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EFFECTS OF FLUID DYNAMICS
ON CLEANING EFFICACY OF
SUPERCRITICAL FLUIDS

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SUMMARY

Pacific Northwest Laboratory (PNL)^(a) and Boeing Aerospace Company are jointly developing a process to clean metal parts using a supercritical solvent. This work is part of a collaborative effort by PNL, Boeing, Inland Technology, Los Alamos National Laboratory (LANL), Sandia National Laboratory (SNL), and other industrial partners to address issues inhibiting the rapid commercialization of Supercritical Fluid Parts Cleaning (SFPC).

During FY 1992, PNL assembled a SFPC test stand to observe the relationship between the fluid dynamics of the system and the mass transfer of a contaminant from the surface of a contaminated metal coupon into the bulk fluid. The bench-scale test stand consists of a "Berty" autoclave modified for these tests and supporting hardware to achieve supercritical fluids parts cleaning. The Berty autoclave is a medium pressure, high-temperature, fixed bed autoclave fitted with a shaft driven impeller and heaters.

Three separate sets of tests were conducted using supercritical carbon dioxide. For the first two tests, a single stainless steel coupon was repeatedly cleaned with organic solvents to remove surface residue, doped with a single contaminant, and then cleaned in the SFPC test stand. Contaminants studied were Dow Corning[®] 200 fluid (dimethylpolysiloxane) and Castle/Sybron X-448 High-temperature Oil (a polybutane/mineral oil mixture). A set of 5-minute cleaning runs was conducted for each dopant at various autoclave impeller speeds. Test results from the first two sets of experiments indicate that precision cleaning for difficult-to-remove contaminants can be dramatically improved by introducing and increasing turbulence within the system. 30% more contaminant was removed during turbulent conditions for both contaminants.

Metal coupons that had been previously doped with aircraft oil at Boeing Aerospace Company's critical cleaning facility were used in a third set of tests. The coupons were placed in the SFPC test stand and subjected to

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different temperatures, pressures, and run times at a constant impeller speed. The cleanliness of each part was measured by Optically Stimulated Electron Emission (OSEE). Results from the third set of tests show that levels of cleanliness attained with supercritical carbon dioxide compare favorably with solvent and aqueous cleaning levels.

In general, the results of these tests show cleaning efficiency can be substantially improved by making relatively small changes in system dynamics. Significant energy savings can be realized by taking advantage of these changes. With further study, quantifiable relationships between system dynamics and cleaning efficiency can be made and energy efficient SFPC systems can be designed.

CONTENTS

SUMMARY	iii
INTRODUCTION	1
EQUIPMENT	5
EXPERIMENTAL PROCEDURES	9
DISCUSSION OF RESULTS	11
CONCLUSIONS AND RECOMMENDATIONS	15
CONCLUSIONS	15
RECOMMENDATIONS	15
REFERENCES	17

FIGURES

1	SFPC Test Stand	6
2	Berty Autoclave	7
3	Impeller RPM vs Percent of Contaminant Removed	12
4	Average Rate of Mass Flux vs Reynolds Number	12
5	OSEE Analysis	14

INTRODUCTION

Degreasing is an essential manufacturing process, particularly in industries fabricating or assembling metal parts. Degreasing is widely used to remove oil and oil-borne solids from parts ranging from transistors, precision equipment, and printed-circuit assemblies to large aircraft and automotive parts. Degreasing is used as both an intermediate process, where gross cleaning is needed for ease of production, and a final production process, where precision cleaning is required before painting, bonding, or plating.

Critical cleaning is contaminant removal to the $\mu\text{g}/\text{cm}^2$ level where surface films are measured to within a few angstroms. Parts requiring critical cleaning include gyroscope bearing surfaces, computer disk surfaces, and precision electronic and optical parts. Critical cleaning typically involves several rinses in an appropriate solvent where very little or no solvent residue remains on the surface of the part being cleaned.

Chlorofluorocarbons (CFCs) have been widely used for precision cleaning of metal parts, circuit boards, and other equipment. CFCs are inert, pure solvents that leave very little residue on the surfaces of the parts being cleaned. However, the production of CFCs is gradually being phased out according to the 1987 Montreal Protocol agreement due to concerns about stratospheric ozone depletion.

Hydrochlorofluorocarbons (HCFCs) have been proposed as a substitute to CFCs. However, at the 1990 London environmental summit, the Montreal Protocol agreement was amended to restrict HCFCs. The new agreement calls for using HCFCs only when other, less ozone-destructive alternatives are not available. The new agreement also calls for the complete phasing out of HCFCs by 2020.

Aqueous emulsion cleaning (AEC) is one alternative to the use of CFCs and HCFCs which does not use chlorinated or ozone depleting solvents. However, aqueous cleaning may not be a suitable alternative for many cleaning applications due to the difficulty of completely eliminating a surface residue. Use of AEC solvents such as detergents, turpenes, and ethanolamines can also present serious health and safety risks to cleaning system operators

due to known or suspected toxicities. Also, because cleaning efficiency deteriorates with loading, AEC solvents, CFCs, and HCFCs must either be regenerated or disposed of when cleaning objectives can no longer be met because solvent loading is excessive. Although the residual from solvent reclamation contains mostly oils and oil-borne particulates, it frequently has to be disposed of as a hazardous waste because of the presence of the solvent.

An attractive alternative to vapor degreasing and AEC is precision cleaning with supercritical fluids. Supercritical fluids parts cleaning (SFPC) makes use of the unique solvent characteristics of fluids near and above their critical point to remove contaminants from the surfaces of metal and possibly plastic parts. Supercritical fluids approach the density and solvating power of the fluid in the liquid phase while maintaining the viscosity and flow characteristics of the fluid in the gaseous phase. Thus, supercritical fluids typically maintain viscosities an order of magnitude less and diffusivities an order of magnitude greater than liquids of similar density [McHugh and Krukonis 1986]. These properties can be dramatically modified by slight changes in fluid density, which is a strong function of changes in pressure and temperature in the near-critical and supercritical range. For any particular contaminant, a slight drop in solvent pressure significantly reduces the solubility of that contaminant in a supercritical fluid. Therefore, it is possible to solubilize a mixture of contaminants from the surface of a part and then selectively reclaim, through slight variations in pressure, each individual contaminant. By dropping the solvent pressure far enough, all contaminants can be separated from the solvent and the solvent can be reclaimed for reuse.

Supercritical carbon dioxide is especially attractive as a solvent for SFPC. Carbon dioxide exists naturally as an environmentally safe, non-flammable, inert gas which, except in extreme cases, poses no threat to exposed personnel. Carbon dioxide is also readily available and relatively inexpensive to use. The critical temperature for carbon dioxide is 31°C , and the critical pressure is 73.8 bar [1070 psi]. Above the critical temperature, it is not possible to compress the fluid enough to force the formation of a liquid phase. At or near the critical pressure, density of the fluid becomes

very pressure dependent; a pressure increase of 50% can produce a four-fold density increase [Motyl 1979]. - Therefore, supercritical fluids such as carbon dioxide can be compressed to near liquid-like densities where they can display good solvent properties.

The use of supercritical fluids as alternative solvents has been of interest for many years. The phenomena of increased solubility in supercritical fluids compared to gases is becoming well known. However, developing large-scale applications requires knowledge of mass transfer rate parameters as well as solubility information. Developing large-scale applications also requires the scaling up of preliminary test runs done in small-scale equipment which may or may not be geometrically similar. To avoid scale-up of SFPC systems from strictly empirical information, engineering data linking system performance with process parameters are needed. These data will ultimately be used to reduce the risk of scale-up by providing the design engineer(s) with empirical correlations between easily measured or estimated process parameters (flow rate, density, pressure and temperature) and a performance based variable (mass transfer rate).

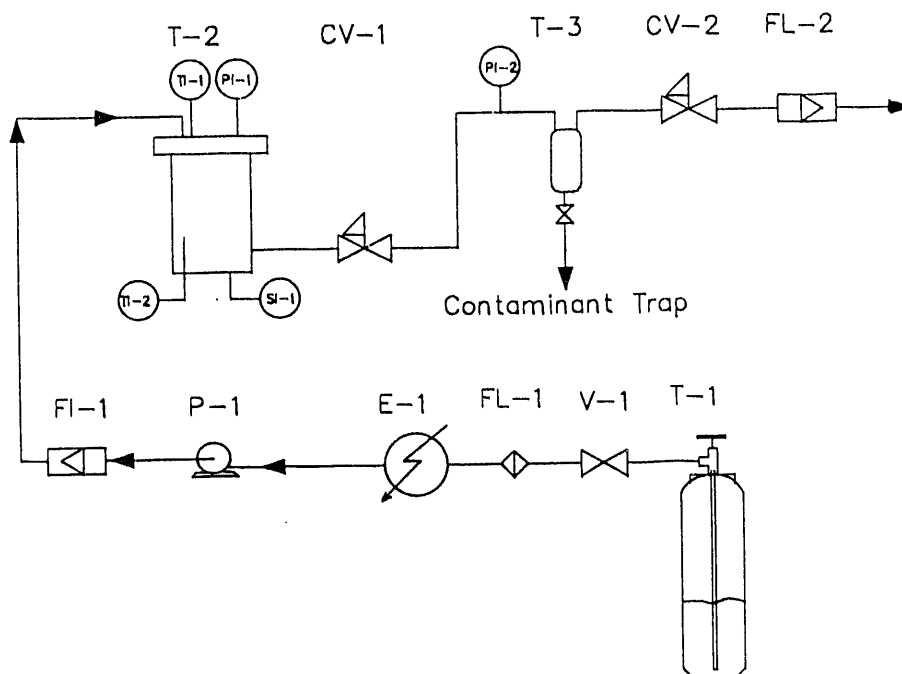
Pacific Northwest Laboratory (PNL), together with Boeing Aerospace Company and Inland Technology, is developing a process to clean metal and perhaps plastic parts using supercritical fluid solvents. This project is part of a collaborative program that also includes Los Alamos National Laboratory (LANL), Sandia National Laboratory (SNL), and other industrial partners to address the technology development issues that inhibit rapid commercialization of SFPC.

During FY 1992, PNL assembled a bench-scale experimental system and conducted experiments to determine the effects of system parameters on SFPC efficacy. Carbon dioxide was the supercritical solvent for these experiments. The objective for FY 1992 was to establish a relationship between the rate of mass transfer of a contaminant from the surface of a contaminated metal coupon to the bulk fluid and the fluid dynamics of the system as determined by the Reynolds number.

EQUIPMENT

The bench-scale SFPC test stand consists of a medium pressure, high-temperature autoclave constructed by Autoclave Engineers and modified for these tests, and supporting equipment to achieve supercritical cleaning (see Figure 1). Carbon dioxide is supplied to the system from standard compressed gas bottles. Carbon dioxide enters the system through a constant-temperature water bath where condensation occurs at 15°C. A refrigeration cooler maintains the temperature at the pump head and in the line from the constant-temperature bath to the pump head. Temperature at the pump head must be maintained in order to insure that fluid entering the pump is in liquid form. Liquid carbon dioxide is then fed through the top and into the autoclave where it is pumped to operating pressure by a high pressure liquid chromatography (HPLC) precision metering pump. Pressure in the autoclave is controlled by a back pressure regulator located downstream of the autoclave. Flow through the autoclave is from top to bottom. A separator vessel collects the dopant as it disengages from the carbon dioxide on pressure letdown. A dry test meter measures the total flow of gas through the system.

The autoclave (see Figure 2) has an internal volume of 433 cc. It is a bolted-closure, 3-inch I.D., fixed bed catalytic reactor constructed by Autoclave Engineers (a "Berty" autoclave). Agitation in the autoclave is supplied by an impeller attached through the bottom of the autoclave to a MagnaDrive assembly. The autoclave rests in a ceramic heater assembly which is capable of heating the autoclave to over 500°C. Rated pressure of the autoclave is 5800 psi at 340°C. Power to the heaters is supplied through a variac which was manually adjusted during testing to control temperature. Impeller speed is controlled by a variable speed controller that is part of the MagnaDrive unit. The only modifications to the autoclave necessary for our testing was to change the MagnaDrive bushings from carbon to nylon, perform a complete polishing of all the interior surfaces of the autoclave, and to fashion a coupon holder to position the coupon in the autoclave in the same orientation for every test run.



Equipment List

CV-1	Back Pressure Regulator (10,000 psi)
CV-2	Back Pressure Regulator (2,500 psi)
E-1	Heat Exchanger
FI-1	Flow Indicator
FI-2	Dry Test Meter
FL-1	10-Micron Filter
P-1	High Pressure Pump
T-1	Supply Tank
T-2	Autoclave
T-3	Separator Vessel
V-1	Needle Valve

Instrumentation

PI-1	Pressure Gauge
PI-2	Pressure Gauge
TI-1	Thermocouple
TI-2	Thermocouple
TI-3	Thermocouple

FIGURE 1. SFPC Test Stand

The high-pressure feed pump is an Eldex model BBB-4 triple head HPLC precision metering pump capable of pumping 100 mL/min at 5000 psi. Liquid enters and exits the pump through manifolds attached at the entrance and exits to the pump heads. High pressure is attained by a positive displacement, reciprocating piston assembly. The pistons are driven by a constant speed motor; volumetric flow control is accomplished by adjusting piston stroke length. Stroke length of the pistons is controlled by precision micrometer adjusters.

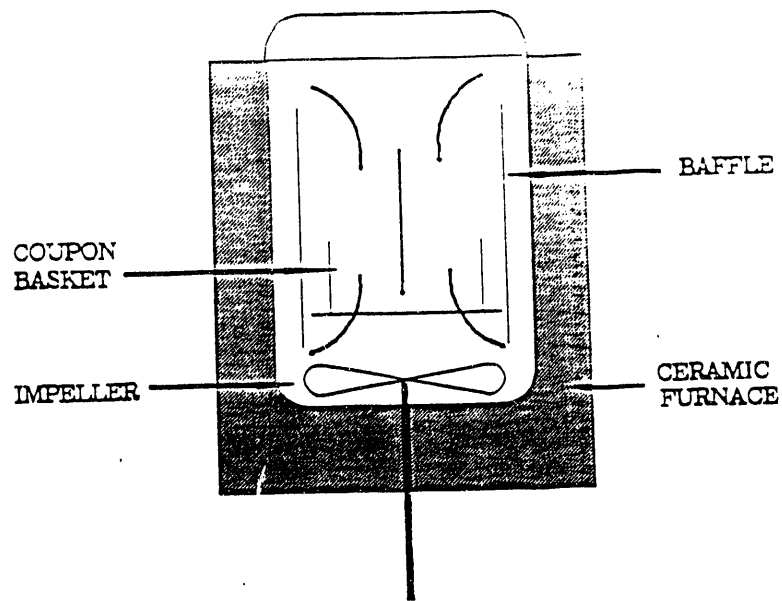


FIGURE 2. Bertly Autoclave

Mass flow through the system is measured with a Model D 6H-SS Micro Motion Mass Flow Meter. Mass flow is reported as a function of twist on the tubes within the meter caused by a Coriolis force on the tubes which is a function of flow through the meter. Accuracy of the meter is within 0.56%.

There are two back pressure regulators in the system, both are models with soft seats. The first is located downstream of the autoclave, is rated to 10,000 psi, and regulates pressure in the autoclave. The second, rated at 2500 psi, controls pressure in the separator vessel.

EXPERIMENTAL PROCEDURES

The same SS coupon was used for the first two sets of experimental runs. Before each run, the coupon was cleaned first in a chloroform bath, rinsed with acetone, and then dipped in an acetone bath. After cleaning, the coupon was weighed to ensure that cleaning had been accomplished to within the limits of our analytical balance. The coupon measured 4 cm x 3.5 cm x 0.1 cm.

The coupon was then doped with one of two dopants by completely submerging the coupon in the dopant solution, patted lightly with a Kim Wipe to remove excess material, and then weighed. Two different doping solutions were used: Dow Corning[®] 200 fluid and Castle/Sybron X-448 High-temperature Oil. The Dow Corning Fluid is a 100 cSt dimethylpolysiloxane, a clear silicone liquid. The X-448 Oil is a polybutane/mineral oil mixture. A set of 5-minute runs was conducted for each dopant at various autoclave impeller speeds.

After doping, the coupon was loaded into the preheated autoclave by placing the coupon onto a holder designed to hold the coupon in a vertical position. The autoclave was always preheated to 41°C to ensure rapid attainment of supercritical conditions. The autoclave's top would then be bolted on and the test started.

Testing proceeded by filling the autoclave vessel and system with carbon dioxide to the first backpressure regulator and venting residual air from the system through a valve at the top of the autoclave. Once the system was filled, the pump was started at an average rate of 57 ml/min of liquid carbon dioxide. Timing of the run began when the pressure gauge located at the top of the autoclave reached 1100 psi.

When pressure in the autoclave reached 1100 psig, the impeller was turned on to a predetermined speed. The autoclave pressure was allowed to reach and maintain 1400 psig for the remainder of the test run. When four minutes and 45 seconds had elapsed, the carbon dioxide supply was turned off and the system vented. When the pressure gauge at the top of the autoclave once again read 1100 psig, the impeller was turned off. Pressure letdown from 1400 psig to 1100 psig typically took 15 seconds, which results in an average run time at supercritical conditions of 5.0 minutes. One volume turnover for

the autoclave (internal volume = 433 ml with baffles and basket in place) is estimated at 7.5 minutes.

When the carbon dioxide was removed from the system, the coupon was removed from the system and immediately reweighed on the same analytical balance. Weight differentials were used to determine mass flux of dopant from the coupon. Impeller speed was used to calculate the impeller Reynolds number for stirred-vessel agitation [Perry and Green 1984].

$$N_{Re} = \frac{D_a^2 N \rho}{\mu}$$

Impeller Reynolds Number

D = impeller diameter	m
N = rotational speed	rev/s
ρ = fluid density	kg/m ³
μ = viscosity	Pa*s

The third set of experimental runs was conducted on coupons that Boeing Aerospace staff had previously doped with aircraft oil. Coupons were placed in the autoclave one at a time and subject to different temperatures, pressures, and run times at constant impeller speed. Cleaned coupons were analyzed by Optically Stimulated Electron Emission (OSEE). This technique effectively measures the relative thickness of films on a flat surface. Boeing contributed use of the OSEE and staff time to perform the analysis.

DISCUSSION OF RESULTS

Both the silicone and high-temperature oil contaminants were difficult to remove using supercritical carbon dioxide as the solvent. Several surface contaminants were examined before choosing the silicone and high-temperature oils. Most contaminants tried were removed too rapidly to observe mass flux by gravimetric analysis. Even by using the silicone and high-temperature oils, scattering of the data occurred. To determine the precise correlation between mass flux and turbulence, a real time analytical method for observing surface contamination needs to be used.

A definite relationship between mass flux of contaminant and system turbulence can be seen from the graphs correlating the data taken from the first two sets of experimental runs. Figure 3 shows that, for equal cleaning intervals, contaminant removal increases as the impeller speed increases up to a maximum efficacy, which depends on the contaminant. The maximum efficacy was reached for silicone oil at a lower impeller speed than for high-temperature oil. Increasing system turbulence beyond this point does not improve mass flux, and would be a waste of power.

Figure 4 shows the relationship between the average mass flux of contaminant during the run and impeller Reynolds number. Even though the silicone and high-temperature oils required more time to remove than other contaminants, the data exhibit significant scatter. This scatter is probably due to the lag-time inherent in pressurizing and depressurizing the autoclave during the cycle. A more fundamental treatment would also correlate the instantaneous mass flux or mass transfer coefficient rather than the mass flux averaged over the cleaning cycle. This requires a real-time analytical method.

The third set of experiments was performed in order to establish cleaning efficacy by supercritical carbon dioxide in comparison with solvent cleaning. OSEE analysis relates the difference between a clean surface and a contaminated one. The cleaner the surface, the higher the OSEE number. Plotting film thickness versus the logarithm of the OSEE reading results in an inverse linear relationship for most contaminants and surfaces.

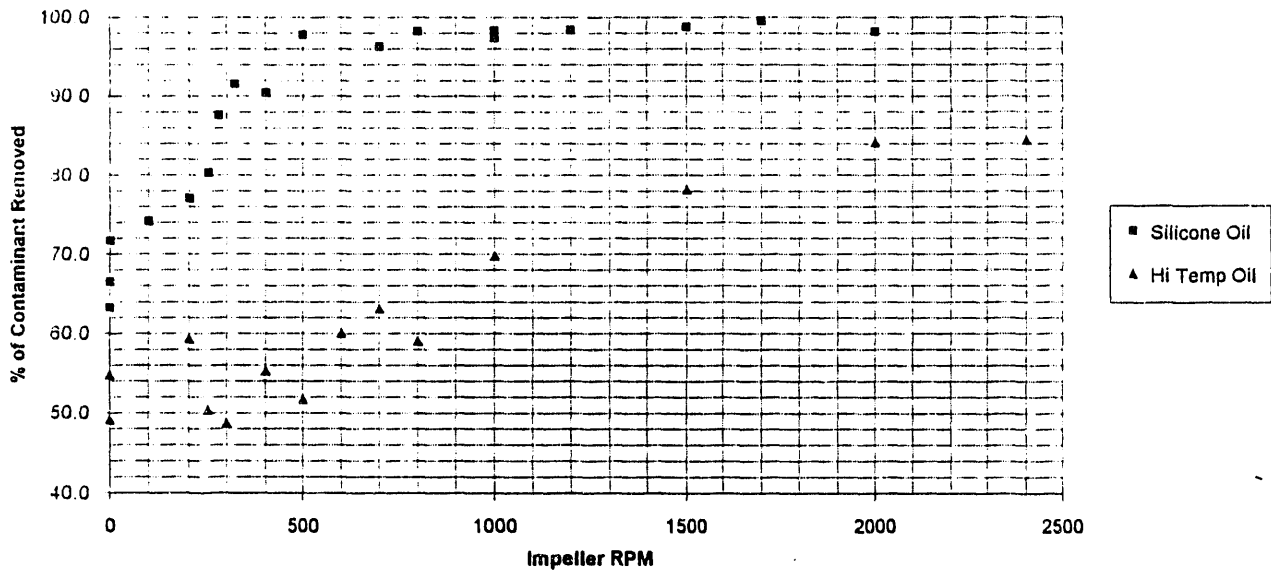


FIGURE 3. Impeller RPM vs Percent of Contaminant Removed

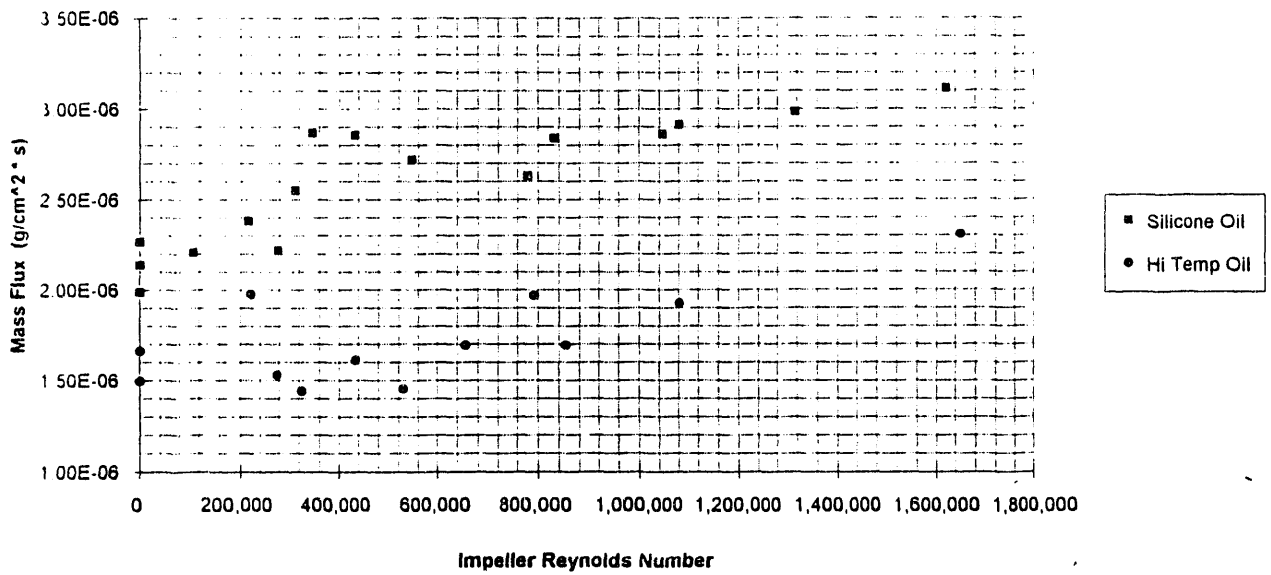


FIGURE 4. Average Rate of Mass Flux vs Reynolds Number

Coupons cleaned by SFPC had surface readings ranging from 90 to 140. A reading of 230 was achieved by washing a coupon in two chloroform baths followed by two acetone washes and then immediately placing the coupon under the OSEE for analysis. Typical readings of 150 were obtained for stainless steel coupons cleaned by Boeing's conventional critical cleaning methods. A plot relating results of the OSEE analysis of coupons cleaned by SFPC to Boeing's conventional critical cleaning method is included as Figure 5. The plot shows that surface cleanliness for coupons cleaned by supercritical carbon dioxide compare very favorably to coupons cleaned by conventional critical cleaning methods.

Results of the OSEE analysis also show that no significant difference in cleanliness levels was achieved by increasing temperature, run time, or pressure. The impact on contaminant removal due to changes in pressure and temperature may have occurred during the early stages of the test runs where the affect was not noticeable. Further changes in temperature, pressure, or run times may have a significant effect on cleanliness levels; however, a real time analysis is needed to accurately quantify how these changes influence mass transfer and ultimate cleanliness.

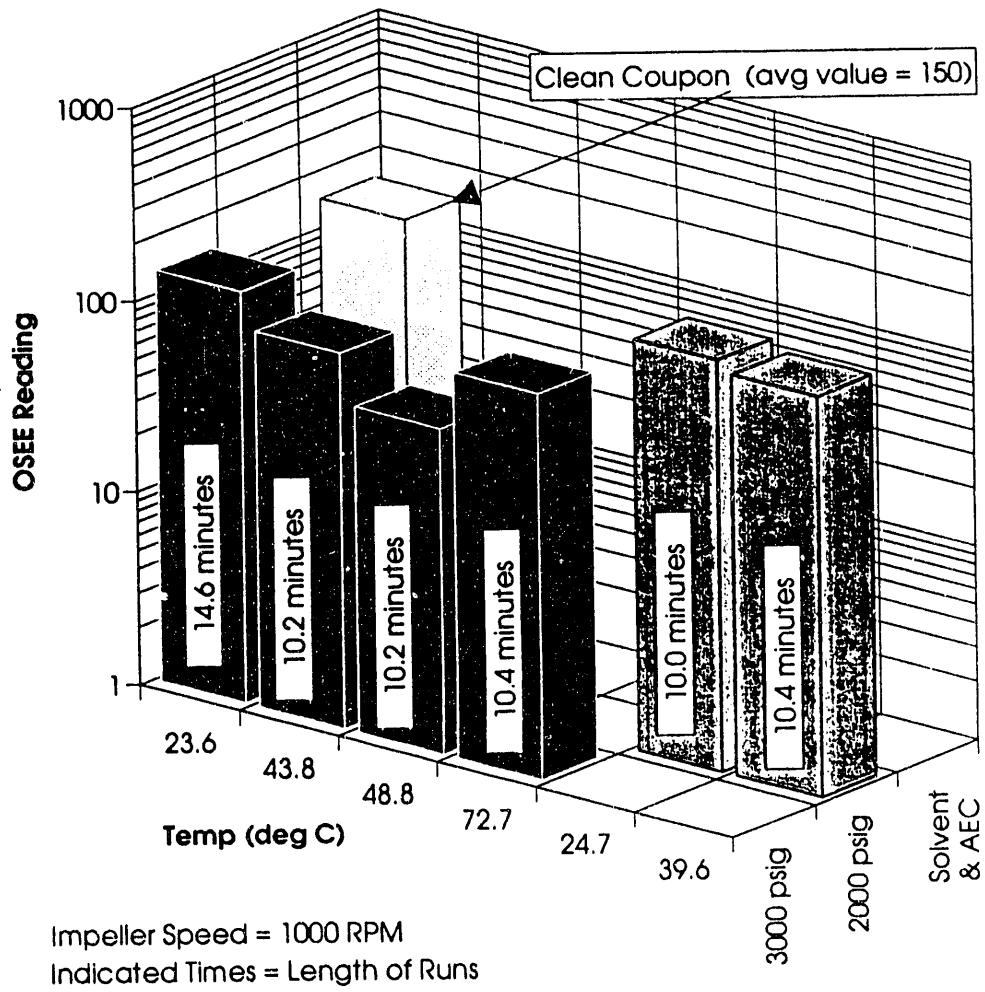


FIGURE 5. OSEE Analysis (Cleanliness level increases with value.)

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

- Power requirements for a SFPC system can be optimized by determining the relationship between mass flux of a contaminant and system agitation. Increasing the internal agitation can significantly reduce the time required to clean a part, but operation above the optimum is a waste of energy.
- Mass flux varies significantly with the type of contaminant being removed. Mass flux is also a function of temperature and pressure. Establishing guidelines for operating temperatures, pressures, and cleaning intervals for different contaminants and mixtures of contaminants could significantly reduce unnecessary energy consumption.
- Cleanliness levels of parts cleaned by SFPC compare favorably to levels attained through AEC and vapor degreasing techniques. SFPC however, is not deleterious to either operating personnel or the environment.

RECOMMENDATIONS

A real time analytical technique needs to be implemented to more precisely determine mass flux of a contaminant from the surface of a part being cleaned into the bulk fluid. Utilizing laser or fiber optic technology to observe a contaminant while it is being removed from the surface would help establish accurate quantifiable relationships between system dynamics and mass flux. An extension of analytical methods used is planned for FY 1993 bench-scale experiments.

Cosolvents may improve cleaning efficiency. Once quantifiable relationships between operating parameters and mass flux are established, the value of using cosolvents could be quantifiably established as well. Studies of cosolvents and hybrid SFPC/aqueous cleaning systems are planned for FY 1993 bench-scale experiments.

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