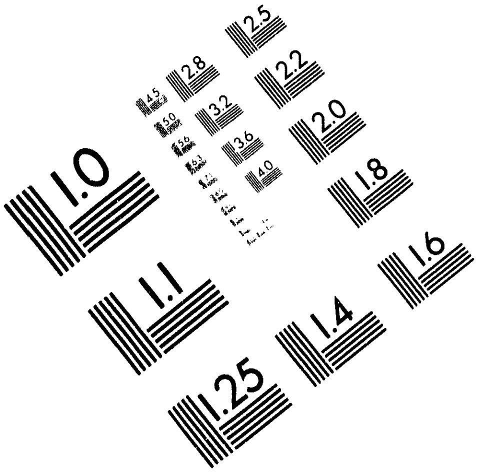

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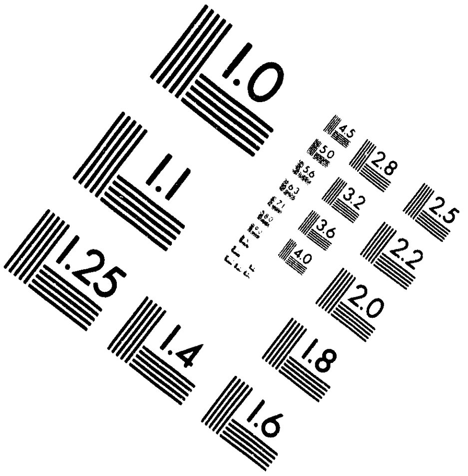

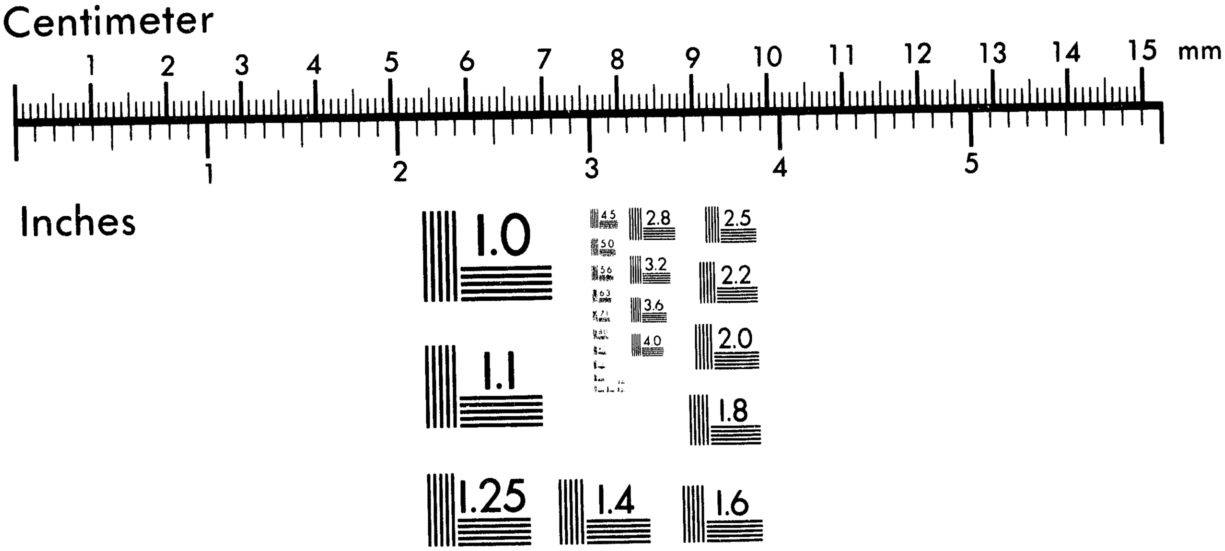

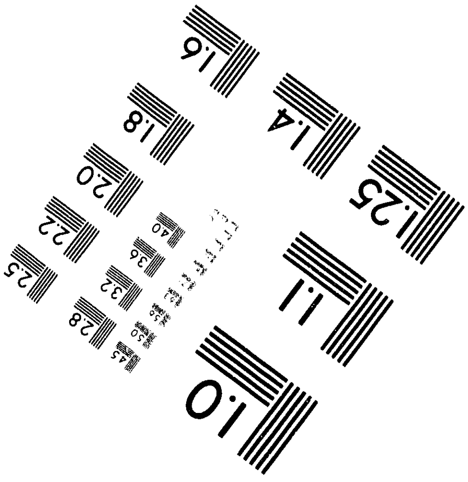

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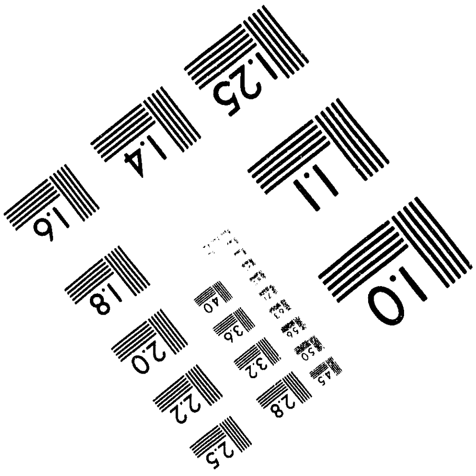

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CONTAMINANT REMOVAL FROM SOLID WASTE BY SUPERCRITICAL CARBON DIOXIDE*

H. Mike Smith and Ronald B. Olson, AlliedSignal Inc., Kansas City Division, Kansas City, MO
Carol L. J. Adkins and Edward M. Russick, Sandia National Laboratories, Albuquerque, NM

INTRODUCTION

Large quantities of solid wastes such as rags, kimwipes, swabs, coveralls, gloves, *etc.*, contaminated with oils, greases and hazardous solvents are generated by industry and the government. At present, these materials must be treated as hazardous waste, and the cost of disposal of such large volumes of hazardous materials is high. If the hazardous components (oils, greases and solvents) could be segregated from the much larger bulk of non-hazardous material, then these solid materials could potentially be handled as sanitary waste, at a significant cost savings. AlliedSignal KCP, a typical DOE manufacturing site, spent several hundred thousand dollars in CY92 for disposal of contaminated solid wastes. Similarly, Naval Air Station North Island, San Diego, also spent several hundred thousand dollars in CY91 for disposal of rags. This amounted to 30-40% of the total hazardous waste disposal costs at this site (these numbers were cut in half due to recycling efforts in CY92 and the base is looking for more cost cutting measures). Hill AFB in Utah, an Air Force Logistics Center, had over a hundred thousand pounds of contaminated rags, coveralls, etc., to dispose of in CY93. In each case, if the hazardous and non-hazardous components could be segregated and disposed of separately, costs would be reduced significantly.

Under the Department of Energy (DOE)/United States Air Force (USAF) Memorandum of Understanding, the objective of this joint AlliedSignal KCP/Sandia National Laboratories project is to demonstrate the feasibility of using supercritical carbon dioxide (SC-CO_2) to segregate hazardous oils, greases, and organic solvents from non-hazardous solid waste such as rags, wipes, swabs, coveralls, gloves, etc. Supercritical carbon dioxide possesses many of the characteristics desired in an "environmentally acceptable" solvent system. It is nontoxic, inexpensive, and recyclable. Carbon dioxide possesses a moderate critical temperature (31°C) and pressure (1071 psi). At 37°C and pressures greater than 2000 psi, the density is greater than 0.8 g/cc. A schematic of an ideal cleaning apparatus is shown in Figure 1. Contaminants dissolved in the supercritical CO_2 solvent are separated out by expansion of the fluid to a subcritical pressure where CO_2 is a gas and the dissolved materials precipitate out (usually as a liquid or solid). The gaseous CO_2 can then be recompressed and recycled.

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*This work was performed in part at AlliedSignal Inc., Kansas City Division, supported by the U.S. Department of Energy under contract number DE-AC04-76-DP00613, and in part at Sandia National Laboratories, supported by the U.S. Department of Energy under contract number DE-AC04-94AL85000.

Efforts to minimize the amount of hazardous waste requiring disposal are not only environmentally and socially conscious, but also minimize the "cradle-to-grave" liability associated with disposal. Regulatory agencies are beginning to allow the use of technology to separate hazardous waste from debris. Not only is the waste minimized due to the segregation of the non-hazardous debris, but if the "debris" can be recycled and reused a number of times before disposal, then sanitary landfill waste will also be minimized. Indeed, the time is right to address the "oily rag" issue!

EXPERIMENTAL EQUIPMENT AND METHODS

The experimental activity currently in progress is directed at determining the extractability and solubility of the major oils, greases, and solvents. Both the "extractability" and the "solubility" of the contaminant affect the cleaning/recycle process. Solubility is a thermodynamic equilibrium property of the solvent-contaminant system. Extractability, on the other hand, is the amount of contaminant that can be removed from the substrate. It is affected by the chemical nature of the contaminant and substrate, and the mass transfer in the cleaning system. The extractability of a contaminant cannot exceed its solubility. The solubility as a function of pressure and temperature determines the conditions that the separator must be operated at in order to achieve a given level of carbon dioxide purity in the recycle. Since the pressure drop must be recovered in the recompression step, the economics of the process are greatly affected by the separator conditions.

At Sandia, a high pressure view cell is used to measure the thermodynamic equilibrium solubility of contaminants in supercritical carbon dioxide. Pressures up to 10,000 psi and temperatures of 100°C can be achieved. Visual determinations of the phase conditions of a contaminant/CO_2 mixture as a function of temperature and pressure are made. The dew point (contaminant solubility in CO_2) or bubble point (CO_2 solubility in contaminant) of the mixture can be measured. From this data, equilibrium phase plots can be constructed as a function of concentration and solubility information obtained

At AlliedSignal KCP, a recycling supercritical carbon dioxide cleaning system was used to measure the extractability of oils, greases, and solvents from laboratory paper wipes as a function of the pressure, temperature, flowrate, and total mass flow of supercritical carbon dioxide. Figure 2 shows the recirculating waste segregation process cycle on a CO_2 phase diagram. The solid waste to be cleaned is placed in the extractor (position 1) and the SC-CO_2 flowing through the vessel dissolves the contaminants and carries them away. When the contaminant laden supercritical fluid expands across the pressure restrictor into the separator (position 2), the dissolved material precipitates out and is left behind in the separator. The gaseous CO_2 is cooled, reliquified (position 3), and then repressurized (position 4) to be used again in the extractor. This recirculating feature allows continual exposure of the contaminated solids to clean supercritical fluid for as long as necessary without consuming large amounts of CO_2. For example, at 75°C and 4700 psi, the cleaning system contains only 15 pounds of CO_2, but in a one hour run, 60 pounds of fluid are circulated through extraction vessel. At the end of a cleaning cycle, the clean solids are removed from the extractor to be reused or discarded as non-hazardous waste. The oils/greases/solvents, now in concentrated form, are drained from the separator and disposed of as hazardous waste.

Oils, greases, and typical solvents common to DOE/USAF facilities were identified. The list included 131 oils and greases in use at the Kansas City Plant and USAF bases. These were sorted by type and by monthly usage in order to allow a priority ranking for the experimental work. By far the most commonly used oils were hydraulic and cutting oils. A similar organic solvent list contained 29 solvents in use within DOE and USAF facilities consisting mostly of cleaning solvents, paint thinners, and aircraft fuels. Isopropanol, methyl ethyl ketone, and perchloroethylene were the most commonly used solvents.

DISCUSSION OF EXPERIMENTAL RESULTS

Twenty-five of the most commonly used oils identified above have been surveyed for solubility and extractability in SC-CO_2. The results have been very encouraging -- in most cases the percent contaminants removal has been > 99%. Only the most viscous, high molecular weight oils have resulted in lower removals, and even these typically exceed 96% at 75°C and 4700 psi. Mild conditions such as 45°C and 2600 psi are adequate for essentially complete removal of most of the contaminants. White paraffin oil has been used as a "standard" contaminant since it is pure and additive-free. The additives present in commercial oils are not typically removed and a stain remains on the rag. The amount of remaining contaminant is extremely small and is typically composed of viscosity modifiers such as highly branched polyisobutylene and polymeric butyl azelate esters. These polymeric materials are not normally considered to be hazardous substances.

Figure 3 shows the equilibrium solubility of three oils of differing viscosity. Lower viscosity oil has greater solubility in SC-CO_2. In a number of cases, solubility "limits" for the range of operating conditions possible in the view cell have been observed. For instance, 2.1 wt.% Mobil vis 300-320 hydraulic oil could not be dissolved under any conditions achievable in the view cell.

Table 1 shows the results of a detailed study of the extractability of five oils ranging in viscosity from < 100 to 1100 (Saybolt viscosity) as a function of the temperature and supercritical fluid density. The extractability for oils of viscosity 365 or less are relatively insensitive to temperature and fluid density variations in the range studied. The high viscosity oil, however, is very sensitive to both these variables because of its much lower solubility. The results in Table 1 were all generated at a total mass flow of 30 liters of SC-CO_2, essentially eight extraction vessel volume exchanges. This data is shown graphically in Figure 4, where the results are compared to the dilution model. The dilution model assumes the contaminant is completely soluble, the input and output flowrates are equal, and the vessel fluid is instantaneously homogeneous as dilution of the contaminant occurs with incoming pure CO_2:

$$Q_n = Q_o \exp(-n)$$

where Q_n is the contaminant concentration after n extractor volume exchanges by CO_2 and Q_o is the initial contaminant concentration. Figure 5 compares the extraction of the same five oils with the dilution model over a range of extraction exchange volumes. Note that again the high viscosity oil is removed more slowly than the dilution model predicts. This is due to its samll solubility. The other four oils follow or exceed the ideal dilution model. Any deviations from the dilution model are due to the fact that residual oil in the extractor condenses on the walls as well as the paper wipe upon decompression. Basically, at an initial contaminant loading of approximately 0.2 wt.%, 95% of the contaminant is removed within three volume exchanges. Clearly, the affect of loading on the extraction rate must be assessed. This data, however, will be highly apparatus specific because mass transfer will dominate.

Table 2 gives the extraction data for 22 common solvents in SC-CO_2 at 45°C and 2600 psi, which are very mild supercritical conditions. The number of vessel volume exchanges was 5.3 in all tests. The dilution model would predict a removal of at least 99.5% under these conditions, and it can be seen that all of the solvents exceeded that level. This result is supported by solubility measurments on some of these solvents (see Table 3). These data indicate that the solvents are soluble to at least 5% by weight at 45°C. Table 4 shows the results for the extraction of five solvents in ***liquid*** CO_2 at 28°C and 1450 psi. These are even milder conditions, but again, removal was complete after 5.3 vessel volume exchanges. These data reproduce the pioneering work of A. W. Francis (*J Phys Chem.*, **58**, 1954, 1099-1114) on the solubility of solvents in liquid CO_2. Any decrease in the system operating pressure would result in a decrease in the capital cost of the full scale system.

CONFORMANCE WITH FEDERAL AND STATE REGULATIONS

The disposal of hazardous solvents is regulated nationally, with additional local regulation possible. In the past, "treatment" of hazardous debris waste and separation into its hazardous and non-hazardous components was not allowed. There are now, however, federal regulations covered in the Federal Register, Vol. 57 No. 168, August 28, 1992, *Land Disposal Restrictions for Newly Listed Wastes and Hazardous Debris*, that specify performance standards for the solvent separation of certain hazardous wastes from non-hazardous debris. As is noted in the Federal Register, the philosophy is as follows (Section V.D.1): "...It is not normally the debris itself that is hazardous, but rather hazardous waste that is contaminating the debris. Thus, the goal of treatment should be to destroy or remove the contamination (if possible) and if this is achieved, to dispose of the cleaned debris as a non-hazardous waste..." 'Performance" standards are established. The requirements for liquid solvent extraction are 15 minutes contact between the debris and solvent, and the contaminant must be soluble to at least 5% by weight in the solvent. The requirements for vapor phase solvent extraction are identical except 60 minutes contact is specified. In each case it is assumed that the contaminants enter the solvent phase and are flushed away from the debris. Since a supercritical fluid is neither a liquid nor a gas, but has solvation powers and densities similar to a liquid and transport properties similar to a gas, the application of this standard to SC-CO_2 would have to be ascertained. However, the performance requirements (time and solubility) can be met for most common solvents (Table 3).

The regulation of oils and grease disposal is addressed primarily by the states. State of Missouri regulations are currently being examined to determine if solid waste contaminated with oils and greases, and "cleaned" by SC-CO_2, could be disposed of in Missouri sanitary waste landfills. The recycle of material -- the reuse of cleaned rags -- is considerably easier than their disposal.

CONCLUSIONS AND FUTURE WORK

The experimental data included here are only a fraction of the total collected to date. However, these results clearly indicate that the concept of separating hazardous waste from non-hazardous solids using supercritical carbon dioxide is even more viable than we had hoped. While much remains to be done, it would appear that the project will be entirely successful in demonstrating feasibility of the concept. For a waste stream consisting primarily of solvents, it should be possible to run at liquid CO_2 conditions, thus literally meeting the requirements of the debris rule.

Research into separator performance is planned for FY95. Again, this is particularly important for the solvents which tend to have higher vapor pressures than the oils and greases. High vapor pressure material will be carried over in a typical pressure reduction separator. This issue must be addressed for several reasons: (1) if the solvent is not removed in the separator, the recycle system reaches a saturation equilibrium concentration and no more solvent is removed from the solid waste; and (2) the solvents are more likely to present a worker safety issue and if the recycle system is saturated, solvent will be vented during the vessel depressurization and the worker will exposed when the vessel is opened.

A second major objective for FY95 is the design of a full scale system (200 liter extractor volume) to be installed in the KCP in FY96. The Waste Management Department of the AlliedSignal KCP has submitted a capital equipment request to install such a system in 1996. They are, in effect, our primary customer. The full-scale unit will serve both as a treatment facility for the Kansas City Plant and a manufacturing-scale demonstration unit for other DOE plants, USAF and other military service facilities, and any other government or private agency interested. The present laboratory cleaning apparatus at AlliedSignal can be used to demonstrate the principle on actual solid waste, but does not have the capacity that a waste treatment unit would require.

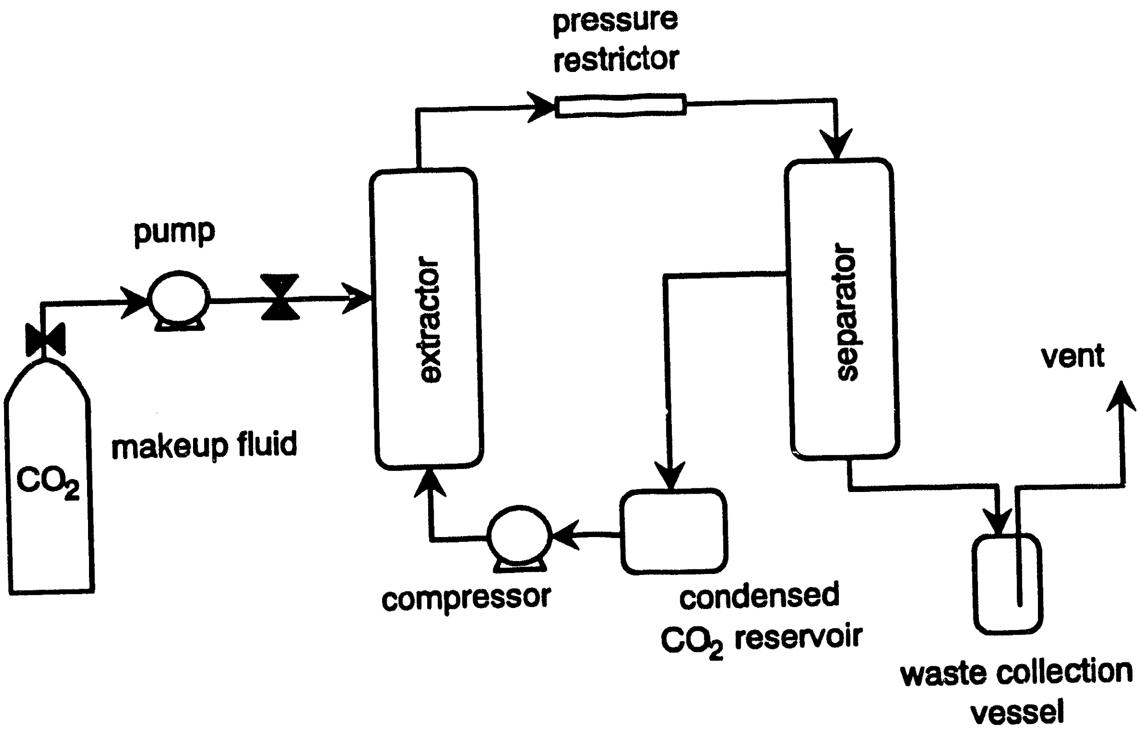

Figure 1. Ideal supercritical carbon dioxide cleaning apparatus.

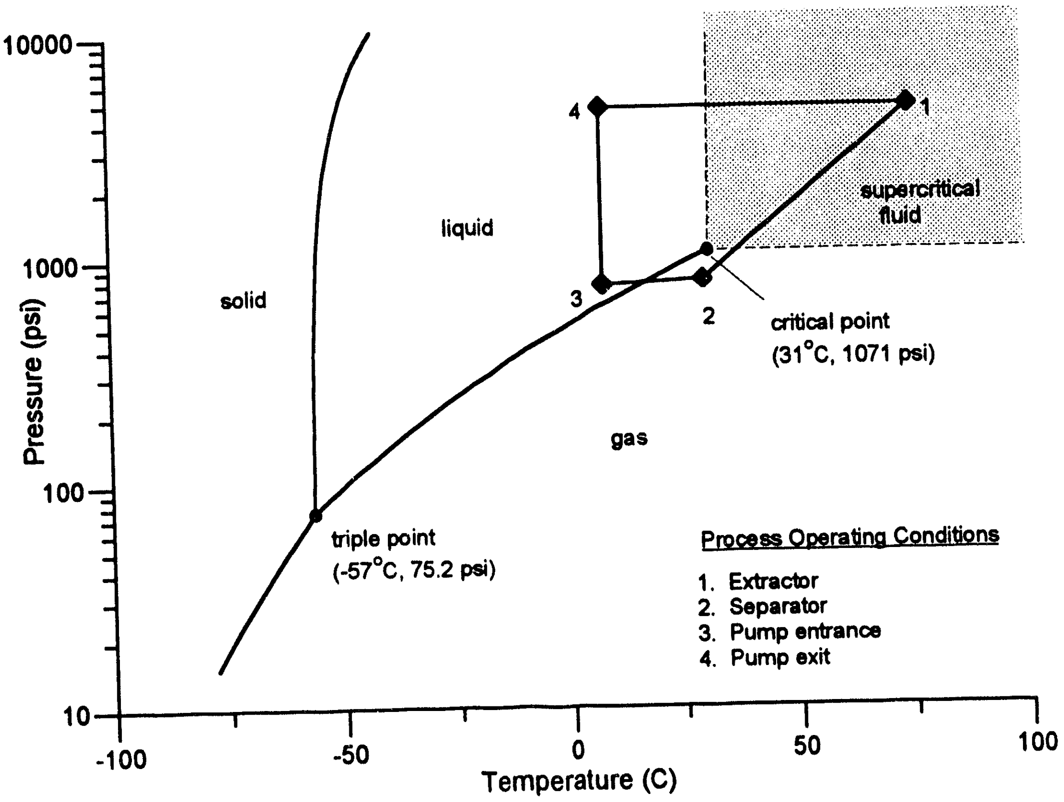

Figure 2. Process Operating Conditions for SC-CO_2 cleaning system.

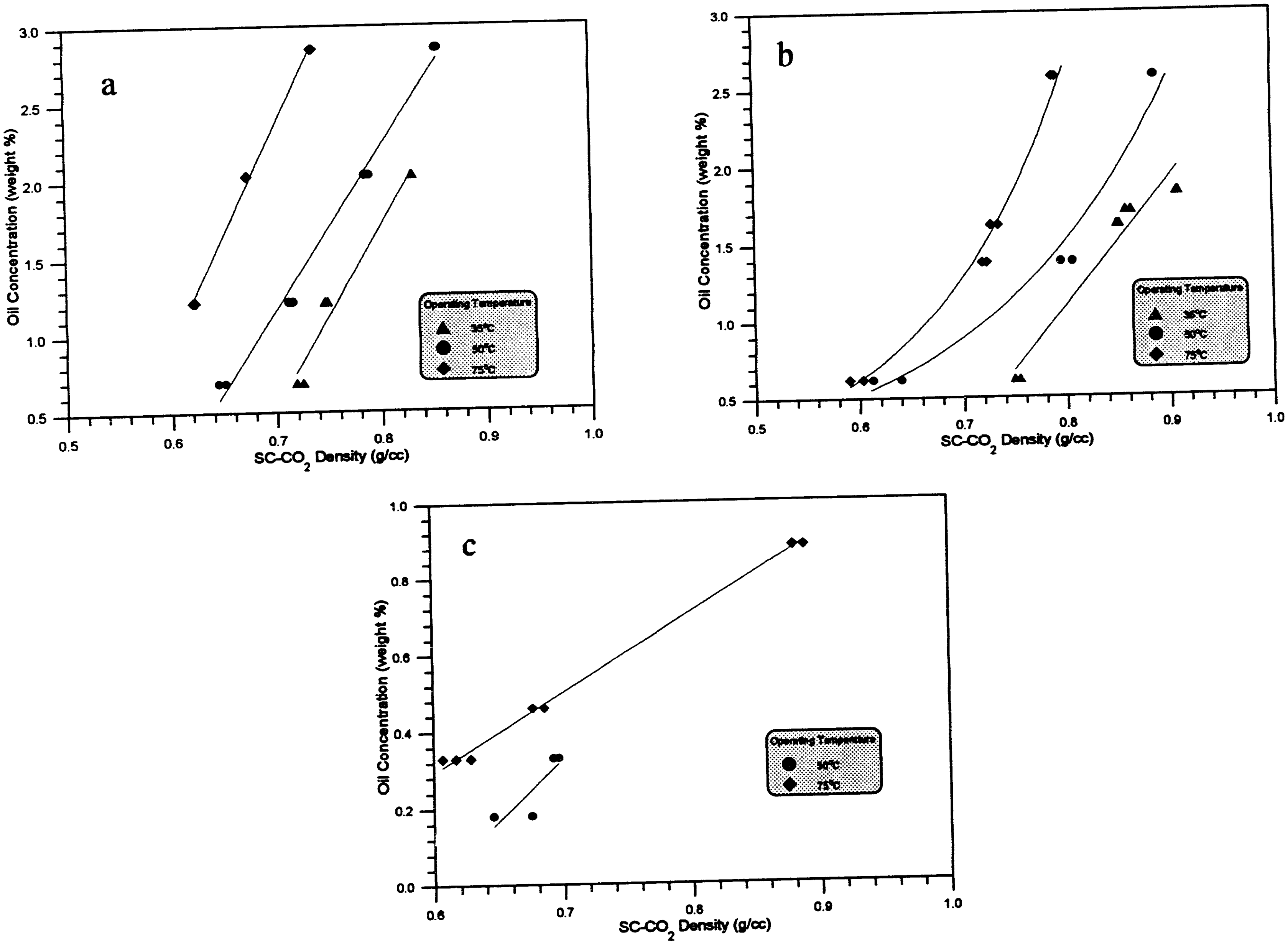

Figure 3. Solubility of (a) light hydraulic oil Mobil vis 145-160, (b) light hydraulic oil Mobil vis 300-320, and (c) general use oil Mobil DTE vis 1045-1165 as a function of the equivalent pure SC-CO$_2$ density.

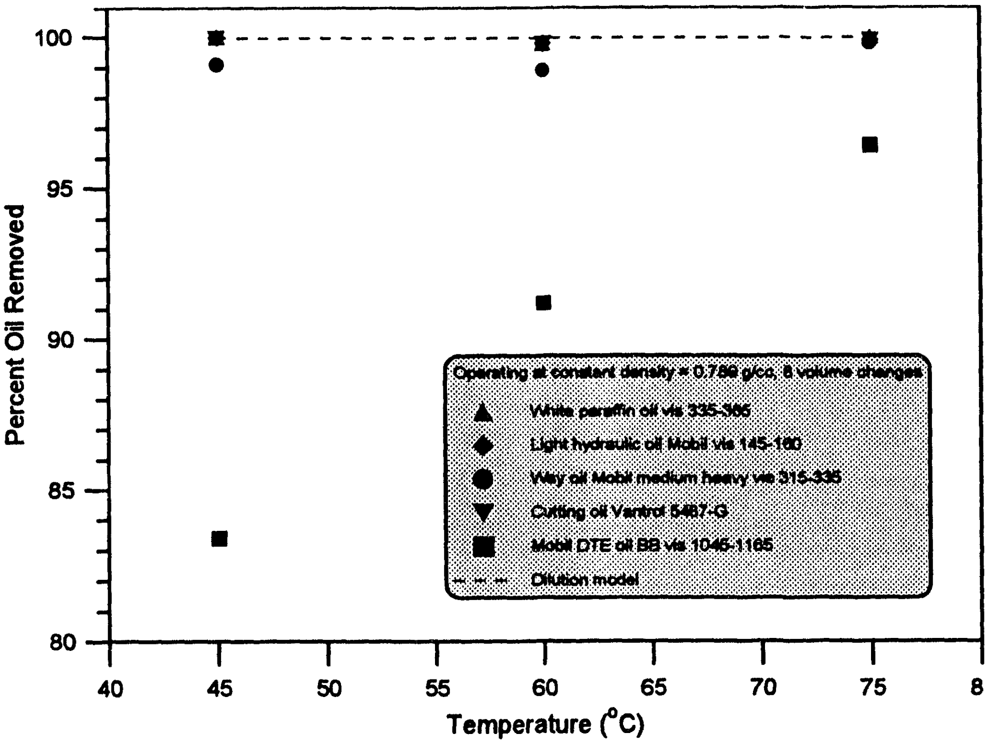

Figure 4. Percent oil removed by supercritical CO_2 as a function of temperature.

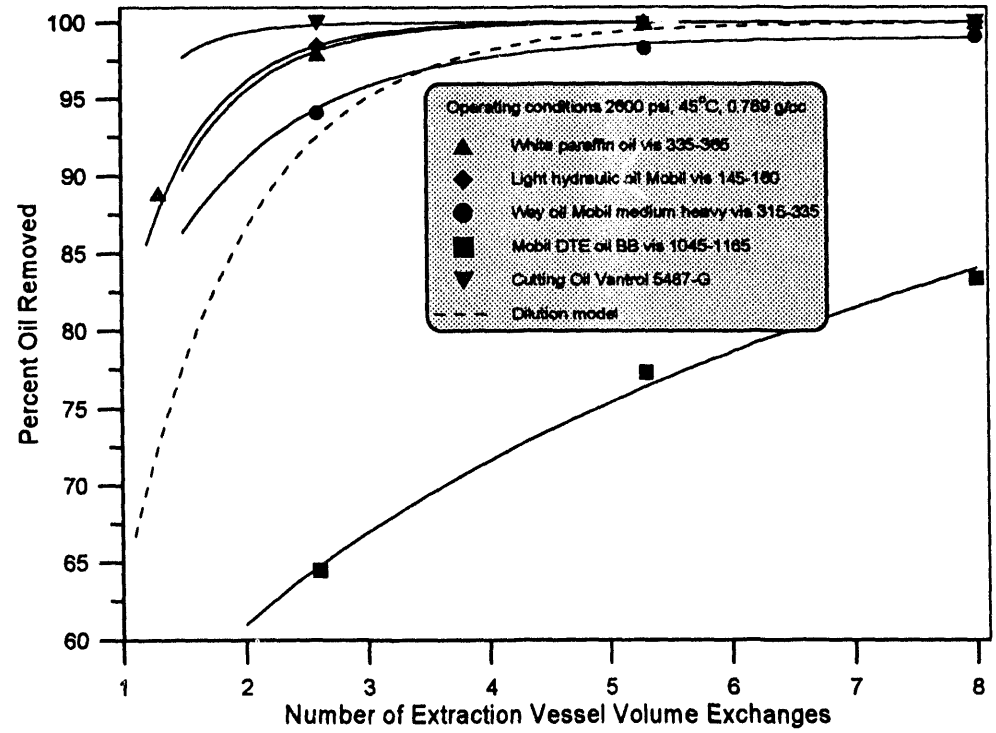

Figure 5. Percent oil removed by supercritical CO_2 as a function of vessel volume exchanges.

Table 1. Oil and Grease Removal Experiments

Temperature (°C)	Pressure (psig)	CO_2 Density (g/cc)	Total Liters CO_2	% Removed				
				Mobil vis 145-160	**Mobil vis 315-355**	**Paraffin vis 335-365**	**Vantrol 5487-G**	**Mobil DTE vis 1045-1165**
45	2000	0.716	30	99.8	97.5	99.7	100	
45	2600	0.789	30	100	99.1	100	100	83.4
45	3400	0.8458	30	99.7	99.0	100	100	
45	4700	0.9048	30	99.7	99.1	100	100	
60	2800	0.7125	30	99.7	98.3	100	99.9	
60	3600	0.7854	30	99.8	98.9	99.8	99.8	91.2
60	4700	0.8475	30	99.6	99.1	100	99.8	
75	2600	0.5732	30	99.6	96.7	99.8	99.8	
75	3700	0.7186	30	99.6	99.2	100	99.9	
75	4700	0.7884	30	99.9	99.8	100	99.9	96.4

Table 2. Solvent Removal Efficiency Screening*

Solvent	Vessel Pressure (psi)	Vessel Temp. (°C)	CO_2 Density (g/cc)	% Removed
Acetone	2600	45	0.7890	100.0
Actrel 4493 (Exxon)	2600	45	0.7890	100.0
Benzene	2600	45	0.7890	100.0
Carbon tetrachloride	2600	45	0.7890	100.0
Chloroform	2600	45	0.7890	100.0
Cyclohexane	2600	45	0.7890	100.0
Ethyl acetate	2600	45	0.7890	99.9
Ethyl lactate	2600	45	0.7890	100.0
Heptane	2600	45	0.7890	100.0
Hexane	2600	45	0.7890	100.0
Iso-octane	2600	45	0.7890	100.0
Isopropanol	2600	45	0.7890	100.0
d-Limonene	2600	45	0.7890	100.0
Methanol	2600	45	0.7890	100.0
Methyl ethyl ketone	2600	45	0.7890	100.0
Methylene chloride	2600	45	0.7890	100.0
Perchloroethylene	2600	45	0.7890	100.0
Tetrahydrofurfuryl alcohol	2600	45	0.7890	100.0
Trichloroethylene	2600	45	0.7890	100.0
Toluene	2600	45	0.7890	100.0
p-Xylene	2600	45	0.7890	100.0
1,1,1 Trichloroethane	2600	45	0.7890	100.0

* 5.3 vessel volume exchanges each run

Table 3. Solubility Check at Approximately 5 wt.% Contaminant Concentration

Solvent	Concentration (wt.%)	Average Pressure at 45°C (psi)
Cyclohexane	5.81	1423
Isopropanol	5.57	1232
Methyl ethyl ketone	5.46	1218
Methylene chloride	5.22	1179
n-Hexane	6.72	1268
Perchloroethylene	5.78	1218
Tetrahydrofurfuryl alcohol	5.00	1690
Toluene	6.34	1241

Table 4. Liquid CO_2 Solvent Extraction*

Solvent	Vessel Pressure (psi)	Vessel Temp. (°C)	CO_2 Density (g/cc)	% Removed
Isopropanol	1450	28	0.7890	100.0
Methyl ethyl ketone	1450	28	0.7890	100.0
Perchloroethylene	1450	28	0.7890	100.0
Toluene	1450	28	0.7890	100.0
1,1,1 Trichloroethane	1450	28	0.7890	100.0

* 5.3 vessel volume exchanges each run

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