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Stripping Organics from Metal and Mineral Surfaces Using Supercritical Fluids

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ABSTRACT

Superalloy grinding swarf was treated with supercritical CO_2 alone, and with various modifiers. Experiments were conducted in a downflow batch mode at pressures of 0 to 5,000 psig, temperatures of 20° to 250° C, and times of 15 to 240 min using up to 25 g of solvent per gram of swarf. Organic dissolution increased with pressure almost linearly to 5,000 psig. Temperature affected dissolution slightly at lower pressure, but not significantly at higher pressure. Certain alcohols used as modifiers dramatically improved organic dissolution. The solvent, modifier, organics, and solids were easily recovered as separate products.

INTRODUCTION

The United States imports many critical metals from potentially interruptible sources because domestic sources for these metals are subeconomic using existing technology. New concepts and methods are needed to process domestic ores or secondary resources. Supercritical fluid extraction is a developing class of extractions having potential applicability to mineral processing.

Although first used as solvent for inorganic salts, supercritical fluids are now used almost exclusively for food and petrochemical separations (1). The Bureau of Mines, U.S. Department of the Interior, is conducting both basic and applied research to determine the applicability of supercritical solvent systems for processing complex ores, secondary sources, and solutions. These studies are being conducted as part of the Bureau's research program to help ensure future supplies of critical and strategic materials by improving domestic supply capabilities.

Supercritical solvents offer several advantages for removing organic materials from metals and concentrates. Carbon dioxide, which is the most widely used supercritical fluid, is inexpensive, nontoxic, noncorrosive, and nonflammable. Because this solvent is insoluble in the organic fraction at ambient conditions, complete separation of the solute and solvent is possible. The organic product is not contaminated with solvent; thus, the organic may become a valuable product rather than a waste. Concurrently, the solvent is not contaminated with organic material; thus, a high proportion of the solvent can be recycled with a minimum of waste.

Although supercritical solvents are attractive in these applications because of their chemical properties, they must be handled in specialized equipment. For example, Friedrich (2) found that pressures on the order of 5,000 psig were necessary to produce seed oil solubilities of 1 pct in supercritical CO_2. Considerable care is always required in constructing and operating equipment at these high pressures.

This paper describes recent research by the Bureau in the application of supercritical CO_2 and supercritical CO_2 with modifiers to deoil superalloy grinding swarf with recycle and reuse of the supercritical fluid, modifier, oil, and swarf.

RESOURCE DESCRIPTION

Superalloy grinding waste is an untapped, high-grade, secondary resource, containing up to 50 pct Co, Ni, and Cr. Approximately 5 MM lb/yr of this material are generated. Since the United States has no domestic mine production of chromium or cobalt (3), recovery of these metal values would significantly improve domestic supply.

The superalloy waste tested in this investigation was a grinding swarf obtained from TRW Inc., Valve Division, Cleveland, OH. The metal fraction contains approximately, in weight percent, 32 Fe, 21 Cr, 16 Co, 12 Ni, and 6 W with minor amounts of aluminum and silicon also present. However, the grinding waste is contaminated with grease, which must be removed to render the scrap metal suitable for reprocessing. The waste is generated during the manufacture of valves for internal combustion engines. This grinding swarf is material filtered from the cutting oil before the oil is recycled. The particle size of the metal fraction is about 45 pct less than 37μm diam (minus 400 mesh); however, the oil causes agglomeration of the swarf into lumps with diameters as large as 3 cm.

In order to use hydrometallurgical techniques to recover the metals, the oil content must be reduced from the 22-pct level present in the filter cake from the production plant to less than 5 pct. Similarly, oil removal would also be necessary prior to a smelting operation to prevent carbide formation in the metal product. Standard solvent degreasing schemes have proven impractical for this waste material because of its small particle size. Liquified gas at the relatively low pressure of 100 psig has been used to remove oil from mill-scale waste. However, it is necessary to distill the solvent for recycle (4). In order to devise a practical system for recovering the strategic and critical metals in this waste, alternative degreasing techniques using supercritical fluid extraction were investigated.

TEST EQUIPMENT

An Autoclave Engineers[a] Supercritical Extraction Screening System, shown in Fig. 1, was modified for these studies. After startup,

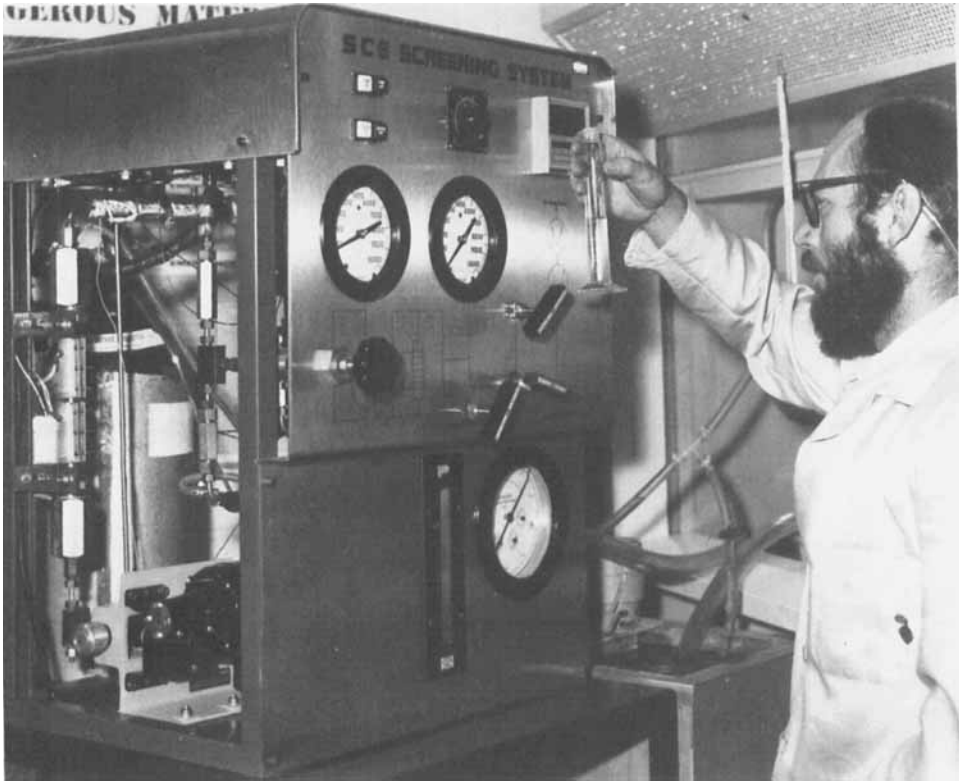

Fig. 1. Supercritical extraction system

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[a] Reference to specific products does not imply endorsement by the Bureau of Mines.

the modified system was operated by remote control. All material that came in contact with the supercritical fluid was constructed of 316 stainless steel.

The extractor vessel, depicted schematically in Fig. 2, was a 1.75-cm-ID by 30-cm-long fixed-bed tubular autoclave with a glass fiber filter in the bottom of the vessel to retain small particles. The sample bed was supported 8 cm above the bottom of the vessel to ensure a uniform bed temperature. The extractor vessel was heated by ceramic heaters secured to the outside of the vessel. A thermocouple between the heater and the vessel wall actuated the temperature controller. Bed temperature was measured directly by a thermocouple inserted into the vessel through the outlet.

Liquid chromatography pumps capable of delivering liquid at rates of 2.76 to 27.6 L/h and at pressures up to 6,000 psig were used to pump liquid CO_2 and modifiers into the system. System pressure was

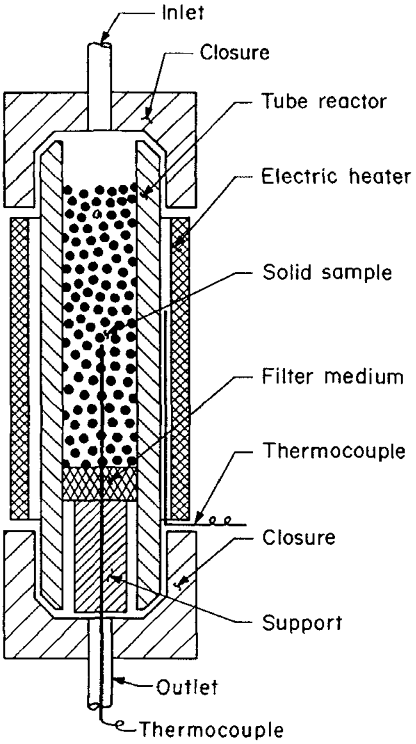


Fig. 2. Extractor vessel

monitored by a pressure gauge on the inlet to the extractor vessel and controlled by a back pressure regulator on the outlet of the extractor vessel. Dry ice formation inside the nozzle of the back pressure regulator was prevented by wrapping the regulator with heating tape. Pressure letdown was accomplished either through the back pressure regulator or through a metering valve.

Solute in the supercritical fluid was captured downstream from the pressure reducer in a separator, which was maintained at room temperature and pressure. Carbon dioxide gas exited through the top of the separator and vented through a dry test meter to measure CO_2 gas consumption.

EXPERIMENTAL PROCEDURE

For these tests, 35 g of superalloy grinding waste was charged to the extractor vessel, which was then sealed into the system. A flow diagram is shown in Fig. 3. The CO_2 tank valve was opened and the pump was turned on to flood the system with CO_2 in a static mode. Heating and pressurizing were then started and operation proceeded by remote control. When the system reached the targeted temperature and pressure, the relief valve on the back pressure regulator opened, allowing the supercritical fluid to flow through the system. The flow rate of the supercritical fluid was constant for each test at approximately 3.5 mol/h. All tests were conducted in a downflow mode on a semicontinuous basis. The extraction period was measured from the time when the targeted temperature and pressure were reached to the time when the pressure was vented during pressure letdown at the

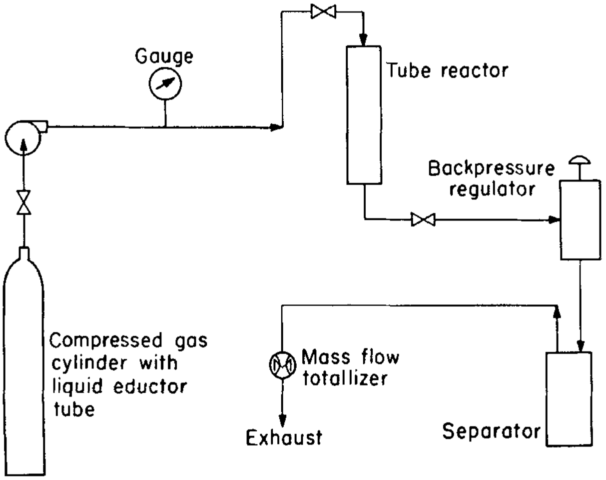


Fig. 3. Supercritical extraction apparatus

end of the test. The extraction period ranged from 10 to 240 min to establish the effect of solvent use on the oil extraction.

Oil content of the supercritical fluid was calculated as the weight of oil lost during extraction divided by the weight of solvent used during the extraction. Solvent use during an extraction was calculated from the volume of gas passing through the dry test meter corrected for temperature and pressure. All gas passing through the system, both during the test and during pressure letdown, was measured by the dry test meter. The amount of oil remaining with the metal swarf after each extraction was measured by washing the solids with perchloroethylene in a Soxhlet extractor; oil content was determined from the weight loss during the Soxhlet extraction.

EXPERIMENTAL DESIGN

The objective of this study was to remove organic materials from metal surfaces. Because the distribution of the compounds on the surface is not known, the data from these studies are not equivalent to equilibrium solubility data using pure compounds. The approach was to maximize organic dissolution in the solvent, and thereby minimize reagent consumption. Variables examined were pressure, temperature, processing time, solvent composition, and volume.

Data were evaluated using a multilevel analysis of variance. Variables producing effects at greater than 95-pct confidence interval were considered to be significant to the extraction.

DISCUSSION OF RESULTS

Initial results using supercritical CO_2 to remove oil from superalloy scrap showed definite extraction, but low solute concentrations. Subsequent test results demonstrated that more rapid oil extraction and increased solvent capacity were achieved by modifying the supercritical CO_2 with a cosolvent.

CO_2 Solvent

Supercritical CO_2 extracted oil from the grinding swarf better than liquid CO_2 at the same density. Using solvent at a density of 0.8 g/cm^3, supercritical CO_2 loaded to 2.33 pct oil; liquid CO_2 loaded to 1.54 pct. As shown in Fig. 4, oil concentration in liquid CO_2 decreased steadily during oil extraction. However, oil concentration in the supercritical fluid (curve "A") initially increased as the extraction process proceeded. Although kinetics of the oil dissolution were not investigated, the initial increase in oil content of the supercritical fluid is believed to result from a higher dissolution rate as contact time between the oil and solvent increased. Because solvent flow rate was constant with respect to time, the horizontal axis of Fig. 4 is directly related to time. The peak in curve "A", therefore, is believed to be a kinetic rather than equilibrium phenomenon.

The data from curve "A" of Fig. 4 are replotted in Fig. 5 (curve A) against unrecovered oil available for extraction. The oil content

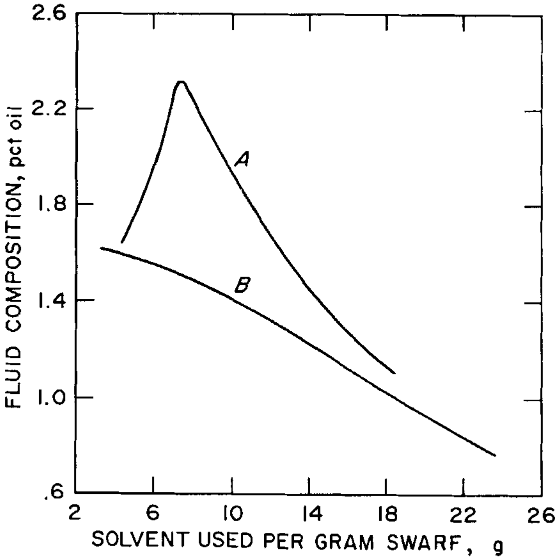


Fig. 4. Phase effect on fluid composition at 0.8 g/cm³.
A. Supercritical CO_2 at 50° C and 5,000 psig
B. Liquid CO_2 at 20° C and 2,000 psig

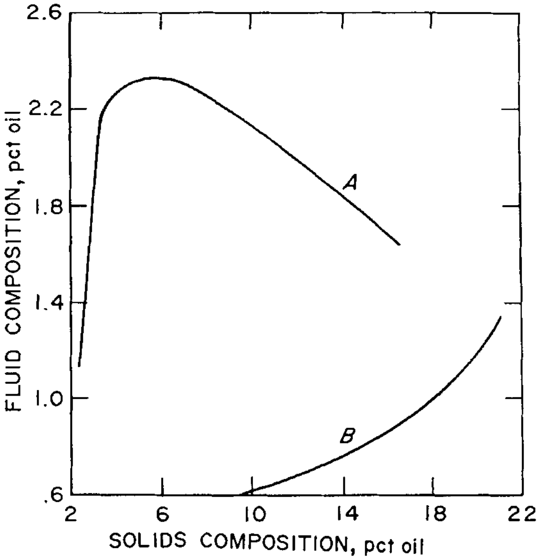


Fig. 5. Oil concentration in supercritical CO_2 plotted against amount of unrecovered oil remaining with the grinding swarf. All extractions were conducted at 50° C in downflow mode at constant solvent flow rate.
A. 5,000 psig
B. 2,000 psig

of the 5,000-psig supercritical CO_2 initially increased as the oil content of the solids dropped from the initial 22 pct level of the feed. This increase, as discussed above, was ascribed to increasing oil dissolution rate as contact time between oil and solvent increased. When the oil content of the solids dropped below 6 pct, which required approximately 30 min and 7.3 g CO_2 per gram grinding swarf, oil concentration in the supercritical fluid began dropping rapidly. During extractions at 2,000 psig (Fig. 5, curve "B"), the oil content of the supercritical CO_2 decreased steadily as the amount of unrecovered oil in the solids decreased. In this case, oil dissolution rate appeared constant during the entire extraction process.

Oil removal at 50° C increased dramatically as the pressure was increased from 0 psig (atmospheric) to 5,000 psig, as depicted in Fig. 6. Oil content in the fluid phase also increased with increased pressure, as shown in Fig. 7. Using 6.3 g CO_2 per gram swarf, oil concentration in the supercritical fluid ranged from 0.85 pct at 2,000 psig to 2.33 pct at 5,000 psig; this is quite an advantage because at atmospheric pressure, the fluid phase contained only 0.29 pct oil at 50°C as a result of the vapor pressure of the oil.

The effect of temperature was dependent on the pressure. Fig. 8 demonstrates that increasing the temperature at pressures of 2,000 psig and below significantly increased the oil dissolution. Increasing the temperature from 50° to 150° C increased the oil content of the fluid from 0.85 to 1.56 pct at 2,000 psig, and from 0.29 to 0.74 pct at 0 psig (atmospheric pressure) due to the increased vapor pressure of the oil. It is important to recognize that in this case, the dissolution of oil in the supercritical fluid appeared to be a function of vapor pressure. At 5,000 psig, the oil content increased from 1.9 to 2.4 pct when the temperature was increased from 50° to 150° C. This increase was insignificant at the 95-pct confidence limit.

Modifiers

Supercritical CO_2 degreased superalloy scrap, but solvent capacity was low. One method to increase the solubility of a solute in a supercritical solvent is to add an entrainer (1) or modifier. The major objective of the next phase of research was to determine the effects of modifiers on oil dissolution in supercritical CO_2.

A baseline study compared oil solubilities in several pure solvents that were considered as potential modifiers for supercritical CO_2. In these tests, 20 g of superalloy swarf was mixed with 100 mL of pure solvent at 23° C and atmospheric pressure for 24 h. Results for five pure solvents are shown in Fig. 9. As the polarity of the pure solvent decreased, the oil solubility increased, as demonstrated by poor oil solubility in methanol, better solubility in methoxyethanol and acetone, and excellent solubility in isopropanol and n-hexane. As shown in Fig. 9, the latter two solvents completely degreased the swarf.

These solvents were next tested as modifiers for supercritical CO_2. Results in Table 1 show that in these tests there was no trend

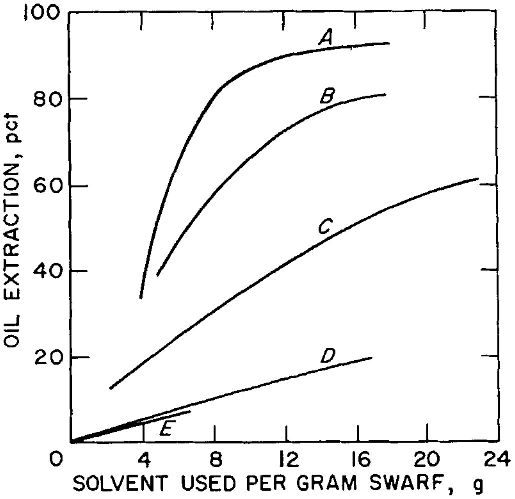
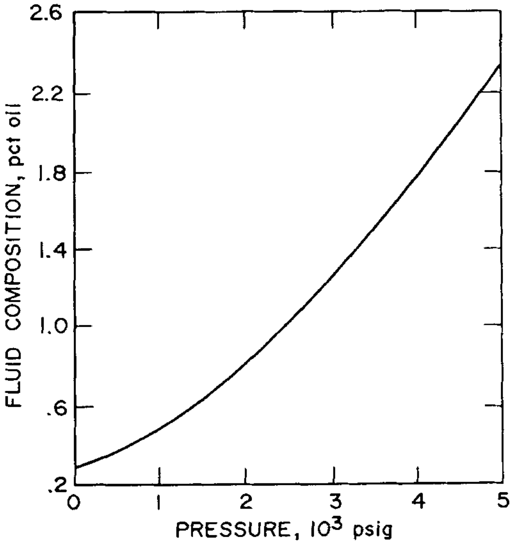


Fig. 6. Pressure effect on oil extraction using supercritical CO_2 at 50° C.

A. 5,000 psig
B. 4,000 psig
C. 2,000 psig
D. 1,500 psig
E. 0 psig



7. Pressure effect on supercritical fluid composition at 50° C using 6.3 g CO_2 per gram swarf

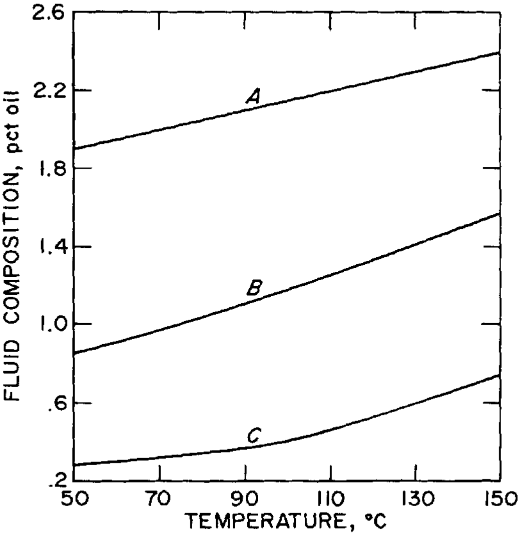


Fig. 8. Temperature effect on fluid composition using 5.9 g CO_2/g swarf.
A. Supercritical CO_2 at 5,000 psig
B. Supercritical CO_2 at 2,000 psig
C. Gaseous CO_2 at 0 psig

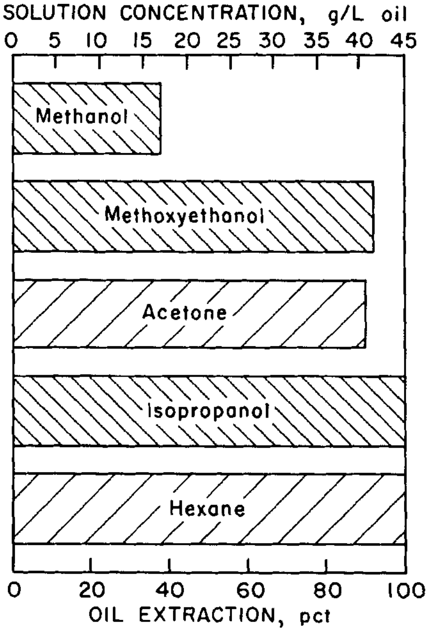


Fig. 9. Oil solubility in pure solvents at ambient conditions

TABLE 1
Comparison of oil content of the fluid extract containing supercritical CO_2 and various modifiers at 50° C and 2,000 psig

Modifier	Modifier concentration, pct	Solvent consumption per gram swarf, g	Fluid composition, pct oil
None...........	0.0	6.3	0.85
Acetone.........	31.1	10.9	.87
N-hexane........	8.5	7.3	[1]>3
Methoxyethanol..	5	5.3	[1]4.0
Isopropanol.....	44.5	5.8	[1]4.1
Methanol........	37.9	3.3	[1]6.3

[1]Complete oil extraction by the end of the test.

linking increased oil content of the extract fluid to decreased polarity. The alcohol functionality appeared to influence oil removal more than polarity of modifiers in supercritical CO_2. Acetone, a relatively polar solvent, did not increase the effectiveness of supercritical CO_2, although oil solubility was high in the pure liquid solvent. Normal hexane, a straight-chain hydrocarbon, and the longer chain alcohols, methoxyethanol and isopropanol, were all effective modifiers; each increased the oil content of supercritical CO_2 from 0.85 pct to better than 3 pct. Methanol, a polar alcohol, was as effective as any of the other modifiers tested, although it displayed the lowest affinity for the oil as a pure liquid solvent. The key advantage of methanol, unlike the other modifiers reported, was its low solvent capacity for oil at ambient conditions allowing simple recovery and immediate recycle of the modifier.

Oil extraction using methanol-modified supercritical CO_2 at 50° C and 2,000 psig is shown in Fig. 10. The addition of methanol decreased solvent consumption and consequently decreased the cycle time required for degreasing.

Composition of the supercritical CO_2-methanol solvent affected oil content of the fluid extract. Fig. 11 shows best oil removal occurred using a solvent composition of 30 to 60 pct methanol when extracting at 50° C and 2,000 psig. Oil extraction decreased dramatically when using methanol levels below this range, and decreased somewhat when using methanol levels above this range.

Increasing the temperature increased the oil content of the mixed solvent and increased the extraction rate, especially when using lower levels of methanol. Fig. 12 shows, within the confidence limits of these tests, that increasing the temperature from 50° to 150° C decreased solvent consumption from 8.1 to 3.5 g per gram swarf for complete degreasing using 30 to 60 pct methanol at 2,000 psig. This corresponds to oil content of the fluid phase of 6.24 pct at 50° C and 6.64 pct at 150° C. The effect was more pronounced when using only 14 pct methanol at 2,000 psig, where oil content of the fluid phase increased from 2.2 pct at 50° C to 4.4 pct at 150° C.

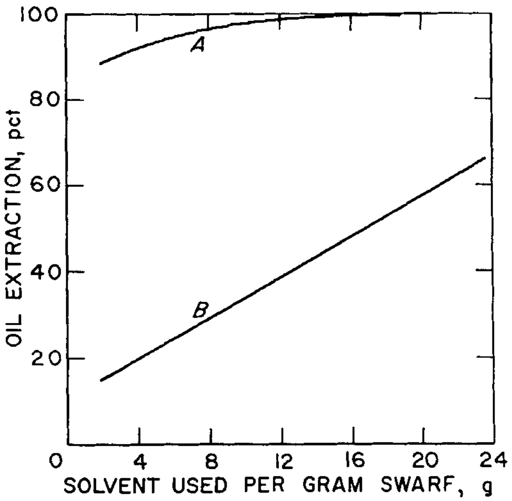


Fig. 10. Methanol modifier effect on oil extraction at 50° C and 2,000 psig.
A. Supercritical CO_2 modified with 30-60 pct methanol
B. Supercritical CO_2

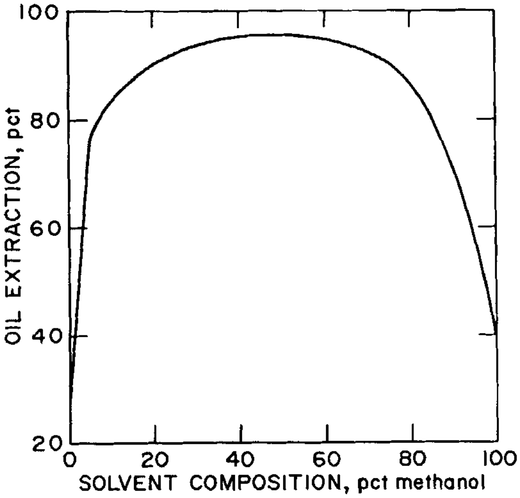


Fig. 11. Effect of solvent composition on oil removal at 50° C, 2,000 psig, and 6.3 g solvent per gram swarf

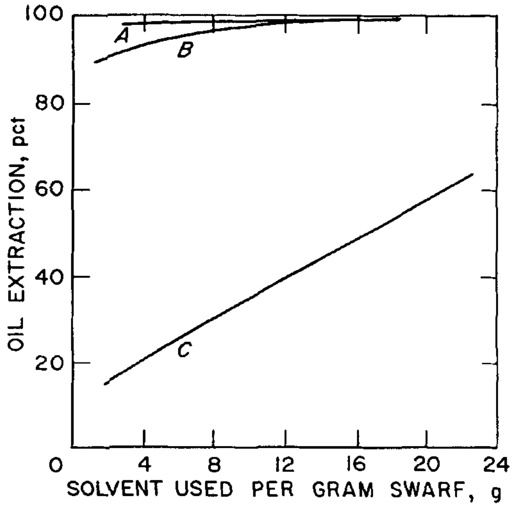


Fig. 12. Temperature effect on oil extraction at 2,000 psig.
A. Supercritical CO_2 with 30-60 pct methanol at 150° C
B. Supercritical CO_2 with 30-60 pct methanol at 50° C
C. Supercritical CO_2 at 50°C

PROCESS IMPLEMENTATION CONCEPTS

Results, shown in Fig. 13, demonstrate that two of the alternatives tested are effective for degreasing grinding swarf produced from superalloy scrap: (1) supercritical CO_2 at 50° C and 5,000 psig, and (2) supercritical CO_2 with 30 to 60 pct methanol modifier at 50° C and 2,000 psig. Each alternative has specific advantages and disadvantages for commercialization.

Supercritical CO_2 is not an electrolyte, so corrosion would be minimal and equipment could be fabricated from low-alloy steel (2). However, the equipment would need to withstand 5,000 psig. Processing time to reduce the oil content from 22 to 5 pct would be about 60 min, which would result in a cycle time of about 90 min.

The supercritical CO_2-methanol solvent is potentially corrosive because of possible liquid methanol condensation in process equipment; thus, this system would need corrosion protection, but would operate at only 2,000 psig. Processing time to reduce the oil content from 22 to 5 pct would be only 15 min, which would result in a cycle time of 45 min.

Both systems, using current technology, would process on a semicontinuous basis using batch extractions. Assuming waste is produced at 1 MM lb/yr, and assuming five batches could be processed daily for 250 d/yr, the supercritical CO_2 system would require a

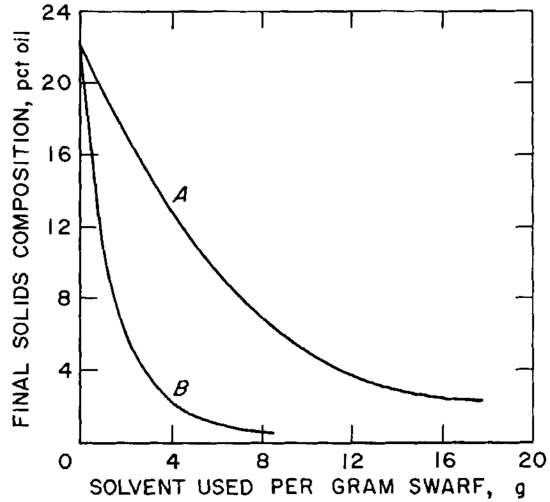


Fig. 13. Alternative oil extractions at 50° C.
A. Supercritical CO_2 at 5,000 psig
B. Supercritical CO_2 modified with 30-60 pct methanol at 2,000 psig

2-ft-ID by 4-ft-long extraction vessel, and the methanol supercritical CO_2 system would require a 2-ft-ID by 2-ft-long extraction vessel. The metal and the oil product are valuable in both systems. Since CO_2 and oil separate readily at ambient conditions, both components would be ready for immediate recycle using straight supercritical CO_2. Methanol is only sparingly soluble in the oil product, which would make direct modifier recycle possible in this case. Either deoiling alternative is advantageous over degreasing with chlorinated industrial solvents, which cannot be separated from the oil, and the oil must be discarded as a waste. Oil stripped from the grinding swarf with a supercritical solvent could either be recycled as a lubricant or burned as a fuel to run the process.

CONCLUSIONS

Supercritical fluids effectively degreased superalloy grinding swarf. Two solvent combinations appeared practical for commercial application. A supercritical CO_2 solvent reduced the oil content from 22 to <5 pct in 60 min at 50° C and 5,000 psig. A mixed supercritical solvent comprising 30 to 60 pct methanol in CO_2 reduced the oil content from 22 to <5 pct in 15 min at 50° C and 2,000 psig. The products CO_2, oil, and methanol (when used) were suitable for immediate recycle without further processing. Both processing alternatives are advantageous over degreasing with chlorinated industrial solvents because the oil can be used as a product, rather than discarded as a waste. The space requirements are also minimal; the extraction vessel to handle 1 MM lb/yr would require no more space than two file cabinets.

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