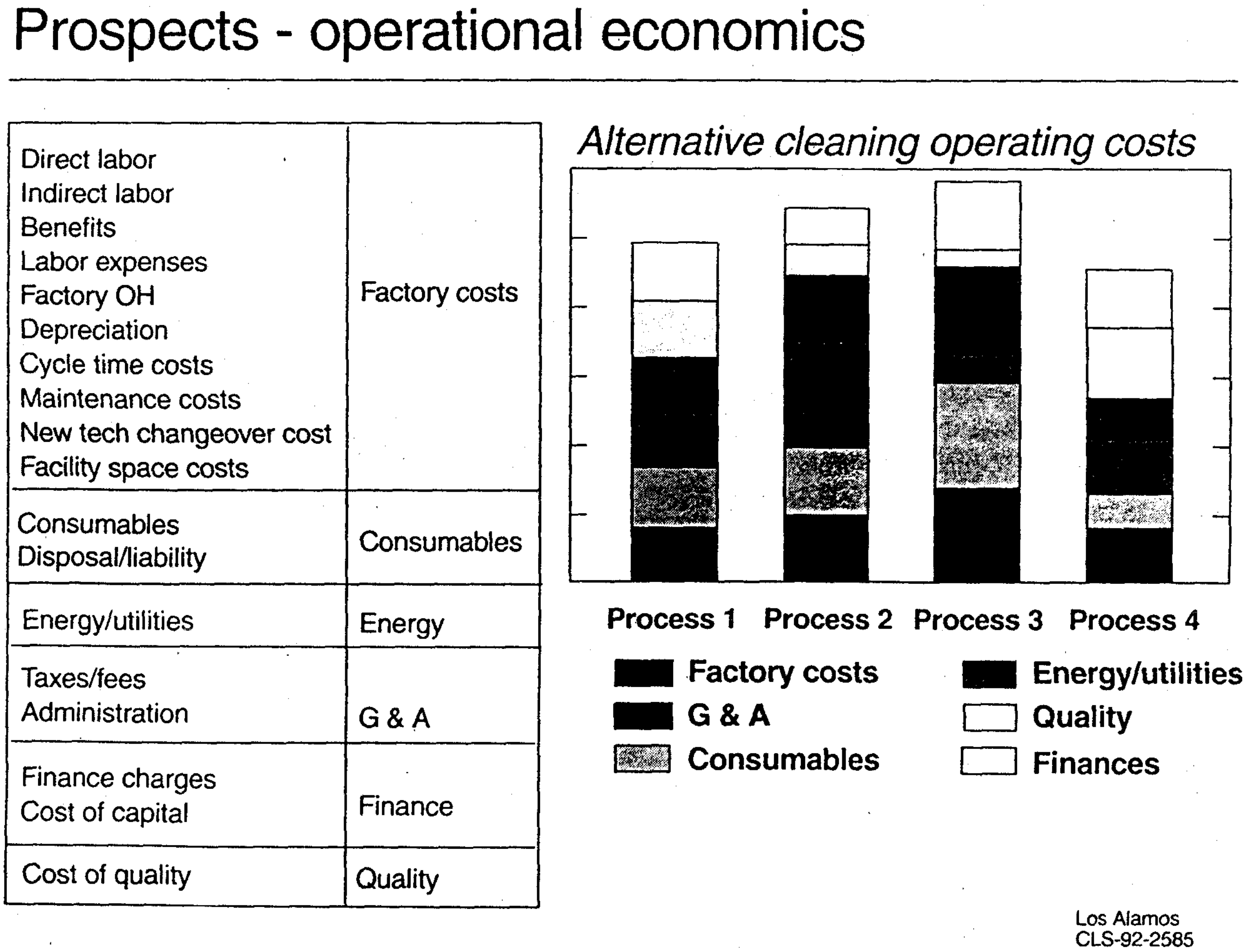
A single-site cost comparison of four cleaning processes used on identical parts indicated supercritical CO_2 was slightly less expensive. Results of this study are shown in Fig. 4. For true economic comparison, however, the entire cleaning process must be considered, including costs arising from solvent handling and disposal, drying equipment, total handling and processing time, dollar value of parts held in the production line for cleaning, space utilization, and energy costs. Obviously, if existing equipment can be retrofit to accommodate an alternative cleaning process, the capital costs of new unit installation can be avoided. This or other economic factors may prove to be the driver for cleaning-method selection. It must be stressed, however, that the entire cleaning process must be evaluated to make an environmentally sound decision on method selection.

A final point in support of using supercritical CO_2 as a cleaning agent is that many of the alternate systems suggested for solvent cleaning have not been tested for toxicity and health effects. Many of these solvents have known health and safety problems; many are considered volatile organic compounds; and all are potentially subject to future regulation as the health and safety factors are identified. Carbon dioxice has been used in a variety of industrial situations for some time, and its health effects and handling requirements are well understood. It is unlikely that CO_2 as a cleaning solvent will be regulated beyond existing standards, thus making it improbable that another cleaning methodology will replace CO_2 cleaning in the future.

Although CO_2 used for cleaning is environmentally benign (CO_2 production distills carbon dioxide from air, so no new carbon dioxide is added to the atmospheric burden), the materials extracted into supercritical CO_2 must be removed before it can be disposed of or recycled for additional cleaning. For compounds with low vapor pressures, this removal can usually be accomplished simply by lowering the pressure of the stream using a simple throttle valve. The pressurized supercritical CO_2 then expands into a large volume. When the pressure and temperature drop below the critical point, the CO_2 will be in the gas phase, and contaminants will form droplets or aerosols in the gas. The concentration of contaminant is determined by its solubility in the CO_2 and by its vapor pressure at the let-down temperature. Allowing the pressure to fall too low is undesirable because energy will be consumed to bring the pressure back to the supercritical range. The expansion of the supercritical fluid is accompanied by a drop in temperature; energy must usually be added at this point to keep the fluid from turning into CO_2 *snow* in the separator. Because the quantity of material remaining in the gas phase will, to a large degree, be determined by the vapor pressure of the contaminant, substances with high vapor pressures will be difficult to remove from the CO_2. Cleanliness is important because *you can't get the dish cleaner than the dish water*, as Murphy's Law of Cleaning states. While feasible from a solubility standpoint, removal of volatile contaminants in CO_2 is not feasible from an operational standpoint.

Our studies on supercritical CO_2 cleaning focused on four areas: materials compatibility, contaminant and substrate removal efficiencies, mechanics of the contaminant removal, and physical parameters determining the effectiveness of the separator. Materials compatibility is a critical issue because many of the substrates being cleaned are organic and the potential for the CO_2 attacking the substrate cannot be ignored. One study centered on components commonly found in the aerospace industry, but many of those materials are used in a wide variety of manufacturing processes. The study was designed to determine the mechanical, electrical, and physical stability of a large number of components and materials when exposed to supercritical conditions. More than 100 materials have been investigated (Table 2), and with few exceptions, all were found to be stable to supercritical CO_2. The exceptions tend to be polymers, and exposure conditions are critical for the amount of change observed. Not all polymers are equally affected, and different formulations of the same basic polymeric formulation react differently. The best counsel is to check specific parts containing polymeric materials on an individual basis.

Millions of potential contaminants can be found on thousands of substrates. Obviously, it is impossible to test removal efficiency for all cases. The most common contaminants tend to be body oils, cutting and machining fluids, oils and greases, adhesives and sealants, and particulate matter. Common substrates are pure metals, alloys, elastomers, polymers, and ceramics. We began the study by investigating the removal of contaminates that are mixtures of compounds from selected matrices. During the study we examined the removal process of specific compounds from selected substrates. The goal was to define a set of conditions that could be used as a guide for the cleaning of substances from surfaces. Rather than determine all possible combinations, we decided to use specific compounds as a guide to a wide variety of mixtures. The principal components of a



Prospects - operational economics

Direct labor Indirect labor Benefits Labor expenses Factory OH Depreciation Cycle time costs Maintenance costs New tech changeover cost Facility space costs	Factory costs
Consumables Disposal/liability	Consumables
Energy/utilities	Energy
Taxes/fees Administration	G & A
Finance charges Cost of capital	Finance
Cost of quality	Quality

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Fig. 4. Economic comparison of alternative cleaning processes. Process 1 is an aqueous process, Processes 2 and 3 are non-aqueous cleaning processes, and Process 4 is supercritical carbon dioxide cleaning. All processes were used to clean identical parts to the same level of cleanliness.

TABLE 2
Materials Tested for Compatibility with Supercritical Carbon Dioxide

Materials tested at 300 atm, 45°C, for 30 minutes
Clad integrated circuits, diodes, chokes, capacitors, resistors
Printed circuit boards including multilayer versions, most common plastics, iron, aluminum, magnesium, copper, stainless, cast aluminum and magnesium, silver, platinum, nickel, chromium
Common rubbers, composite materials, glass, sapphire, quartz
Silicon adhesives, epoxies, composite sealants, most coax cables

mixture can be easily determined by using modern analytical methods such as FTIR and GCMS or by consulting the material safety data sheet (MSDS) supplied with the product. Although some components in the mixture may be proprietary, the major constituents are listed, along with health, safety, and handling information.

When coupled with the individual compound data identified in the recent study, the MSDS information serves as a guide for selecting the initial set of conditions for removing compounds from surfaces. Using a selection of extraction conditions, we determined the removal process for more than 150 compounds from a variety of surfaces. This data will be available shortly and will serve as a guide to customizing CO_2 extraction conditions for a variety of cleaning problems.

In general, the results indicate that, as expected, high-polarity compounds extract more slowly from surfaces than do low-polarity compounds when pure CO_2 is used as the extractant. Modifying the polarity of the CO_2 forces a compromise on the amount and rate of extraction of mixtures having a range of polarities in the constituent compounds. As the solvent polarity increases, more-polar compounds become more readily extractable and less-polar compounds become less readily extracted. The extraction process becomes one of compromise in removal efficiency, with the polarity of the CO_2 the determining factor. As expected again, porous surfaces clean more slowly than smooth surfaces. The two most difficult surfaces to clean appear to be cast metals, which tend to be porous, and ceramics, particularly those with rough surface. High-fired ceramics (glasses) have the same cleaning properties as very smooth surfaces.

The surface extraction of substances is governed by a variety of physical and chemical factors. The density of the supercritical fluid relates most closely to the chemical factors, but parameters such as mass flux rates from the surface are governed to a large degree by the rate of fluid flow at the boundary layer, and the boundary layer is controlled by the rate of bulk flow past the surface to be cleaned. A recent study performed at Battelle Pacific Northwest Laboratories has vividly demonstrated this effect. Cleaning rates can be significantly enhanced by increasing the mass flow rate of the fluid past the surface to be cleaned. Other mechanical aspects of the cleaning process such as the ratio of dead volume in the cleaning cell to part surface area need to be evaluated. Some observers suggest that the removal rate for contaminants from the surface is very rapid for smooth surfaces, and that the majority of the extraction time is spent clearing the extraction chamber of the extracted material. These topics are food for future research.

Research being performed in the Department of Energy program includes determining the best design for the separator portion of the equipment. In the case of precision cleaning, it is probably necessary to use CO_2 that is very clean; for the recycle of CO_2, it must remain clean during use. Current studies indicate that the concentration of low vapor pressure compounds must be kept below 1 part per million to achieve cleanliness levels at or below 1 microgram per square centimeter. Design of a separator system that can accomplish this while using minimal energy is not a simple task.

CONCLUSIONS

Supercritical carbon dioxide is an excellent solvent for precision cleaning, particularly for porous, intricate parts or parts that are relatively accessible by conventional solvents. The economics of the entire cleaning process may dictate the use of CO_2 in cleaning uses other than precision cleaning. Work in progress will clarify the areas for the application, but current indications are that the applicability will be large.

ACKNOWLEDGMENTS

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