

# **CF SYSTEMS** **CORPORATION**

## **The Treatment of Organic Bearing Wastewater in the Chemical Industry Using Liquefied Gas Extraction**

GMM 001 0052

✓

By  
**William E. McGovern**

**CF SYSTEMS**  
CORPORATION

140 Second Avenue, Waltham, MA 02154-1100

380708



## INTRODUCTION

Recent effluent limitations imposed by the EPA on a large sector of the U.S. chemical industry will mandate more stringent standards for wastewater treatment prior to discharge. As a result of these new regulations, cost-effective processes capable of removing priority pollutants and other non-biodegradable organics from industrial wastewater will be in significant demand. On November 5, 1987, the EPA published its final ruling: *Effluent Limitations Guidelines, Pre-Treatment Standards for the Organic Chemical, Plastics and Synthetic Fibers Industry* (OCPSF), which will significantly reduce the allowable discharge of priority pollutant organics to either navigable waters or municipal sewage treatment plants. According to EPA estimates,<sup>1</sup> the quantity of priority pollutant organics discharged to surface waters and sewers will be reduced by over 73% at the end of a three year timetable already in effect under the new regulations. The cost of compliance will be high, with an average estimated capital expenditure of over one million dollars per facility.<sup>2</sup>

The use of liquid carbon dioxide as an extraction solvent for the separation and recovery of organics has been of interest for a number of years, and it is currently being used in the food industry for the decaffeination of coffee and the extraction of hops in beer-making operations.<sup>3</sup>

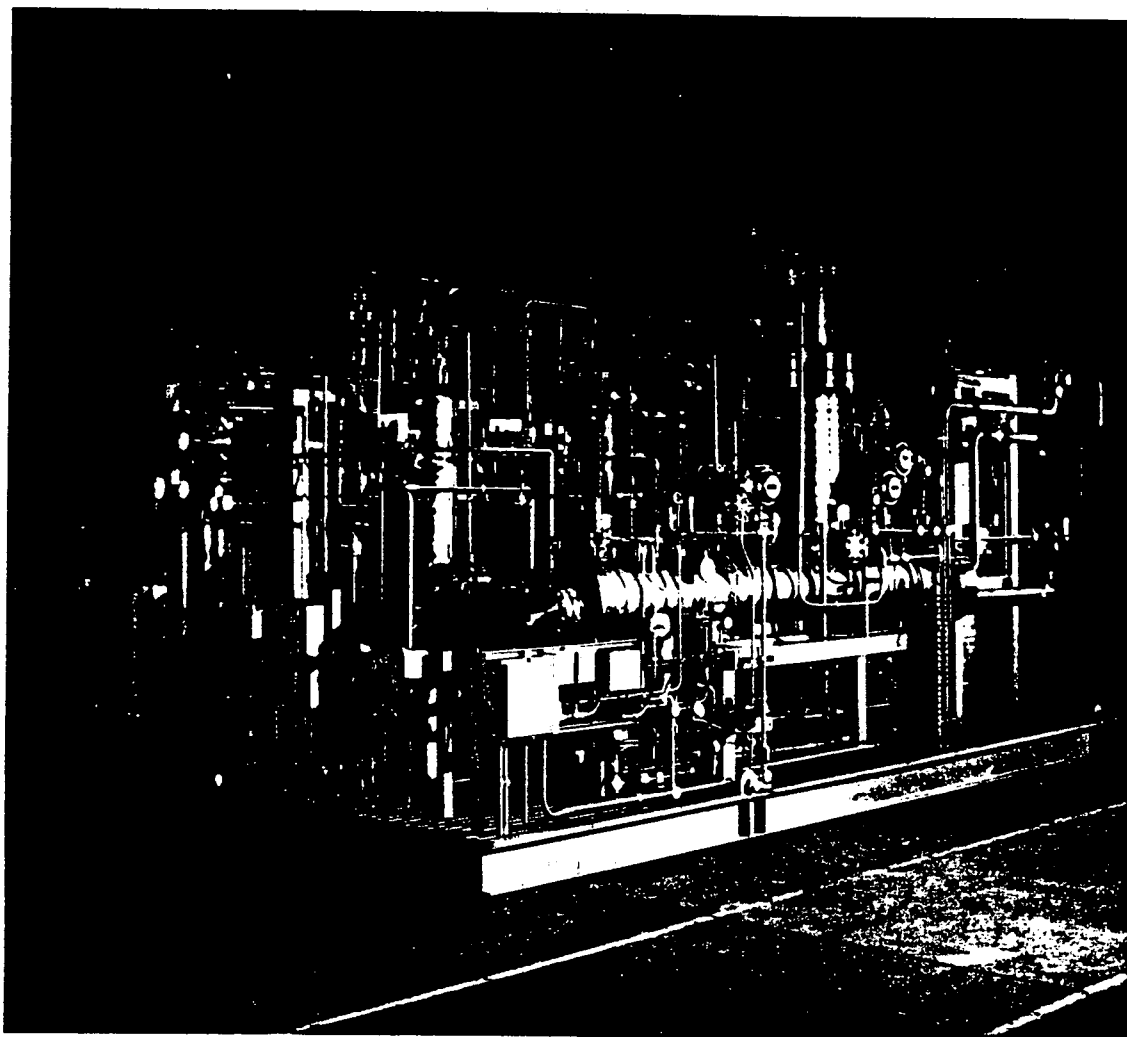
Liquid CO<sub>2</sub> is an ideal choice as an extraction solvent because of its high solubility for a broad range of organic compounds, and its ability to work efficiently at ambient temperatures. In addition, CO<sub>2</sub> is non-toxic, non-flammable, and easy to separate from the extracted organics. Table 1 lists a few examples of organics miscible in liquid CO<sub>2</sub>, and illustrates the solubility of CO<sub>2</sub> for a wide variety of organic compounds.<sup>4</sup>

TABLE 1  
EXAMPLES OF ORGANIC COMPOUNDS MISCIBLE IN  
LIQUID CO<sub>2</sub> AT 25 DEGREES C AND 65 ATM

Compound	Class
Acetaldehyde	Aldehyde
Acetic Acid	Carboxylic Acid
Acetone	Ketone
Acrylonitrile	Nitrile
Benzene	Aromatic
Butyl Alcohol	Alcohol
Chlorobenzene	Halogenated Aromatic
Chlorophenol	Halogenated Phenol
Dimethylformamide	Amide
Ethyl Acetate	Ester
Propylene	Olefin
Pyridine	Heterocyclic

GMM 001 0053

A commercial scale treatment unit, utilizing liquid CO<sub>2</sub> as an extraction solvent to separate organics from industrial wastewater (Figure 1), has recently been leased to a commercial waste treatment company by CF Systems Corporation of Waltham, Massachusetts. This paper presents a process description of the first CF Systems organics extraction unit designed specifically for the treatment of organic bearing wastewater.



**FIGURE 1**  
**WASTE TREATMENT UNIT DESIGNED AND BUILT BY CF SYSTEMS CORPORATION**

GMM 001 0054

## The Extraction and Separation Process

Figure 2 is a simplified flow diagram of the CF Systems extraction process utilizing liquid  $\text{CO}_2$  as a solvent to extract and separate organics from wastewater.

As shown in Figure 2, organic-bearing wastewater is continuously fed into the top of the extractor and flows down the column through a series of sieve tray downspouts. Simultaneously, liquid  $\text{CO}_2$  is fed into the bottom of the extractor, and jets upward through perforations in the sieve trays due to its buoyancy. During this countercurrent contact between  $\text{CO}_2$  and wastewater, organics are extracted from the water phase to form a  $\text{CO}_2$ /organics phase, or extract, which continuously exits from the top of the extractor.

As the extract flows from the extractor to the separator vessel, it passes through a pressure reduction valve. In the separator vessel, liquid  $\text{CO}_2$  is flashed and converted to vapor, while the liquid organics are collected in the reboiler section and continuously removed as a concentrated stream. The  $\text{CO}_2$  vapor leaving the top of the separator vessel is continuously fed to a compressor, recompressed, heat exchanged in the reboiler and then reused as fresh solvent, resulting in a totally enclosed solvent recycle system.

Both the concentrated organic stream from the reboiler section and the water effluent from the bottom of the extractor vessel are reduced in pressure prior to being pumped off-skid.

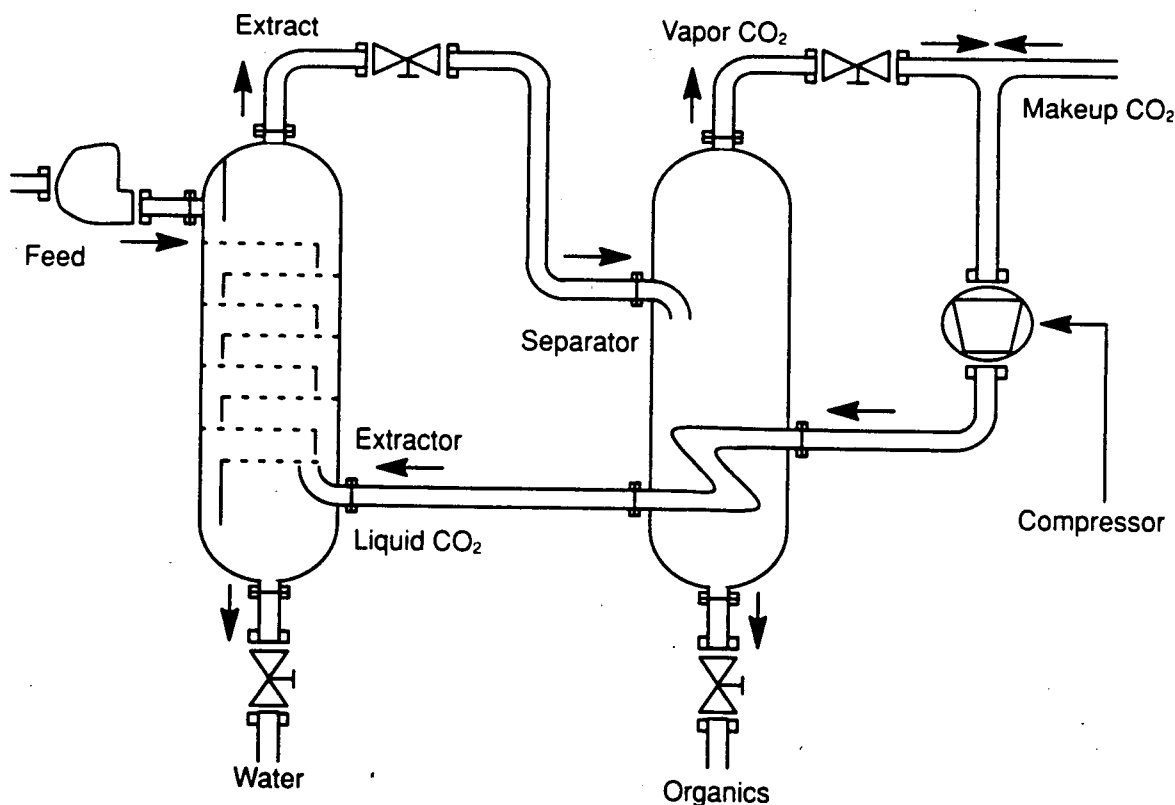


FIGURE 2  
CF SYSTEMS WASTEWATER TREATMENT FLOWCHART

CF Systems operates a one gallon per minute liquid-liquid extraction pilot plant utilizing liquid carbon dioxide as the extraction solvent. The pilot plant flow diagram (Figure 3), shows a countercurrent sieve tray extractor, a solvent recovery still and a vapor recompression cycle. The extractor is a windowed vessel, 2 meters tall and 10 centimeters in diameter with a tray stack of eight sieve trays with downcomers. The solvent recovery still is 10 centimeters in diameter and 1.5 meters high, with a reboiler section containing a heat exchange surface area of 5500 cm<sup>2</sup>. Extractions are conducted at ambient temperature and at pressures of 900 to 1200 psig.

The extract passes through a decanter to remove any entrained water before entering the solvent recovery still. In the still, the extract experiences a pressure drop which causes the CO<sub>2</sub> to vaporize, leaving the organics to concentrate in the reboiler. Vaporized CO<sub>2</sub> exiting the top of the still is recompressed and then heat exchanged with the contents of the reboiler. In the still heat exchanger, the hot CO<sub>2</sub> gives up its heat of compression to help boil off dissolved CO<sub>2</sub> from the organic liquid concentrate.



## STUDY I — EXTRACTION OF AN ACRYLONITRILE WASTEWATER

This pilot study investigated the use of liquid CO<sub>2</sub> as an extraction solvent to extract and separate organic nitriles from a 125 gpm waste stream generated at a large chemical production facility. The plant currently deep well injects the wastewater and is seeking an alternative method of treatment. The extraction of organics using liquid CO<sub>2</sub> would result in reduced toxicity and would allow the facility to send the treated wastewater (raffinate) to on-site biotreatment. As an added benefit, the extracted organics could be credited as a recovered byproduct. The simulated industrial test stream contained acrylonitrile, acetonitrile and ammonium sulfate, and had the following composition:

### Acrylonitrile Wastewater Feed Composition

Acrylonitrile	275 ppm
Acetonitrile	355 ppm
Ammonium Sulfate	2.0 wt. %
Water	97.9 wt. %

### Operating Procedure

The distribution coefficient (DC) is a measure of the relative solubility of an organic in CO<sub>2</sub> vs. water. Empirical determinations of the distribution coefficient were performed in the laboratory, and indicated that the extraction of both acrylonitrile and acetonitrile could be easily achieved using liquid CO<sub>2</sub>. The distribution coefficient data is given below:

	Feed Concentration	Distribution Coefficient
Acrylonitrile	1654 ppm	5.5
	997 ppm	4.5
Acetonitrile	2099 ppm	0.9
	1750 ppm	0.6

From the distribution coefficient data, it was concluded that a solvent-to-feed ratio of 1.5:1 would be sufficient to extract the dissolved organics. Pilot plant stream samples of the feed, raffinate and extract were taken at 10 to 15 minute intervals during experimentation to determine extraction efficiencies and to obtain mass transfer data. All samples were analyzed using a gas chromatograph.

## Results

Tables 2 and 3 list the concentrations of acrylonitrile and acetonitrile in the feed and raffinate during this extraction. Also listed is the percent removed of the organic through the extractor, where removal is defined as  $(X_f - X_r)/X_f$  or more simply,  $1 - (X_r/X_f)$ . As predicted by the distribution coefficient data, acrylonitrile extracted more efficiently than acetonitrile, and in one pass through the pilot scale extractor, 99% of the acrylonitrile and 89% of the acetonitrile were extracted.

From the results of this study, it was concluded that a commercial scale extraction unit could easily achieve >99.9% removal of acrylonitrile and >99% removal of acetonitrile from an actual process wastestream.

**TABLE 2**  
**ACRYLONITRILE CONCENTRATION HISTORY**

Time (min)	Feed (ppm)	Raffinate (ppm)	Removal ( $1 - X_r/X_f$ ) %
5	—	2.0	99
15	267	2.6	
30	292	2.7	
40	288	3.3	
50	261	2.4	

**TABLE 3**  
**ACETONITRILE CONCENTRATION HISTORY**

Time (min)	Feed (ppm)	Raffinate (ppm)	Removal ( $1 - X_r/X_f$ ) %
5	—	26	89
15	342	27	
30	370	38	
40	368	50	
50	340	39	

## STUDY II — THE EXTRACTION OF ORGANICS FROM WASTEWATER AT A HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL (TSD) FACILITY

### Background

In this study, CF Systems was contracted to produce a process design package for a CO<sub>2</sub> extraction unit to be used at a hazardous waste treatment and disposal facility, to treat wastewater containing from 5% to 30% organics by weight. The extracted organics were to be used as incinerator fuel, and the water was to be suitable for sewer discharge. To provide the design information for this solvent extraction unit, a series of pilot plant experiments were run to determine optimal operating conditions. The data from this study resulted in the design and construction of a commercial scale wastewater extraction unit, utilizing liquid CO<sub>2</sub> as the extraction solvent.

### Results

Analytical results from the pilot scale extraction of the wastewater using a solvent-to-feed ratio (S/F) of 1.5 to 1 are shown in Table 4, with concentrations given in parts per billion.

TABLE 4  
CF SYSTEMS — PILOT STUDY RESULTS  
CONCENTRATION IN PPB  
S/F = 1.5

Positive Identification (GC/MS)	Feed	Raffinate	Percent Removal
Chloroform	2,690	121	98.2
1,2 Dichloroethane	1,160	ND	>99.3
Methylene Chloride	2,730	150	97.1
Toluene	1,140	52	98.3
Tentative Identification (GC/MS)			
Propane, 1-Methoxy	988	113	87.2
Propanal, 1 Methyl	17,200	485	97.0
Propanamide	53	NI	—
Pentanone, 4 Methyl	1,304	NI	—
Furan, Tetrahydro	5,680	236	96.1

ND: Not Detected (detection limit 8 ppb)

NI: Not Identified

GMM 001 0059



Results from Table 4 show that in a single pass through the 2.0 meter, eight tray extractor, a significant reduction in volatile organics occurred.

The laboratory DCs and the pilot scale data indicate that a commercial scale extractor, with proper tray design, would extract at least 99.9% of the organics listed here, using a S/F ratio of 1.5:1.

### Calculated Performance Data

Table 5 lists the distribution coefficients and calculated percent removals for some important industrial solvents, including seven regulated priority pollutant organics named in the EPA's recent effluent limitation guidelines for the OCPSF industries.

The distribution coefficient (DC) is defined as the weight fraction of organic in the liquid CO<sub>2</sub> phase, divided by the weight fraction of organic in the water phase at equilibrium. The DC may be used to calculate the liquid CO<sub>2</sub>-to-feed (S/F) ratio required to obtain essentially complete removal (99.99%) of an organic from wastewater. Alternatively, the DC may be used to calculate the percent removal of an organic from wastewater at a constant (S/F) ratio (the results shown in Table 5 were determined using a S/F ratio of 1.5).<sup>5</sup> The removal rates in Table 5 could be improved by adjusting parameters such as the number of trays in the extraction column or the S/F ratio.

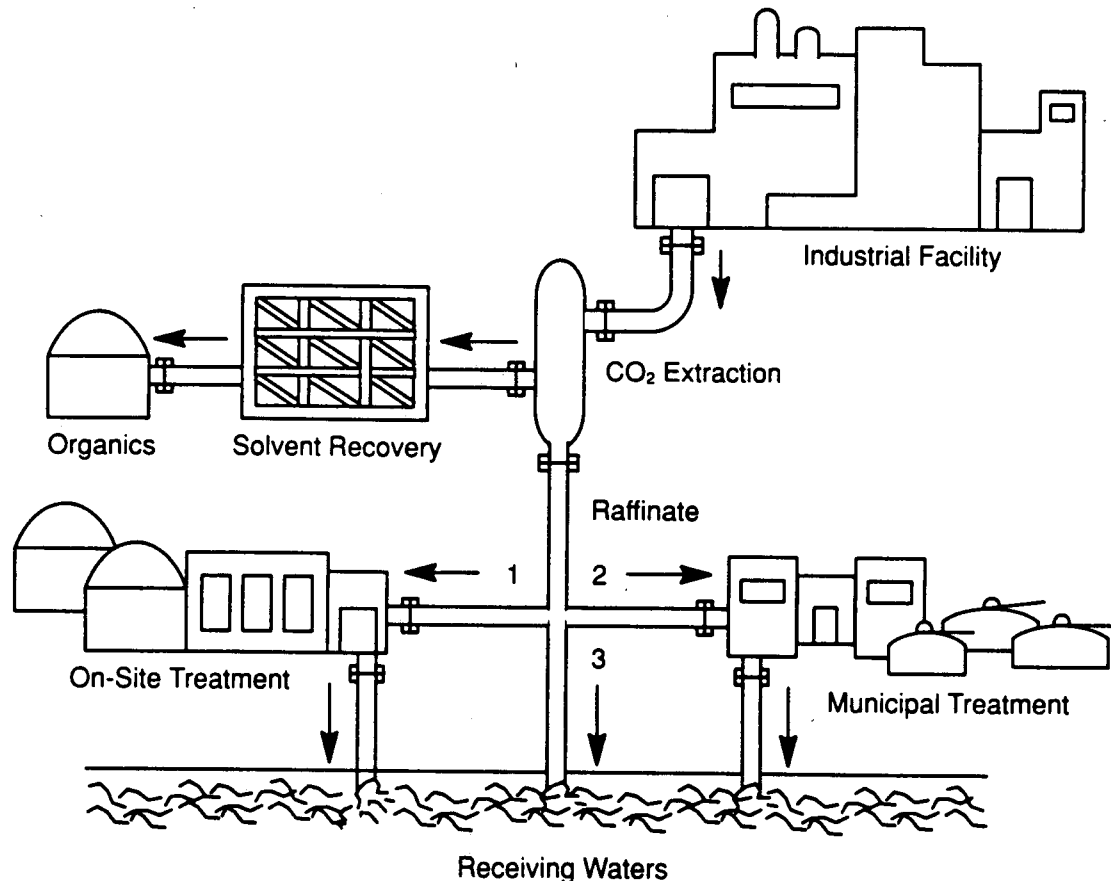
TABLE 5  
CALCULATED EXTRACTOR PERFORMANCE

Organic Compound	Distribution Coefficient	Percent Removal
Methanol	0.1	14.0
Phenol*	0.3	38.0
Acetone	1.1	99.7
Acrylonitrile*	5.0	>99.9
Trichloroethylene*	17.0	>99.9
Methylene Chloride*	74.0	>99.9
Benzene*	290.0	>99.9
Diethyl phthalate*	472.0	>99.9
Toluene*	505.0	>99.9

\*Priority Pollutants

## On-Site Treatment of Industrial Wastewater

Figure 4 illustrates three treatment applications using CO<sub>2</sub> as the solvent to extract and separate organics from industrial wastewater. In many cases, the feed to a CO<sub>2</sub> extraction unit would be an isolated process waste stream rather than the total plant effluent, thereby maximizing the opportunity for organics recovery. For the three applications shown, CO<sub>2</sub> extraction may be used to remove priority pollutant organics from wastewater in order to meet regulatory standards, and/or to recover CO<sub>2</sub> extractable organics for value.



**FIGURE 4**  
**CF SYSTEMS CORPORATION WASTEWATER TREATMENT LIQUID CO<sub>2</sub> EXTRACTION**

### Application: NPDES Discharge

For those industrial facilities discharging wastewater directly to surface waters, the discharge is governed by a permit issued under the National Pollutant Discharge Elimination System (NPDES), usually monitored by an agency of the state in which the facility is located. As a result of the recent EPA (OCPSF) regulations, NPDES permit effluent limitations are now

being expressed in terms of the maximum allowable concentrations of individual priority pollutants. This means that regulatory agencies will now be monitoring wastewater effluents for the concentration levels of over 60 individual organic chemicals, such as acrylonitrile and benzene, in addition to testing for conventional parameters such as biological oxygen demand and total suspended solids. The result is an increased emphasis on processes capable of removing priority pollutant organics prior to either direct discharge or final treatment in an on-site wastewater treatment plant.

Surveys conducted by the EPA indicate that the majority of OCPSF industrial facilities currently utilize some form of on-site organics treatment prior to direct discharge. For the most part, however, these treatment systems were originally designed for reductions in bulk organic loadings, usually expressed as biological oxygen demand, and are not well suited for the removal of individual priority pollutant organics. In cases where industrial facilities have on-site treatment systems already in place, CO<sub>2</sub> extraction can be utilized as an upstream primary treatment process. In this configuration, a CF Systems extraction unit reduces the organic loading to on-site wastewater treatment systems, and maximizes the potential for organics recovery.

### **Application: Sewer Discharge**

In the case of facilities discharging wastewater to municipal sewage treatment plants, CO<sub>2</sub> extraction is a flexible treatment alternative that will allow plants to conform to the EPA's stringent pre-treatment standards governing the discharge of priority pollutants. Unlike most conventional pretreatment methods, when waste streams vary in the concentration and composition of organics, a CO<sub>2</sub> extraction unit will adjust to the new level of organic loading without interruption.

In addition to regulated organics, liquid CO<sub>2</sub> extracts a broad range of organic compounds from wastewater that are generally considered incompatible with sewer operations. These compounds include aromatics, halogens, furans and nitriles. For this reason, the technology has been well received by both managers and operators employed at publicly owned treatment works (POTWs).

For industrial facilities faced with shipping large volumes of wastewater off-site for treatment, because of either high organic loadings or the presence of priority pollutants, CO<sub>2</sub> extraction can be a cost-effective on-site, pre-treatment alternative. By removing the small volume of organic material for dispatch to off-site treatment, and discharging the larger volume of remaining water to a POTW, substantial reductions in off-site treatment costs can be achieved. In addition, the liabilities associated with over-the-road transport of hazardous waste are reduced. In cases where the extracted organics can be recovered for value, or used on-site as fuel, off-site treatment costs and the associated liability may be reduced to zero.

## **Application: Deepwell Injection**

For those industrial facilities using deepwell injection to dispose of wastewater, a CO<sub>2</sub> extraction unit presents a unique opportunity for pre-treatment. This is due to the fact that CO<sub>2</sub> is capable of extracting virtually all of the compounds proposed for regulation in the EPA's August 27, 1987 ruling regarding the monitoring of Class 1 injection wells.<sup>6</sup> In the proposed ruling, the EPA targeted the F001 through F005 solvent wastes, dioxin containing wastes, and the "California List" wastes for regulation and monitoring. By using CO<sub>2</sub> extraction to remove organics prior to deepwelling, the potential for downwell plugging and the migration of organic pollutants to groundwater is significantly reduced.

## **Application: On-Site Incineration**

When on-site incineration is used for the treatment of process wastewater, the energy costs associated with burning the water fraction of the waste are high. The use of CO<sub>2</sub> extraction to separate the organic portion can be a cost-effective pre-treatment alternative. After removing the organic fraction from a wastewater stream, the water may be discharged to either surface waters or to a POTW, and the organics may be used as liquid fuel in the existing incinerator. The cost savings of using a CO<sub>2</sub> extraction unit to pre-treat incineration feed will depend on the total volume of wastewater being incinerated and its organic loading.

## **Conclusions**

In order to comply with recent effluent limitations imposed by the EPA on the organic chemical industries, manufacturing facilities will be seeking out treatment processes capable of removing priority pollutant organics from process wastewater prior to either final treatment or direct discharge.

Utilizing CO<sub>2</sub> extraction to treat process wastewater allows for the recycle and recovery of organic chemicals for value.

The use of liquid CO<sub>2</sub> extraction can be a cost-effective approach to wastewater treatment, particularly when used as a primary treatment process to recover organics from process wastewaters prior to either final treatment or direct discharge.

GMM 001 0063

## References

1. U.S. Environmental Protection Agency, "Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works," February 1986 EPA/530-SW-86-004.
2. U.S. Environmental Protection Agency, "Economic Impact Analysis of Effluent Limitations Guidelines and Standards for the Organic Chemicals, Plastics, and Synthetic Fibers Industry," September 1987 EPA 440/2/87-007
3. de Filippi, R.F., Moses, J.M., "Extraction of Organics from Aqueous Solutions Using Critical Fluid Carbon Dioxide." Presented at the Fourth Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, Tennessee, May 12, 1982.
4. Francis, A.W., Journal of Physical Chemistry, Vol. 58, 1099 (1954).
5. McGovern, W.E., Moses, J.M., "The Treatment of Solvent Contaminated Waste Using Liquefied Gas Extraction." Presented at the Third Annual Waste Source Reduction Conference and Exhibition, Worcester, Massachusetts, October 23, 1986.
6. U.S. Environmental Protection Agency, "Underground Injection Control Program; Hazardous Waste Disposal Injection Restrictions; Amendments to Technical Requirements for Class 1 Hazardous Waste Injection Wells; and additional monitoring requirements applicable to all Class 1 wells; Proposed Rule." 40 CFR Parts 124, 144, 146 and 148.

GMM 001 0064