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Project Summary

Pilot Plant Evaluation of Critical Fluid Extractions for Environmental Applications

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Liquefied gas solvents were used in a pilot plant study to extract oil from mill scale (a steel mill by-product) and bleaching clay (a vegetable oil filtering media). The process, operated on a semi-batch cycle, involved two extractors and a solvent recovery system. The results of the extraction experiments demonstrated the feasibility of condensed gas extraction. Preliminary economics indicate attractive payback on full-scale plants—about 23 months for a mill scale extraction facility and 17 months for a bleaching clay plant.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In recent years, several studies have been undertaken by the U.S. Environmental Protection Agency for uses of critical-fluid extraction technology for waste treatment. For solvent extraction, the process has unique advantages in facilitating recovery of by-products and minimizing solvent residues because of the high solvent volatility. Prior studies sponsored by EPA and others have focused on coupling extraction with adsorption; i.e., using critical fluids to strip and regenerate adsorbents which selectively trap organic pollutants from liquid and vapor effluents.

More recently, the direct extraction of liquid and solid wastes has been considered. A range of applications of critical-fluid extraction to environmental problems have been evaluated by Critical Fluid Systems, Inc. under EPA sponsorship. In a recent EPA study, laboratory scale extractions were conducted on: 1) mill scale from steel production/processing, and 2) bleaching clays from vegetable oil and specialty oil production. Both of these wastes contain significant amounts of oil and constitute major solid waste disposal problems. The laboratory studies showed that extraction of oil from these wastes was feasible using Solvent-12 or propane; preliminary economic evaluations were favorable.

The present study extends these evaluations to the pilot scale. The residual oils on both mill scale and bleaching clays are soluble in Solvent-12 well below critical conditions. This allows processing at ambient temperatures and at pressures that do not require exotic materials or methods of construction. All of the economic advantages of supercritical extractions still exist (simple solvent recovery, high purity, desolventized products) with the added benefit of lower compressor costs. In many situations, the compressor will be the only energy consumer in the process. This energy consideration is the prime factor in making condensed gas solvent extraction, as well as near- and supercritical solvent extraction, so economically attractive.

Nature of the Wastes

Steel Mill Scale Oily Wastes

The steel industry is a major producer of oil-containing solid wastes. A variety of waste streams exist. The major problems stream is that of mill scale. Mill scale is waste iron oxides contaminated with lubricating oil. It results from surface contamination of steel stock as stock is formed into product during rolling and handling. Mill scale represents 1.5 to 10% of the total raw steel production of a plant. As the percentage increases, so does the incentive to recover this waste and turn it into saleable product. About half of the scale currently generated is in fact recycled to the blast furnaces, most by way of a sintering operation. The other half is stockpiled.

Only half of the mill scale is reprocessed because the sintering operation is adversely affected by high oil content. The oil is volatilized during sintering and recondenses in the plant off-gas. Without treatment this produces a visible plume and is an obvious source of pollution. When bag houses are used, the oil condenses and impairs bag house operation.

Several de-oiling methods have been tested. Water washing with hot alkaline solution can remove at best 90-95% of the oil on mill scale fines at low cost. The solids would then be suitable for recycling, but the oily solid disposal problem becomes an oily water disposal problem. Thermal incineration of the oily mill scale is a very effective de-oiling method, but the energy costs of the incineration and the subsequent off-gas treatment could quickly offset the economic advantages of raw material recycling. A direct fired kiln has been reported in commercial use.

Another possibility is liquid solvent washing using a chlorinated hydrocarbon solvent. The solvent would be used to strip the oil off the mill scale fines, making them suitable for the sintering operation. The solids would have to be thoroughly desolventized, however, and the solvent would have to be recovered from the product oil in order that the oil could be recycled. The energy costs for these operations would have to be evaluated and carefully compared to the recovered raw material value. The costs of solvent makeup must also be taken into account.

An alternative that appears economical exists, based on condensed gases. The effectiveness of the conventional solvent process can be coupled with the economic attractiveness of critical fluid extraction to yield a process that holds the promise of efficient extraction at reasonable processing costs. This process uses sub-cooled condensed gases as the solvent. After extraction, the clean scale is depressurized to atmospheric conditions. Residual solvent vaporizes within a short time, leaving the de-oiled scale ready for recycling. The oil-laden solvent is sent to a still where the oil is concentrated and the solvent vaporized for reuse.

The energy for this vaporization comes from the superheated compressor discharge, which is routed through heat exchange coils in the base (reboiler section) of the still. Thus the only energy input into the system is the compressor.

Bleaching Clay Oily Residues

The refining of a number of synthetic and natural oils includes a processing step to decolorize, or bleach, the refined product using special clays. These clays are composed of very fine (<400 mesh) diatomaceous earth particles and any of a number of additives. These materials adsorb impurities from the product. The clay is mixed with the oil, then the suspension is filtered. The resulting clay filter cake contains 30 to 60% (by mass) occluded oil, and thus represents a pollution problem as well as a yield loss. About 0.5 kg of clay is used per 100 kg of refined oil product in vegetable oil processing.

There are a number of incentives for recovering this oil. The first of these incentives is the potential savings in hauling and landfill costs. The mass of material handled would be substantially lower and, with the waste clay itself being de-oiled, would require less sophisticated landfilling techniques for its disposal. The cost per kilogram of disposal would be lower as would the total amount of waste to be disposed of.

A second incentive is the recovery of the bleached oil product. This product could be added to either refined or crude oil, depending on its quality, and thus improve overall plant yield. The de-oiled clay may also be reusable if its activity has not been entirely spent.

A final incentive to de-oil spent bleaching clays is one of safety. The stored oily clay waste can undergo spontaneous combustion. This possibility would be lessened, if not eliminated, by de-oiling the material. Currently, water is added to the clays to inhibit spontaneous combustion. This adds to the mass to be disposed of and so to disposal costs.

There appear to be no de-oiling schemes in current industrial usage. As with mill scale, incineration is an option, but the higher oil content may incur higher costs in off-gas cleanup. Conventional halocarbon solvent extraction is a possibility, but removing solvent from the de-oiled clays would be difficult due to the small pores in the clays. These pores would adsorb and hold solvent by capillary condensation. The solvent-bearing clay may present a worse pollution problem than the starting material.

Sub-cooled condensed gas extraction has shown promise as a de-oiling technique for bleaching clays. Laboratory scale runs produced product oil of a somewhat higher quality than the process refined oil, presumably due to the longer contact time of the occluded oil with the still-active clay. Condensed gas extraction of bleaching clays offers the same process economic advantages outlined for mill scale de-oiling, and so was chosen for further experimentation.

Pilot Plant Description

The solids extraction plant used for this study is a unit, primarily carbon steel, mounted on a steel framework (skid) measuring 3 by 2.5 m. The primary equipment in the plant is a bank of three extractors, a reboiler/still unit, a vertical surge vessel, a compressor and compressed gas storage vessel, a pump, piping, and valves. (See Figure 1.)

The solvent first passes through a mass flow meter. This is used as an input to a computer controller which, in turn, outputs a signal to a transducer. The pneumatic control signal from this transducer is sent to a valve that controls flow.

The solvent next enters the inlet line to the extractor bank. The three extractors include two 15 cm dia x 1.5 m long schedule 80 units with six inlet and six outlet ports, configuration allowed for upflow, downflow, and crossflow experimentation. The third extractor was of the same length and schedule, but had a diameter of 7.6 cm. This allowed for higher velocity experimentation in either upflow or downflow modes. This smaller column was not equipped for crossflow work.

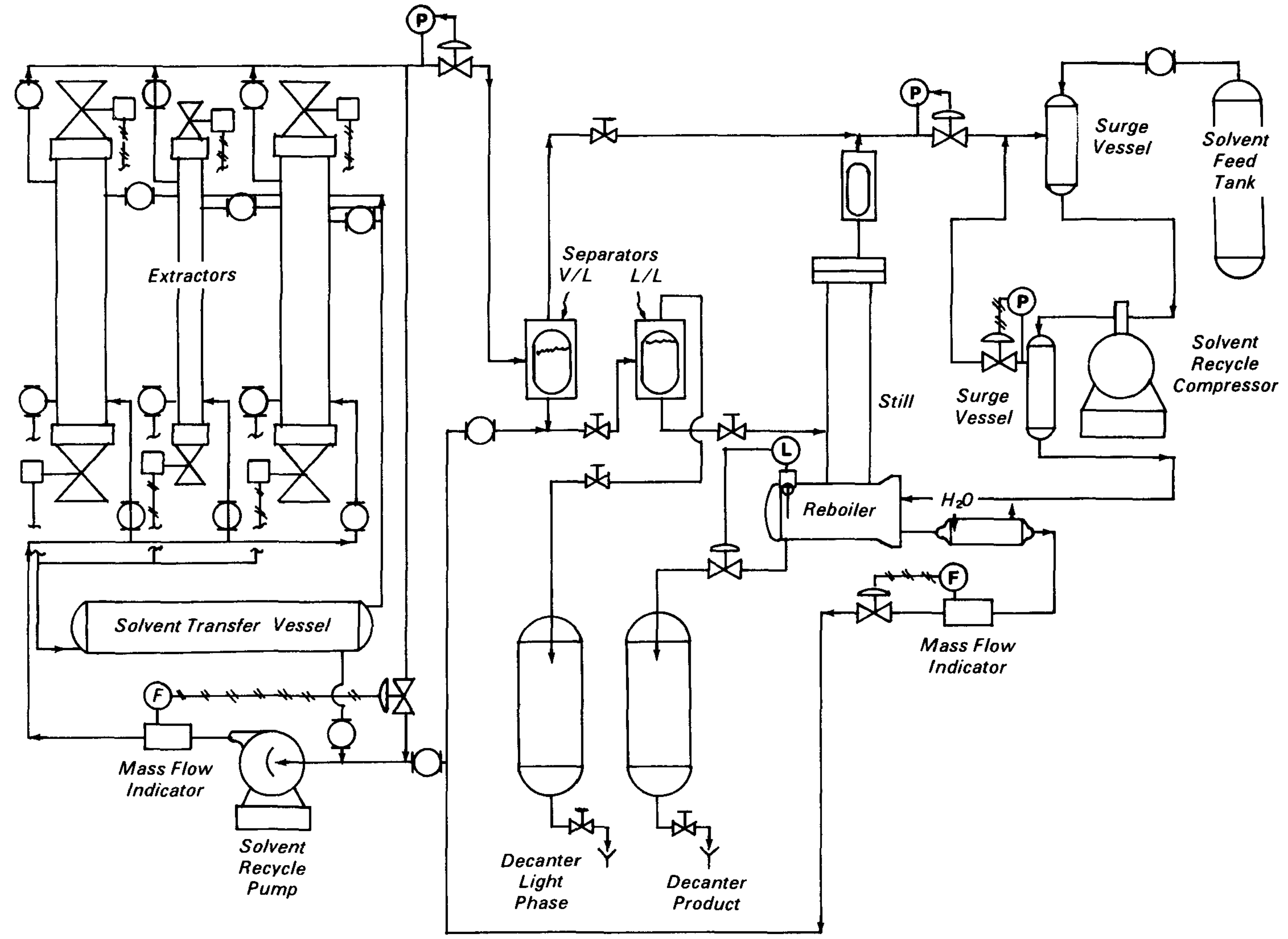

Figure 1. *Simplified process flow diagram.*

The solvent is directed through a loaded extractor, where it picks up oil from the solid charge. Pressure is maintained by a backpressure control valve at the column exit manifold. This controller ensures that the solvent passes through the extractor in a liquid phase. The solvent/oil mixture flows through the pressure control valve and into a series of two vapor/liquid separators. These separators allow any solvent vapor to enter the still tower at a point above the liquid solvent inlet, and keep flow at the liquid solvent inlet smooth.

The still/reboiler unit is a stainless steel unit capable of operating at pressures in excess of 10 mPa. (This work was carried out at pressures of less than 700 kPa.) It is a 10 cm diameter tower, 2.5 m high and coupled at its base to a kettle-type reboiler containing 13 m of 1.3 cm diameter heat transfer coils. These coils allow efficient heat transfer from the superheated compressor discharge to the contents of the reboiler. Solvent is boiled off and the extracted oil is concentrated in this reboiler. As oil builds up in the reboiler, a level control valve opens to allow an oil/solvent mixture to flash into the product receiver. In our pilot plant system, this solvent is vented to the atmosphere. The still pressure is maintained at a pressure about 250 kPa less than the extractor pressure by another (independent) backpressure control valve. The solvent vapors from the reboiler (and vapor/liquid separators) flow through this valve and into a vertical compressor inlet surge vessel.

The compressor inlet surge vessel is another 15 cm diameter steel vessel, 1.5 m high. This acts as a trap to prevent liquid carryover (if any) from the still from reaching the compressor. It also dampens out the pulsations of the compressor, thus isolating the still from pressure variations. The solvent vapors pass through a filter before entering the compressor.

The compressor is an oilless piston compressor capable of delivering 85 LPM (free air flow) and having a maximum discharge pressure of 1700 kPa. The output of the compressor is sent to a 110 L surge vessel. The pressure in this surge vessel is maintained at 1400 kPa by another backpressure control valve that vents excess compressor capacity to the compressor inlet surge vessel.

The superheated compressed solvent gas flows into the coils of the reboiler and is there liquefied as it gives up its latent heat to the solvent/oil mixture in the reboiler. The coils are followed by another vapor/liquid separator. This separator serves to collect non-condensable gases and ensure that only liquid solvent flows to the flow meter, and so through the system for another extraction cycle.

Pilot Plant Operation

The first step in the extraction experiment was to load the extractor with a known amount of feed. This was accomplished by weighing starting material in a transfer vessel and pouring the material into the extractor. A large funnel kept transfer losses to a minimum. Samples of the feed were taken at this time. When the transfer was complete, the transfer vessel was reweighed. The charge to the extractor was then calculated and noted, as was the height of feed in the extractor.

The extraction plant was then started up in a bypass mode. No solvent was put through the bed of solids during this start-up phase. The flow of solvent was cycled through the piping until pressures and flow rates achieved steady state. Not until this steady running condition was achieved would extraction begin.

The extraction cycle was begun by filling the column with solvent. This was done by the pump from the solvent storage vessel or, if the solvent volume in that vessel was inadequate, from the main solvent supply tank. Filling the column generally took about 5 minutes. Pumping was continued until the pressure in the column was higher than the vapor pressure corresponding to ambient temperature, typically greater than 500 kPa. A valve at the top of the column was then cracked to relieve any trapped air. The column was ready for extraction.

The inlet and outlet valve arrangement for the given experiment was set and the bypass valve switched to extraction. The solvent mass flow totalizer was re-zeroed at this time. The experiment continued for the prescribed time, and then flow was once again diverted to the bypass mode. The total solvent throughput was noted, and the extractor drained of solvent.

Removal of solids was straightforward. After a final check that there was no pressure in the extractor, the top cover was opened. The height of residue was noted and the top of the bed of solids examined visually for evidence of channeling or agglomeration. A sample of the top of the bed was taken.

The bottom cover was next removed and the solids collected in a weighed container. This procedure required care in the case of bleaching clay because this material rarely poured out of its own accord. The solids would be prodded from the bottom with a rod to break up any bridging, and then prodded from the top to start the flow. Any solids escaping the collection vessel were swept up and added to the residue. The column sides were examined for adhering residue and cleaned (scraped) when necessary. Samples of the bulk residue were taken by a cone and quartering technique in an effort to get a representative sample for moisture and oil analysis.

Results

Extraction rate data were taken by grab sampling the extract stream at various times during the extraction cycle. The sample's solvent was vented, and the concentration of oil in the extract was calculated. When these data were plotted against time, an exponential decay in concentration with time was observed (Figure 2).

Extraction efficiency data were based on Soxhlet extraction feeds and residues. A composite sample of feed was taken as the column was loaded; a similar sample of residue was taken at the conclusion of the run. These samples were then analyzed for their oil content. We defined extraction efficiency as the quantity of oil removed divided by the quantity of oil available for extraction as determined by the Soxhlet analyses.

Table 1 provides extraction efficiency data. As shown, the extraction for mill scale was quite efficient: half the runs gave greater than 90% oil extraction. On the other hand, the bleaching clay was more difficult to extract: most values were less than 50%. Note that, although the bleaching clay extractions were less effective, larger amounts of oil were recovered due to the much greater oil content of the bleaching clay waste. In addition, these efficiencies are based on a limited extraction period. Figures 3 and 4 show the cumulative oil extracted as a function of time for mill scale and bleaching clay, respectively. Note that, for mill scale (Figure 3), only 60 minutes was required to achieve maximum ex-

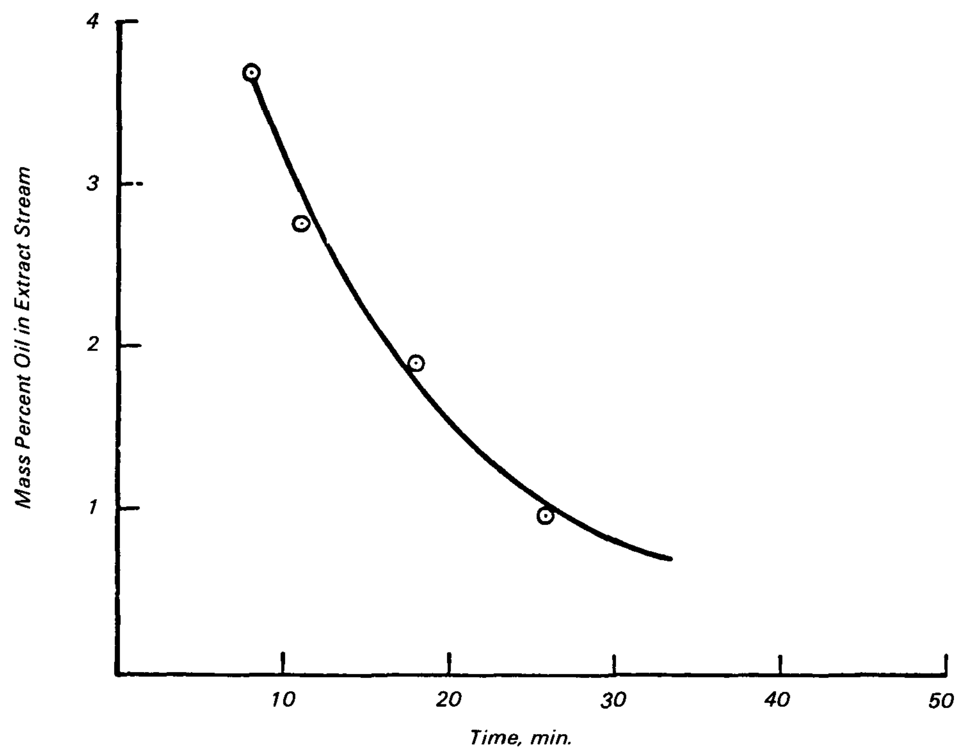

Figure 2. Decay in extract oil concentration with time during mill scale extraction.

Table 1. Extraction Efficiencies

Waste	Run No.	Oil in Waste, %	Extraction Efficiency, %
Mill Scale	30	1.2	75
	31	1.2	93
	32	0.9	80
	35	2.4	97
	36	1.2	93
	37	1.0	80
Bleaching Clay	51	24.7	34
	52	17.4	40
	53	18.7	19
	54	18.6	43
	55	18.4	40
	56	20.2	65
	57	22.5	59
	58	16.1	45

traction. For bleaching clay (Figure 4), the extraction curves were still rising when the run ended.

The overall lower oil reduction efficiences for bleaching clays (when compared to mill scale data) may be attributed to the nature of the feed. Bleaching clay is a very fine, porous material. The presence of fine pores throughout the particle adds another term to the overall mass transfer coefficient of oil from the particle to the solvent. In addition to particle-to-solvent mass transfer through the boundary layer of the individual particle, there exists an intra-particle diffusional resistance. The oil trapped in internal pores must diffuse through the particle matrix in order to be extracted. This resistance term will be independent of flow conditions as long as the oil at the particle boundary layer is removed as fast as the internal pore diffusion brings oil to the particle surface.

Preliminary Economic Analysis

Mill Scale

A preliminary design was prepared for a mill scale de-oiling plant for the purpose of a process feasibility study. The proposed plant would process 80,000 metric tons of mill scale per year with a nominal oil content of 5%.

Capital costs, operating costs, and expected credits combine to provide a net credit of over $900,000/yr. A dollar value cannot, however, be attached to the credit for the elimination of a hazardous waste. This benefit of mill scale de-oiling will become an overriding factor in the implementation of de-oiling technology.

Bleaching Clay

Preliminary design of a vegetable oil extraction facility has been completed for a 3,600,000 kg/yr plant.

Capital costs, operating costs, and expected credits combine to provide a net credit of over $800,000/yr.

Conclusions

1. Steel mill scales containing several percent residual oil can be de-oiled to levels acceptable for sinter-plant feed using condensed dichlorodiflouromethane (Solvent-12), at ambient temperatures, and pressures of about 700 kPa. The maximum pressure requirement of such a system is 1400 kPa.
2. The rate of mill scale extraction is proportional to flow rate. Ninety percent extraction occurred in 30 minutes at 1.6 kg/min and in 60 minutes at 0.9 kg/min.
3. The rate of mill scale extraction was increased by a static soaking period before extraction.
4. Preliminary economic evaluation indicates that credits for de-oiled mill scale and fuel quality oil proprovide an attractive payout for a plant de-oiling 80 metric tons per year of 5% oil mill scale feed.
5. Bleaching clays used in vegetable oil processing can be de-oiled using the condensed gas extraction process.
6. Extraction efficiency of bleaching clay is primarily a function of contact time.
7. Preliminary economic analysis indicates that product recovery credits and disposal cost reduction make condensed gas extraction attractive.

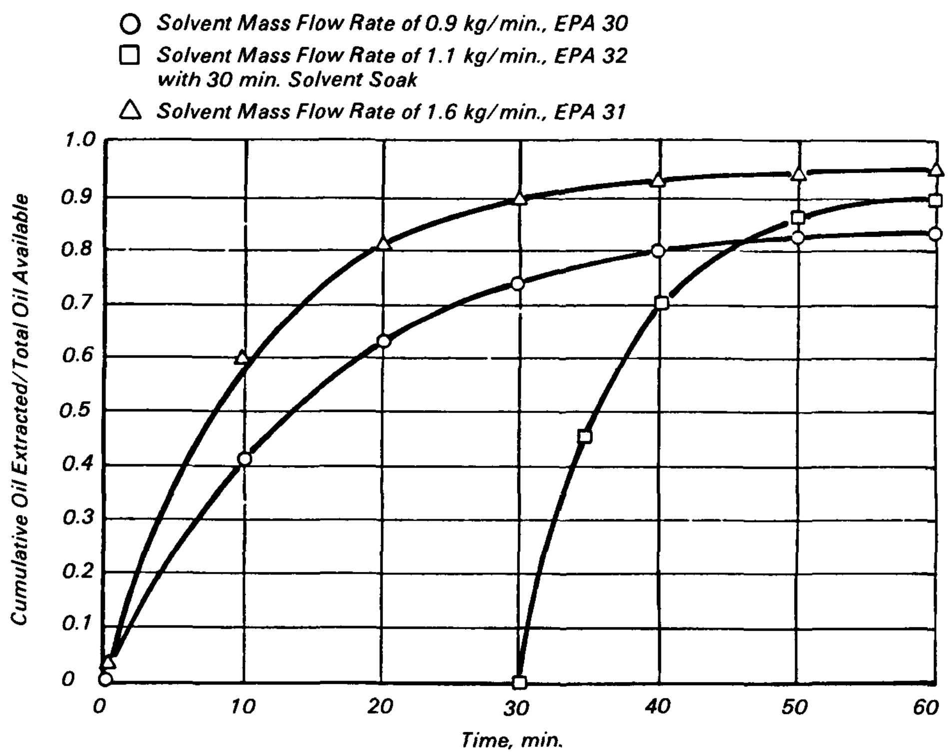

Figure 3. *Cumulative oil extracted from mill scale as a function of time.*

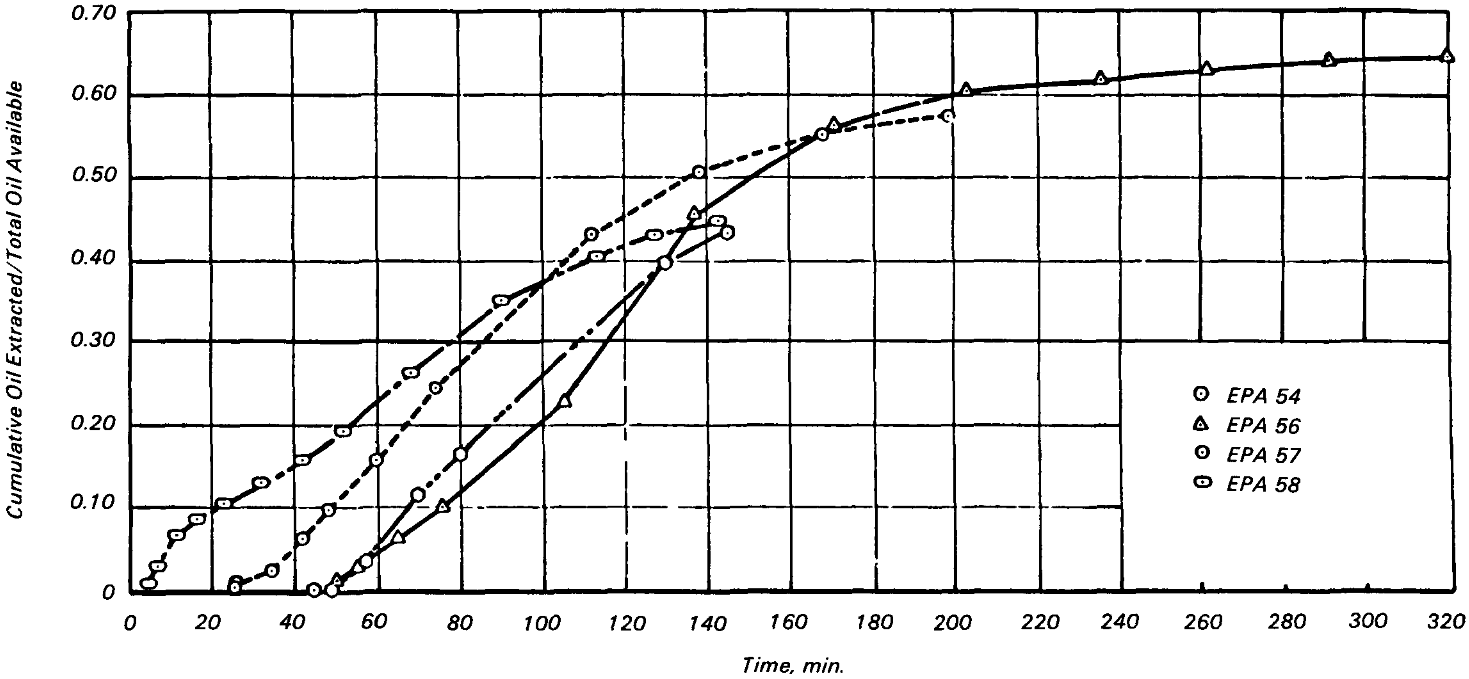

Figure 4. *Cumulative oil extracted from bleaching clay as a function of time.*

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The complete report, entitled "Pilot Plant Evaluation of Critical Fluid Extractions for Environmental Applications," (Order No. PB 85-233 484/AS; Cost: $11.50, subject to change) will be available only from:

National Technical Information Service
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