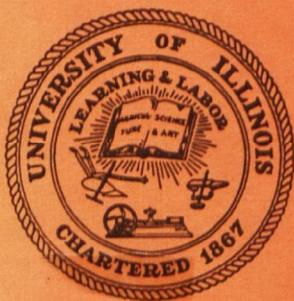


UIIU-ENG 91-0107
HWRIC TR 006

APPLICATIONS OF SUPERCRITICAL FLUID PROCESSING TO ENVIRONMENTAL CONTROL

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Publication No. UILU-ENG 91-0107

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Publication No. HWRIC TR 006

December 1991

Final Report

**APPLICATIONS OF SUPERCRITICAL FLUID PROCESSING
TO ENVIRONMENTAL CONTROL**

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The information described in this report has been funded in part by the United States Environmental Protection Agency under assistance agreement EPA Cooperative Agreement EPA CR 812582 to the Advanced Environmental Control Technology Research Center. Additional funding was provided by the Illinois Hazardous Waste Research and Information Center. Although the report has been reviewed internally with respect to its technical content, it has not been subjected to either organization's required peer and administrative review. Therefore, it does not necessarily reflect the views of the organizations and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

Environmental control and waste remediation are of immediate technological and political interest. One technology which has great potential is contaminant removal and separation with supercritical fluids (SCF's) or supercritical fluid extraction (SFE). In order to take advantage of this technology, both a fundamental understanding of phase equilibria and applicable engineering design data are required. This report documents an extensive study into both aspects culminating in the design and economic evaluation of a SCF regeneration process for granular activated carbon (GAC).

We determined solubilities of relatively non-volatile solid compounds in supercritical fluid solvents, exploring effects of solvent properties, solute properties, and the nature of the critical region. Cosolvents added to an SCF were shown to enhance solubilities and increase selectivities through specific intermolecular interactions. Vapor pressure measurements and spectroscopic investigations also aided the understanding of solubility enhancement. The data were used to test and develop equations of state for calculating phase equilibria in systems containing a supercritical fluid.

The ability of supercritical CO₂ to remove model contaminant compounds from GAC and subsequently drop out most of the contaminant in a liquid phase has been investigated in a pilot scale apparatus. Typical desorption profiles indicate approximately 85% removal of contaminants 2-chlorophenol and toluene from the carbon. The presence of water on the GAC was shown to inhibit slightly the efficiency of the desorption. The desorption results have been interpreted with a generalized desorption-mass transfer model.

The results of the pilot scale studies have been applied to the design of a fixed-site GAC regeneration unit consisting of a three element desorber with two stage flash separation. Optimization of the process centers around minimizing the cost of recycling the SCF through an efficient recompression scheme and regeneration cycle configuration in the desorber unit. An economic evaluation shows a processing cost of 10.6¢/lb GAC which compares favorably with thermal regeneration and incineration. This non-destructive process allows re-use of the GAC while maintaining a high adsorbate capacity, which reduces carbon replacement costs and significantly decreases the need for carbon disposal by landfill or incineration.

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I. INTRODUCTION

Environmental control and waste remediation are of immediate technological and political interest. The problem of removing potentially toxic compounds from waste streams or spill sites is exacerbated by their low concentrations and even lower allowable limits, which for some compounds is defined as zero. With legislative controls on emissions and liability for contamination, the demand for economical treatment processes is growing stronger.

Although removal of contaminants from waste streams is often considered an economic liability, these problems have several potential solutions, some of which can be profitable. For instance, DuPont is recycling the wastes from their acrylonitrile and adipic acid processes to recover dibasic ester, 2-methylpentamethylenediamine, and acetonitrile which will yield an estimated \$70 million in profits for 1990 (Reisch, 1990). This solution shows a creative yet serious response to a problem which, until recently, has been ignored by industry and the government. Other wastes may not be amenable to such a solution but the renewed commitment to clean-up is motivation for development of separation and treatment technologies.

One technology which has great potential is contaminant removal and separation with supercritical fluids (SCF's) or supercritical fluid extraction (SFE). In this process, a gaseous component is compressed and heated to a pressure and temperature above its critical point where it has a substantial density and high compressibility. The density of the SCF is intermediate between that of a gas and a liquid, allowing the dissolution of non-volatile solid compounds up to 1-2 mole percent. The high compressibility in the supercritical region gives substantial changes in density with small changes in pressure or temperature, allowing the solvent power of the fluid to be "tuned" so that contaminant mixtures may be separated in a series of steps. The thrust of this project has been to investigate experimentally and theoretically the solubility enhancement of non-volatile model contaminant compounds in pure SCF's and cosolvent/SCF mixtures. Using a well defined progression of experiments, we have developed a basic understanding of the physico-chemical properties that influence phase behavior in supercritical systems.

Detoxification of soils, sludges and adsorbents such as granular activated carbon (GAC) appear amenable to SCF extraction. Detoxification processes will primarily be batch operations with widely varying feedstocks, a situation that demands a flexible separation strategy. Supercritical fluid extraction and separation may prove economically viable in such circumstances as indicated by model compound solubility studies and laboratory scale feasibility studies demonstrating its use for the regeneration of GAC.

Supercritical fluid regeneration of GAC was first investigated by DeFilippi and co-workers (1980,1983) using pesticides from industrial wastewaters and model compounds (DeFilippi, et al.,

1980; DeFilippi and Robey, 1983). Regeneration with CO₂ maintained a stable working carbon capacity after 31 cycles while thermal regeneration typically reduces capacity 5-10% per cycle. An economic analysis showed that the processing costs depend predominantly on the specific waste properties and the regeneration throughput. These costs were competitive with thermal regeneration. All of their regeneration experiments, however, were performed at either 120°C or 225°C, which corresponds to reduced temperatures of 1.29 and 1.64, respectively. The reduced temperature is the operating temperature divided by the critical temperature of the solvent. Most of the unique characteristics of these fluids, such as high compressibility and high diffusivities, appear in the region of reduced temperature between 1.01 and 1.1 and many workers have since demonstrated the ability to extract contaminants from GAC and soil at these conditions (Brady, et al., 1987; Dooley, et al., 1987; Tan and Liou, 1988, 1989a, 1989b; Hess, et al., 1991). We demonstrate here a pilot scale study of the SCF regeneration of GAC at 40°C ($T_r = 1.03$). The data obtained from this study are coupled with economic analyses and computer aided design packages to produce a scaled up design of a fixed-site unit to carry out this process.

II. BENCH-SCALE SCF STUDIES

A. SUMMARY

We undertook a concerted effort to understand the phase behavior in solid-SCF systems. We determined solubilities of relatively non-volatile solid compounds in pure and cosolvent-modified supercritical fluid solvents. Cosolvents (typically 1-5 mole percent of a small polar compound) added to an SCF were shown to enhance solubilities and increase selectivities through specific cosolvent-solute interactions. Vapor pressure measurements of several solutes were determined to help isolate the effect of solute properties on the phase equilibria. Spectroscopic investigations also aided the understanding of solubility enhancement by giving information about the local environment around a solute in solution. Correlation of the solubility data has shown that although cubic equations of state are very popular for calculating phase equilibria, they do not completely describe the solid-SCF system due to the molecular asymmetry of size and energy.

B. RESULTS AND DISCUSSION

1. Solubility of Model Compounds

To establish a database suitable for correlation, interpolation and/or prediction of solubilities, it was necessary to measure first the solubilities of a variety of solutes in several supercritical fluids. We made measurements using a gravimetric, dynamic flow technique in several apparatuses capable of operating in different temperature ranges (Johnston and Eckert, 1981). This

arrangement allowed the study of near room temperature fluids (Carbon Dioxide, Ethane, Ethylene, Fluoroform, Sulfur Hexafluoride), moderately high temperature fluids (Ammonia, Butane), and a very high temperature fluid (Ethanol). Solubilities were measured for 21 solid compounds in one or more of the solvents as shown in Table 1. In general, the solutes were chosen to exhibit a variety of physical and chemical properties such as molecular size, polarity, acidity, basicity, and hydrogen bonding ability. The matrix of solubilities is not full due to either immeasurable solubility in a given solvent or the probable formation of a liquid phase in the system.

In terms of the absolute magnitude of solubility, the solvent power for the non-polar room temperature fluids appears to increase in the order $\text{SF}_6 < \text{CO}_2 < \text{C}_2\text{H}_6 < \text{C}_2\text{H}_4$. Solubilities are generally higher in the moderate temperature fluids ammonia and butane than in ethane. The solvent power of fluoroform increases with the dipole moment and is a better solvent for polar solutes but not as good as carbon dioxide for non-polar compounds. For solutes of low volatility, the absolute solubility will depend greatly on the choice of solvent since solubility always increases with temperature at constant density. This indicates that although carbon dioxide is a convenient solvent because it is non-flammable and non-toxic, butane ($T_c = 152^\circ\text{C}$) may be a better choice for many environmental applications.

The effect of solute properties on solubility is essentially two-fold: solubility depends on the solute's volatility or vapor pressure and also on the strength of solute-solvent intermolecular forces. In order to compare the latter effects, a dimensionless enhancement factor is used which is defined as the ratio of a solute's partial pressure in the supercritical phase to its ideal gas partial pressure or vapor pressure (Eq. 1).

$$E = \frac{y_2 P}{P_2^{\text{sat}}} \quad (1)$$

By factoring out the solute's volatility, the enhancement factor allows comparison of solvent and secondary solute effects. Empirically, there is a linear relation between the log of the enhancement factor and solvent density. In fact, for the non-polar and polar solutes shown in Fig. 1 in supercritical CO_2 , the enhancement factor plots almost coincide indicating that differences in solubility are due primarily to vapor pressure differences. Non-linear behavior is noted for high solubilities (10^{-2} - 10^{-1} mole fraction) as in the case of naphthalene in supercritical ethylene. The enhancement in pure fluids is relatively independent of solute structure but is sensitive to solvent polarity and density.

Table 1. Solid-SCF Systems Investigated
Temperatures (C) for which Solubility Data have been taken

Solute	CO ₂	C ₂ H ₆	C ₂ H ₄	CHF ₃ ^d	SF ₆ ^d	C ₄ H ₁₀	NH ₃ ^e	CH ₃ OH ^e
Naphthalene	45 ^a	20,25,35,45 ^b	25,45,50 ^c		50			
Anthracene	30,50,70 ^b	30,35,50,70 ^b	50,70,85 ^c			162,182 ^e	142,162	
Phenanthrene	30,50,70 ^b	30,40,60 ^b	25,45,70 ^{b,c}	30,50				
Fluorene	30,35,50,70 ^b		25,45,70 ^b					
Pyrene	35,50,70 ^b		45,75 ^b					
Acridine	35,50,70 ^d		35,50 ^d		50			
Phenazine	50 ^g							
Dibenzofuran	35,50,70 ^d		35,50 ^d	30,50	50			
Thianthrene	50,70 ^e							
9-Fluorenone	35,50 ^d		35,50 ^d	30,50				
Dibenzothiophene	35,50,70 ^e							
Hexamethylbenzene	30,50,70 ^b		25,45,70 ^b					
Carbon Tetrabromide	35 ^d		12,25 ^d					
Triphenylene							142	
Dodecahydrotriphenylene							162,182	
Xanthone							157	
Thioxanthone							162,182	
Anthraquinone						155,165 175,185 ^f		
5,6 Dimethylbenzimidazole						155,165 175,185 ^f		
9,10 Phenanthrenequinone						165,175 ^f		
6,13 Dihydrodibenzo[b,i] phenazine								275

^aZiger, 1983; ^bJohnston, et al., 1982; ^cJohnston and Eckert, 1981; ^dEckert, et al., 1985; ^eHess, 1987; ^fAlferi, 1989; ^gVan Alsten, 1986

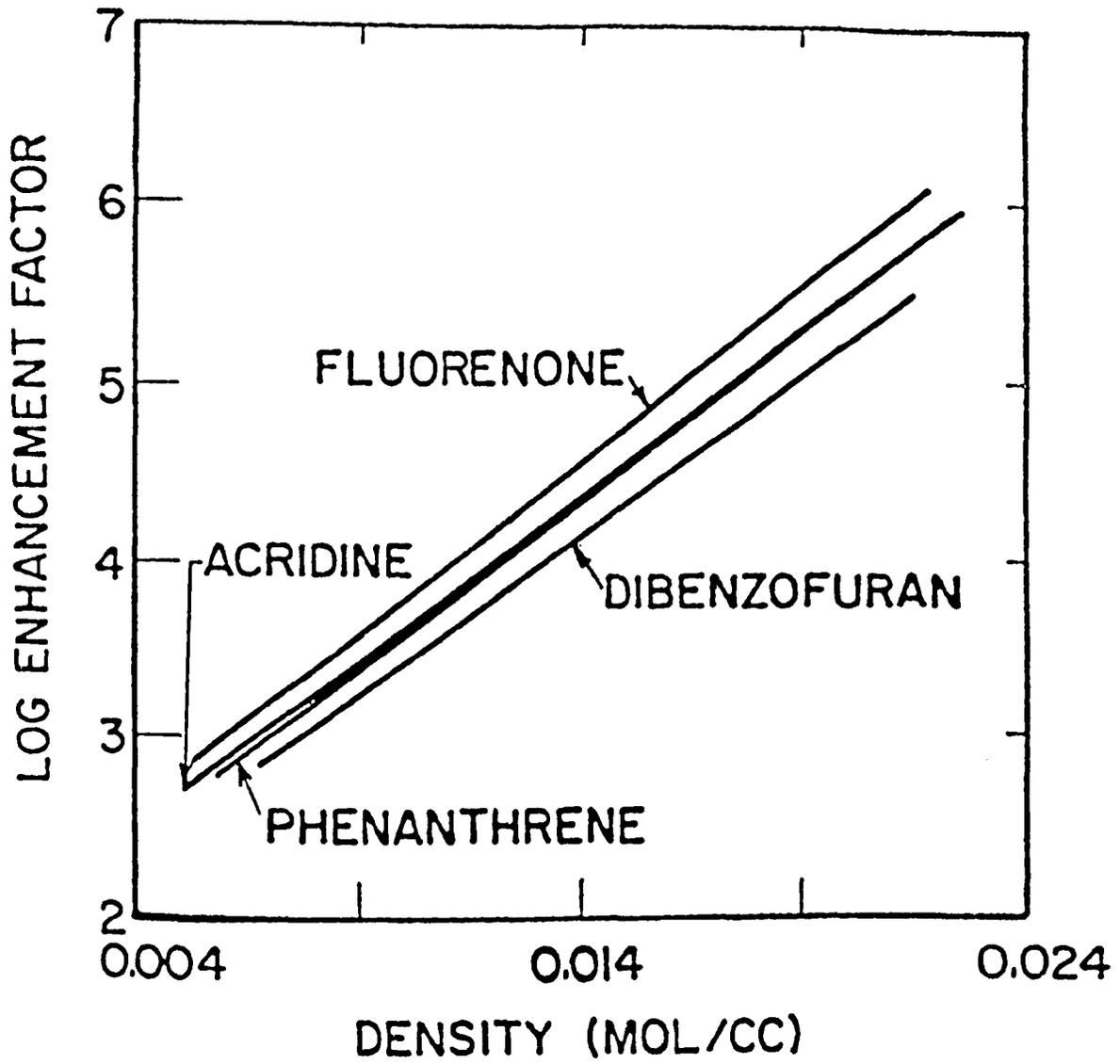


Figure 1. Enhancement Factors for Model Compounds in Supercritical CO₂ at 50°C

2. Cosolvent Effects on Solubility

In pursuit of further solubility enhancements and solute selectivities, cosolvents (also known as entrainers) may be added to an SCF. Cosolvents are normally used at concentrations of 1-5 mole percent with methanol and acetone being typical examples. In the case of a non-polar solute containing no functional groups, the cosolvent induced solubility enhancement is quite similar for all cosolvents and depends only on the concentration of cosolvent. This type of enhancement apparently results from alteration of the solvent properties rather than any specific interaction.

In the case of a polar or heterocyclic solute, the nature of the cosolvent does become important in the magnitude of the enhancement factor. If the solute is capable of participating in hydrogen bonding or dipole-dipole interactions, a complementary cosolvent can be chosen to take advantage of this property. This has been demonstrated in the case of 9-fluorenone/ CO_2 /MeOH and Acridine/ CO_2 /MeOH (Van Alsten, 1986). It is these types of specific interactions that allow one to tailor a solvent/cosolvent mixture to enhance the solubility of a particular solute. The preferential enhancement of one solute from a mixture of solutes then leads to novel separation process. The selectivity for acridine from a mixture of acridine and anthracene is shown in Fig. 2 (selectivity = solubility of acridine/solubility of anthracene). The addition of 1% methanol as a cosolvent in supercritical CO_2 yields a substantial increase in the selectivity of acridine. This enhancement is due presumably to a specific hydrogen bonding interaction between the hydroxylic proton in methanol and the unpaired electrons on the amine nitrogen in acridine whereas anthracene is not capable of participating in such an interaction.

3. Vapor Pressure Measurements

As mentioned previously, the volatility of a solute is the primary physical property that determines its solubility in an SCF and is a necessary piece of information for calculating the enhancement factor. Therefore, previously undetermined vapor pressures of model compounds used in the solubility studies were measured. Vapor pressures were measured for 10 compounds using a transpiration technique which allowed accurate measurements down to 5 millipascals. Measurements were obtained for temperature ranges of interest for SCF processes as long as the solute exhibited a pressure of a few mPa. The data have been recently published so only a summary of the compounds and temperatures studied is given in Table 2 (Hansen and Eckert, 1986; Alferi, 1989). These data also provide a good measure of the heat of sublimation which can be used to correlate energy parameters for equations of state. This property will always be a critical factor in process design and feasibility studies for proposed SCF processes.

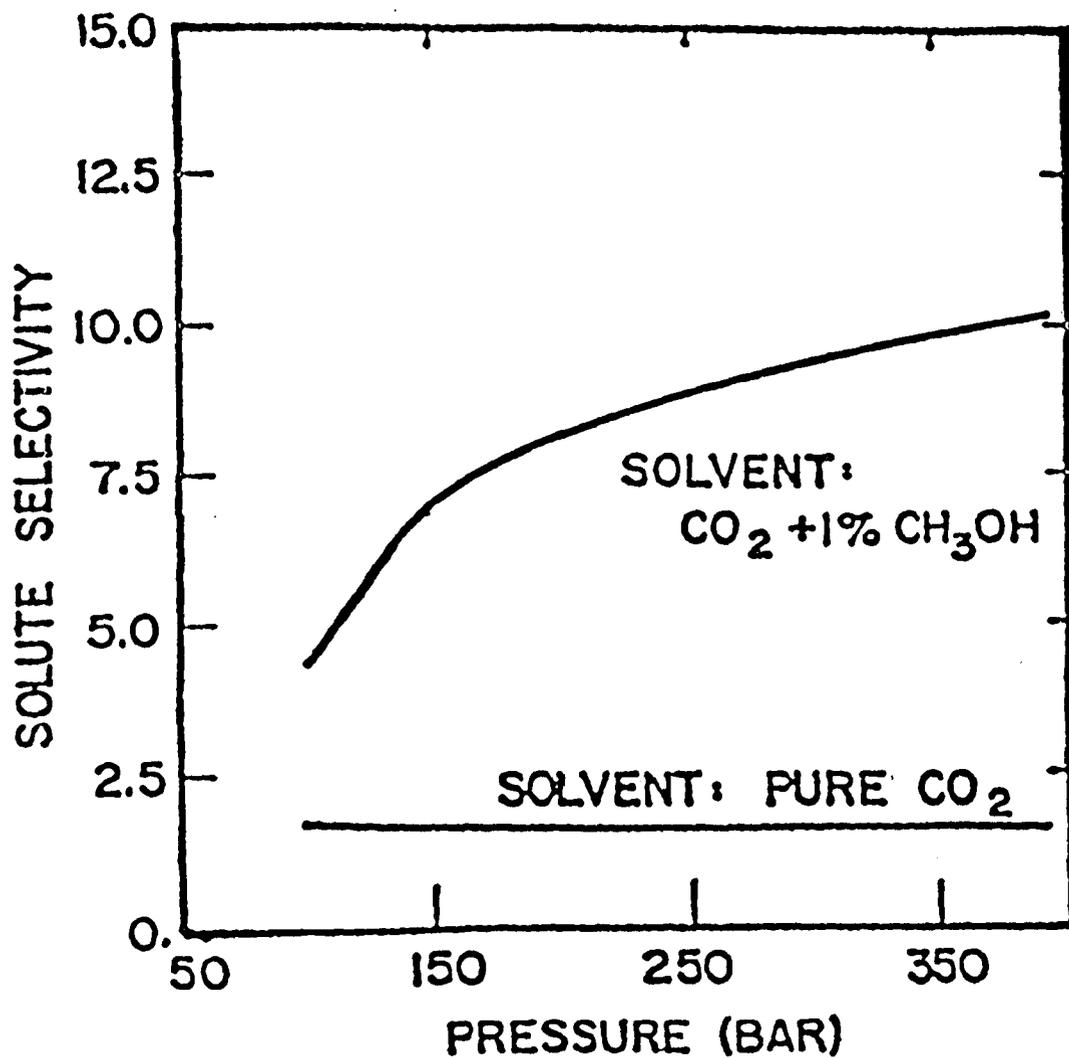


Figure 2. Selectivity for Acridine from an Acridine/Anthracene Mixture

Table 2. Summary of Vapor Pressure Studies	
Compound	Range of Temperature (C)
Anthracene	40-90
Carbazole	110-180
Dibenzofuran	30-70
Dibenzothiophene	30-75
5,6-Dimethylbenzimidazole	110-180
9-Fluorenone	25-70
9,10-Phenanthrenequinone	140-190
Thianthrene	45-110
Triphenylmethane	30-85
Xanthone	110-160

4. Spectroscopic Measurements

Of the possible mechanisms for solubility enhancement, that of solvent "clustering" has recently been given much attention. Measurements of the partial molar volume at infinite dilution for four solutes in supercritical CO₂ show a large negative dip in the near-critical region where the isothermal compressibility of the solvent diverges to positive infinity. This was originally interpreted in terms of the solvent clustering about the solute molecule and therefore reducing the total volume of the solution (Eckert, et al., 1983,1986b). A solvent cluster of about 100 solvent molecules was put forward although at present this number seems excessive. Recent spectroscopic measurements in our laboratories and others (Brennecke, et al., 1990; Kim and Johnston, 1987; Yonker and Smith, 1988; Kajimoto, et al., 1988) have probed the local environment around a solute in the same highly compressible region and do indeed indicate an excess number of solvent molecules near the solute over what would be determined from the bulk density. This local density reaches approximately 3-4 times the bulk density in the region where the fluid has a high compressibility. Hence, there is now a substantial body of experimental evidence for the idea of clustering which would help explain enhancement factors for solutes in pure supercritical fluids.

5. Models for SCF Phase Equilibria

The most widely used method for calculating high pressure gas phase thermodynamic properties is the cubic equation of state (e.g., van der Waals, Soave-Redlich-Kwon, Peng-Robinson). Various attempts have been made to modify the molecular interactions in these models to describe more accurately the phase equilibria in the asymmetric solid-SCF system. Examples of this are the Carnahan-Starling van der Waals equation (Johnston and Eckert, 1981) and the Augmented van der Waals equation (Johnston, et al., 1982). It is also possible to adapt lattice theories which impose a certain structure on the solution since the SCF is quite dense. An example of this is the decorated lattice gas (Gilbert and Eckert, 1986). These models have had limited success in correlating the solubilities or enhancement factors but are not yet predictive and do not correlate cosolvent effects very well.

An approach for including cosolvent effects which appears promising is to treat the cosolvent-solute interaction by the law of mass action with an equilibrium constant and couple this chemical equilibrium with an equation of state that handles the physical interactions. These so called chemical-physical models are very versatile but suffer from too large a number of adjustable parameters. It may be possible to reduce the number of adjustable parameters, however, by measuring equilibrium constants spectroscopically (Eckert, et al., 1986a). It is likely that the most profitable applications of SCF technology will need to make use of cosolvent effects to "tailor" a solvent for a particular solute and this type of model will likely be useful in the development of these applications.

C. CONCLUSIONS

A substantial body of good experimental data for solubilities in pure and mixed SCF's over a wide range of temperature has been established. This database along with vapor pressure measurements has provided a proving ground for equation of state development. Spectroscopic measurements have shown detailed molecular interactions of solutes in SCF's which can be used to explain enhanced solubility and lead to further development of models. As a result of this work, we can estimate from limited data the feasibility of applying SCF processing to a given separation.

III. PILOT-SCALE RESEARCH PROGRAM

A. SUMMARY

The ability of supercritical CO₂ to remove model contaminant compounds from GAC and subsequently drop out most of the contaminant in a liquid phase has been investigated in a pilot

scale apparatus. Model compounds, 2-chlorophenol and toluene, were chosen to represent common features of hazardous waste chemicals such as aromaticity, acidity, and chlorination. Contaminants were adsorbed onto GAC through either direct contact or by entrainment in a gas stream. Typical desorption profiles indicate an 85% removal of the compound from the carbon. The presence of water on the GAC was shown to inhibit slightly the efficiency of the desorption. Methanol was used as a cosolvent for a desorption of 2-chlorophenol in which the carbon showed a net weight gain. This indicates that although methanol can enhance the solubility of model compounds in an SCF the GAC has a strong affinity for methanol which competes with the solvation process. The desorption results have been interpreted with a generalized desorption-mass transfer model.

A series of near-critical vapor-liquid equilibrium measurements have been carried out on the 2-chlorophenol/ CO_2 system. The effects of the presence of water as an impurity and methanol as a cosolvent were also investigated.

B. EXPERIMENTAL

The pilot plant is a two-part apparatus designed to carry out SCF regeneration of GAC and near-critical gas/liquid separations on a scale such that the data may be used directly in design calculations for a detoxification unit with reasonable scale-up factors (Fig. 3). The two units are a GAC regeneration or desorption bed and a contaminant separation flash vessel, which may be operated separately or together. In addition to the pilot plant, another apparatus was constructed similar to that used by Tan and Liou (1989a) for preparing "contaminated" GAC by adsorbing the model compound onto the GAC from a nitrogen stream.

For GAC regeneration, liquid CO_2 was pumped to operating pressure and brought to temperature in a series of steam and cooling water heat exchangers. The system temperature and pressure were monitored with a thermistor probe (OMEGA OL-703) and pressure transducer (OMEGA PX302-3 KGV), respectively. Methanol was injected during the heat up stage by means of a high pressure syringe pump (ISCO μLC -500). The GAC bed consisted of an 18" long 3/8" OD x 0.305" ID piece of stainless steel tubing which was loaded with a preweighed sample of contaminated GAC. Glass wool plugs held the GAC in place during operation. An in-line high pressure UV monitor (Milton Roy Critical Extraction Monitor) was located downstream of the GAC bed to determine the concentration of contaminant in the SCF as a function of time. The output from the UV had to be back calibrated from the final contaminant concentration determined gravimetrically due to instrument deficiencies. Finally, the fluid mixture was flashed to atmospheric pressure through a micrometering valve where the contaminant dropped out of solution and was collected in a cold trap. The gas flow rate was monitored with a wet test meter.

The GAC was Calgon F-400 and was washed with distilled water once to remove fines, dried under vacuum, then kept in a desiccator until ready for use. No screening for particle size was carried out. Carbon dioxide was bone dry grade (99.0%) from Linde. The 2-chlorophenol (99+ %), methanol (99.9%), toluene (99+ %), and water (HPLC grade) were obtained from Aldrich Chemical Company and were used as received.

For near-critical vapor-liquid separation, CO₂ was pumped through the heat exchangers and flashed through a micrometering valve into a separation vessel at a lower, but still elevated pressure. The gas phase from the separation vessel was recompressed and recycled to provide a recirculating flow while the liquid phase was pumped back to the top of the vessel to wash the gas stream. Once the desired conditions stabilized, the contaminant was injected into the stream and allowed to distribute between the two phases in the separation vessel. The vapor phase was then sampled and analyzed by gas chromatography. When water or methanol was used, it was added before the contaminant, and analysis was carried out before the contaminant was introduced.

C. RESULTS AND DISCUSSION

1. Adsorption/Desorption Studies

Regeneration experiments with CO₂ were carried out for 2-chlorophenol, 2-chlorophenol with methanol cosolvent, toluene, and toluene in the presence of water at 40°C and 104 bar. Since the temperature and pressure effects could be nominally predicted, these studies concentrated on flow rate effects and desorption profiles.

In order to model the rate of desorption it is also desirable to know the adsorption profile to help establish the equilibrium. We carried out the adsorption of 2-chlorophenol from supercritical CO₂ at 173 bar and 50°C. This adsorption profile resulted in a maximum loading of 0.80 g/g GAC and was modeled with a Toth isotherm which correlates the data very well (Fig. 4). To expedite preparation, further samples of GAC for the regeneration studies were prepared in a low pressure system using nitrogen as the carrier.

Using the nitrogen adsorption method, 2-chlorophenol showed a loading of 0.53 g/g GAC, while toluene adsorbed at 0.37 g/g GAC. These loadings were reproducible to within 2%.

The regeneration efficiency of CO₂ is defined as the percent of the initial concentration removed during regeneration. The desorption profile for toluene is shown in Fig. 5 along with literature data for this system (Tan and Liou, 1989b). The data are plotted as a function of a dimensionless volume (volume of fluid at bed conditions/volume of GAC) in order to compare between our data and the literature data. There is quite good agreement with the literature despite

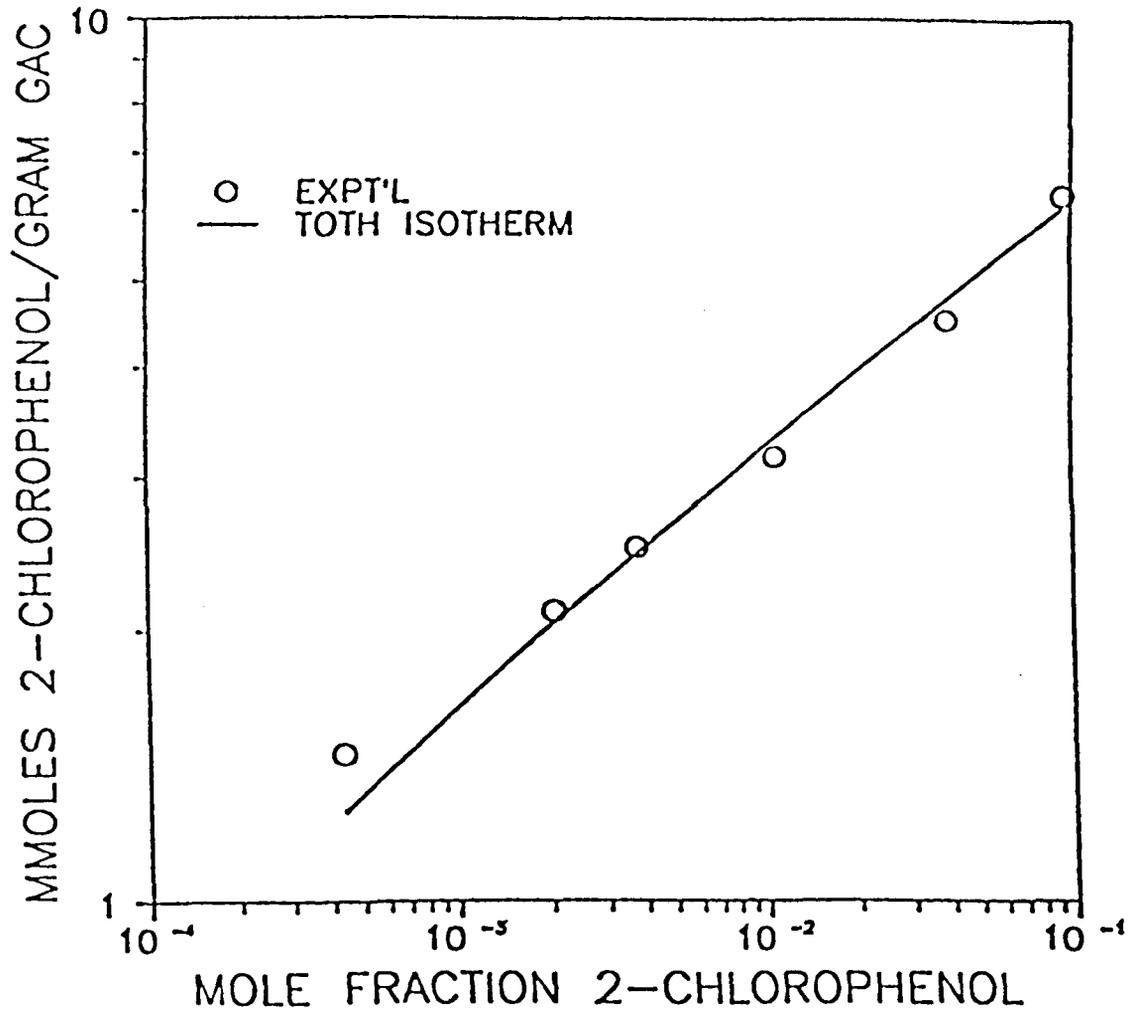


Figure 4. Adsorption of 2-Chlorophenol from Supercritical CO₂

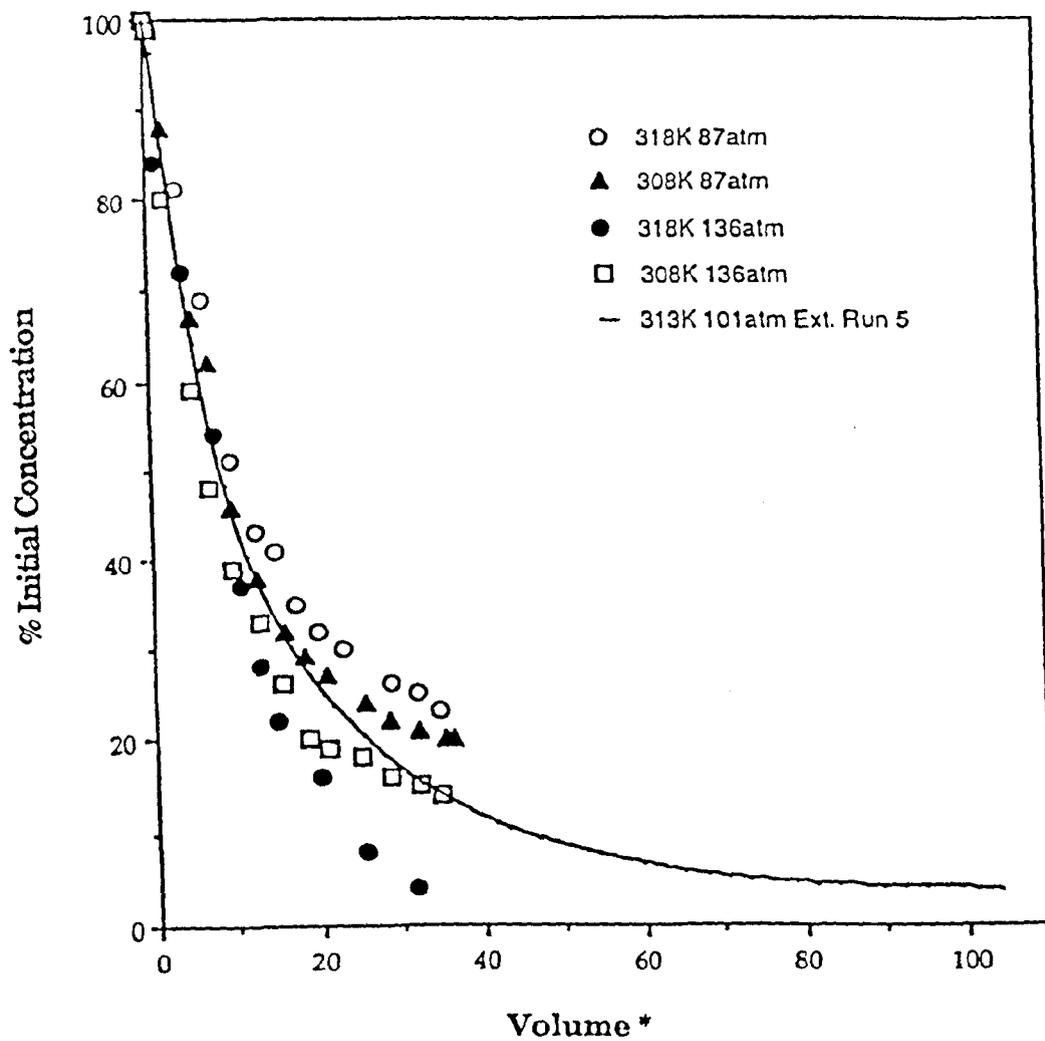


Figure 5. Desorption of Toluene with Supercritical CO₂, Symbols are Data of Tan and Liou (Volume* = Dimensionless Volume Defined in Text)

differences in temperature, flow rate, and GAC. Figure 6 shows the effect of water on the desorption of toluene. The regeneration efficiency was 96% without water and 85% with water but the initial rates of desorption (indicated by the slope of the desorption profile) are similar for both cases. Water apparently has a shielding effect for low concentrations of toluene.

Efficiencies of 85% and 89% were observed for 2-chlorophenol. In early studies the flow rate of CO₂ was varied to attempt to reach the mass transfer limit in terms of superficial velocity of solvent. This is the point at which the solvent velocity is too fast for the concentrations in each phase (adsorbed and SCF) to equilibrate. We were not able to attain velocities sufficiently large to deviate from an equilibrium desorption process. Methanol was added as a cosolvent to try to increase the regeneration efficiency but it appears to adsorb onto the carbon from the SCF phase and does not help. The GAC actually gained weight during a desorption run using methanol as a cosolvent.

The regeneration efficiency is apparently determined by two competing effects, solvation and adsorption. The solvation is dictated by thermodynamic equilibrium and can be estimated using the models described above for solid-SCF phase equilibria. Generally, high pressures will give higher solubilities of contaminants. The adsorption is determined strongly by the characteristics of the GAC which are by no means general. Such things as surface area per unit volume, heat treatment, and particle size, affect the adsorption/desorption properties but little can be done to predict these effects. Usually adsorption/desorption experiments must be carried out for compounds of interest and the results fit to a model, as was shown above, which can then be extended in pressure and temperature space for that compound only. Through repetitive cycles, other investigators have demonstrated sufficiently that SCF regenerated carbon retains consistently higher adsorption capacity than steam regenerated carbon (DeFilippi, et al., 1980; Tan and Liou, 1988).

2. Near-Critical Gas/Liquid Separation

The systems studied for separation include 2-chlorophenol/CO₂, 2-chlorophenol/water/CO₂, and 2-chlorophenol/methanol/CO₂. The concentrations of water and methanol were both 5 mole percent. The results from these experiments are shown in Fig. 7 as vapor concentration vs. liquid concentration. For a successful separation to occur, the contaminant must preferentially distribute into one of the two phases leaving the other phase relatively pure. This distribution will show up as a deviation of the data from the 45° line, which in the figure rises steeply away from the data due to the scale of the axes. The data indicate that most of the contaminant is in the liquid phase and that it would be possible to recycle the vapor phase as a solvent and concentrate the contaminants in a liquid phase.

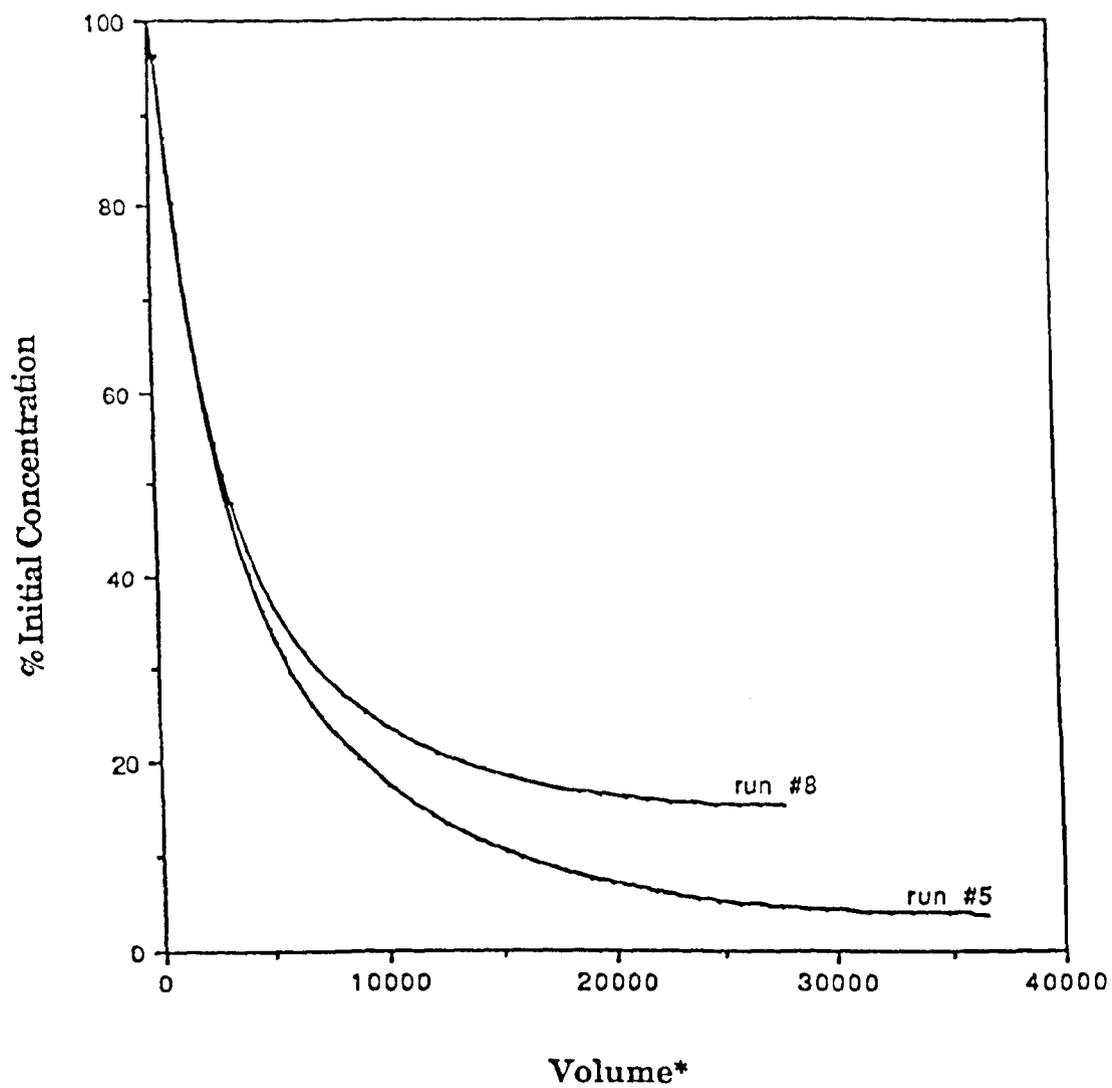


Figure 6. Desorption of Toluene in the Presence (#8) and Absence (#5) of Water
(Volume* = Dimensionless Volume Defined in Text)

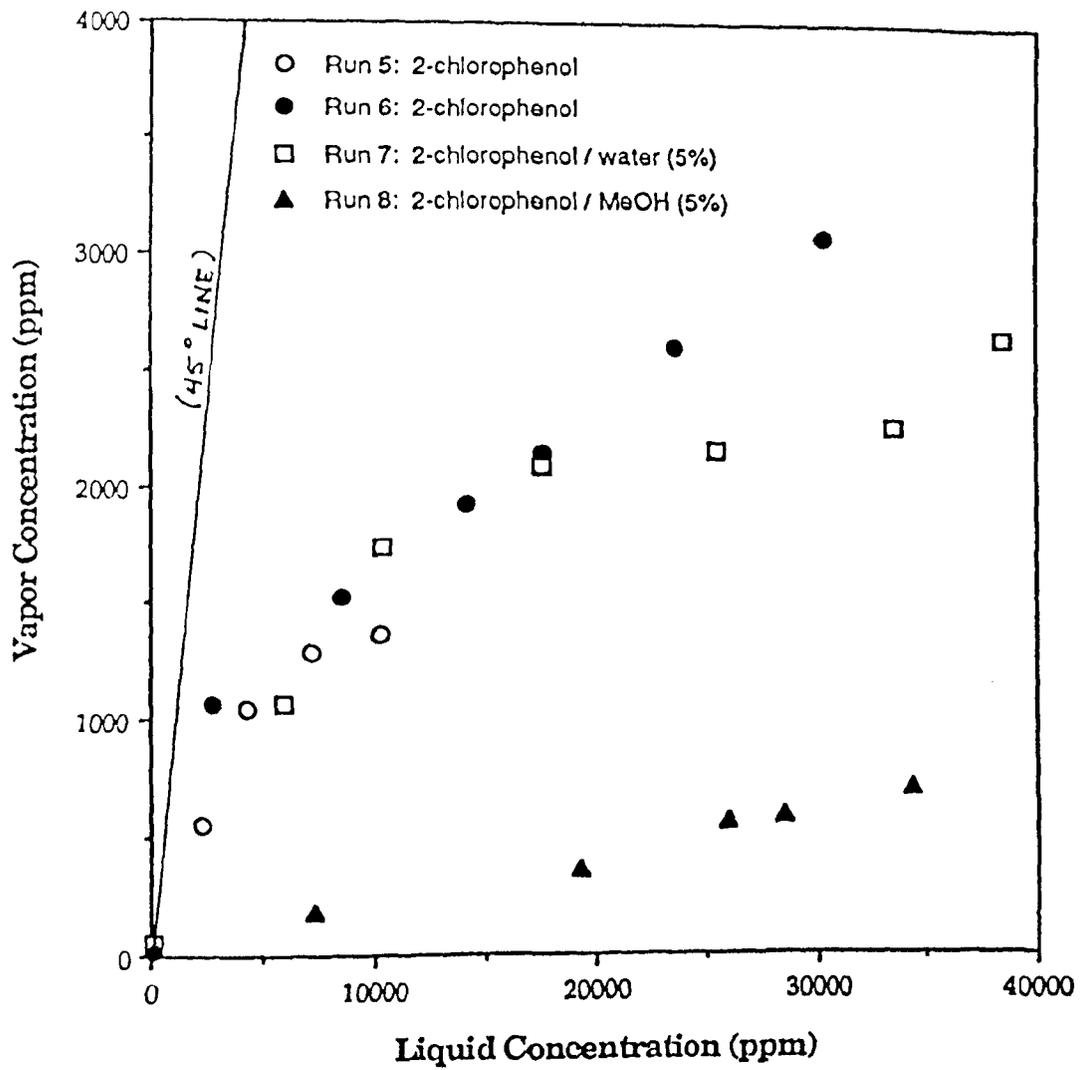


Figure 7. Vapor-Liquid Equilibria in the 2-Chlorophenol/CO₂ System

D. MODELING OF RATE PROCESSES

Several recent publications discuss models for supercritical regeneration of GAC; Tan and Liou (1988) present a model for the desorption of ethyl acetate which assumes no axial dispersion and which approximates the desorption kinetics as being linearly related to the adsorbed concentration. The resulting equation for desorption bed outlet concentration, $C(L,t)$ is:

$$C(L,t) = \frac{1-\alpha}{\alpha} C_{a_0} \left[\exp\left(-k\left(t - \frac{\alpha L}{u}\right)\right) - \exp(-kt) \right] \quad (2)$$

where k is defined as the kinetic desorption constant given by:

$$\frac{\partial C_a}{\partial t} = -kC_a \quad (3)$$

Recasens, et al. (1989) improved upon this model by incorporating the solid-SCF equilibrium and external mass transfer coefficient explicitly, assuming a parabolic concentration profile inside the particles. Analytical solutions were developed for two cases: 1) where equilibrium desorption occurs and is controlled by the external and intraparticle mass transfer rates and 2) where a first-order irreversible desorption step is controlling. The first of these is found to effectively describe the supercritical desorption of ethyl acetate. The solutions for exit concentration and desorbed fraction from carbon with an initial concentration C_{a_0} are:

$$\begin{aligned} \frac{C(L,t)}{C_{a_0}/K} &= \frac{b'}{b+b'} \exp[-(b+b')\theta] [\exp(b+b') - 1] \\ &+ \exp[-(b+b')(\theta-1)] \sum_{m=0}^{\infty} (-1)^{m+1} \left(\frac{b}{b'}\right)^m \frac{A_m(b') A_m[b'(1-\theta)]}{(m!)^2} \end{aligned} \quad (4)$$

where

$$\begin{aligned} \theta &= \frac{tu}{L\alpha} \\ b &= \frac{3k_p L\alpha}{r_0(\beta + \rho K)u} \\ b' &= \frac{3(1-\alpha)k_p L}{r_0 u} \end{aligned} \quad (4a)$$

and A_m is related to the incomplete gamma function and is calculated from:

$$\begin{aligned} A_0 &= 1 - \exp(-w); & m=0 \\ A_m &= A_{m-1}(w) - w^m \exp(-w); & m \geq 1 \end{aligned} \quad (5)$$

The equilibrium constant K rigorously denotes the equilibrium between adsorbed concentration and concentration in the pore fluid:

$$C_a = KC_{\text{pore}} \quad (6)$$

The desorbed fraction is given by Eq. 7. We found the first four terms in the summation sufficient to approximate the series.

$$\begin{aligned} F &= \frac{b}{b+b'} \left[1 - \frac{\exp[-\theta(b+b')][\exp(b+b') - 1]}{b+b'} \right] \\ &+ \frac{1}{b+b'} \sum_{m=0}^{\infty} \frac{A_m(b') A_m[b(\theta-1)]}{(m!)^2} \\ &- \frac{b}{(b+b')b'} \exp[-(b+b')(\theta-1)] \sum_{m=0}^{\infty} (-1)^{m+1} \left(\frac{b}{b'} \right)^m \frac{A_m(b') A_m[b(1-\theta)]}{(m!)^2} \end{aligned} \quad (7)$$

In this work the data for SCF regeneration of GAC adsorbed with 2-chlorophenol has been modeled with these equilibrium desorption/mass transfer equations. Optimal fits for the equilibrium constant K and the overall mass transfer coefficient, k_p , were obtained by visual inspection using MathCAD software on a Compaq 286 computer. It is apparent the observed desorbed fraction may be reasonably predicted for a range of K , k_p combinations, but in order to simultaneously model the exit concentration, the values are constrained to a single pair. Figures 8 and 9 display a series of data in comparison with predicted values. The fitted values for equilibrium and mass transfer coefficients are $2.5 \times 10^{-2} \text{ m}^3/\text{kg}$ and $5.7 \times 10^{-7} \text{ m/s}$, respectively. These were used in the design study to determine cycle times and regeneration effectiveness for various fluid flow rates and bed lengths. Representative results for $u = .05 \text{ m/s}$ and 10 m bed length are shown in Figs. 10 and 11.

Concentration vs. Time

2-Chlorophenol Extraction

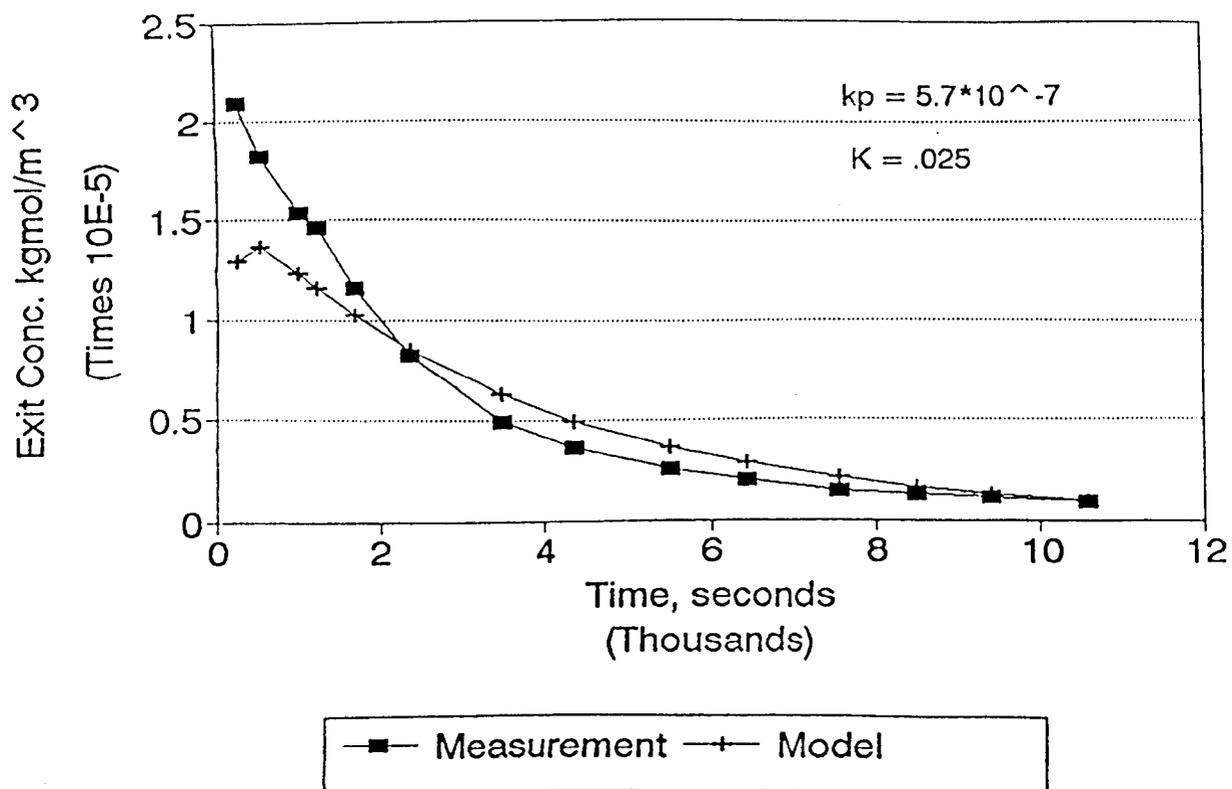


Figure 8. Model Correlation of Exit Concentration Data for 2-Chlorophenol

Desorbed Fraction vs. Time 2-Chlorophenol Extraction

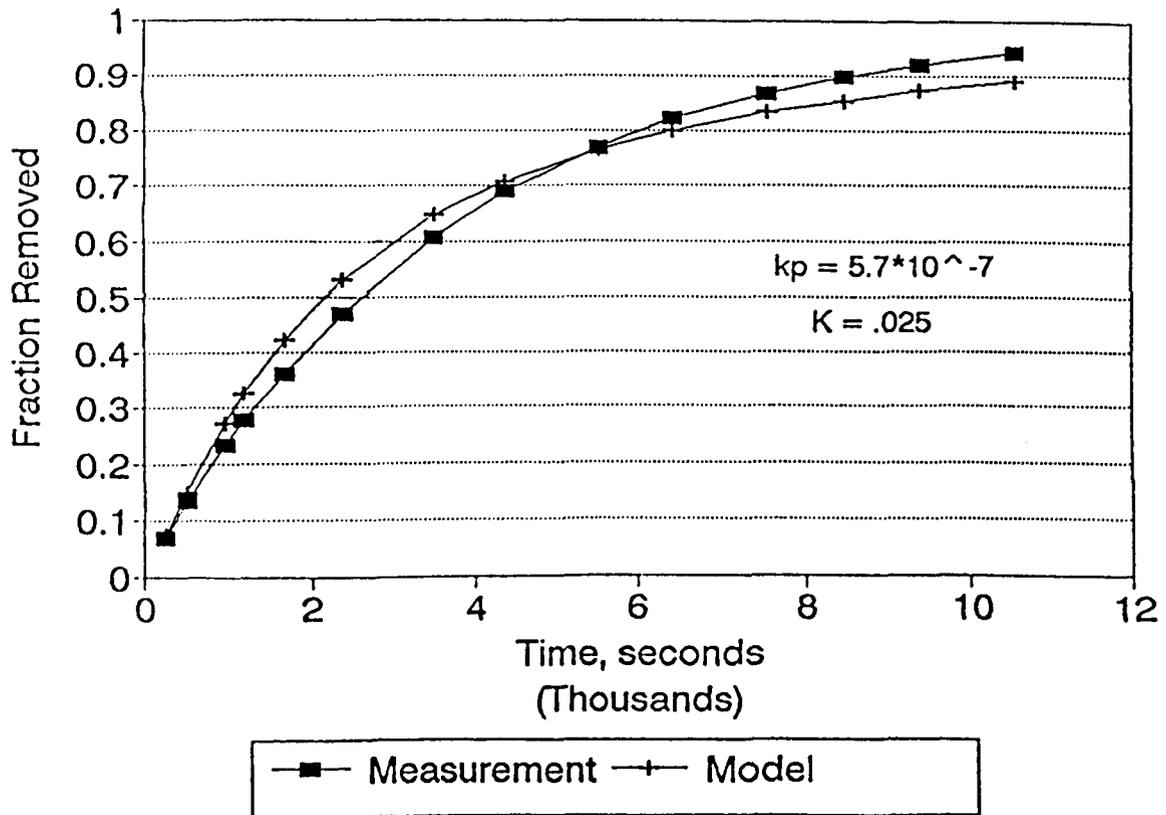


Figure 9. Model Correlation of Desorbed Fraction of 2-Chlorophenol

Concentration vs. Time

Plant Design Case

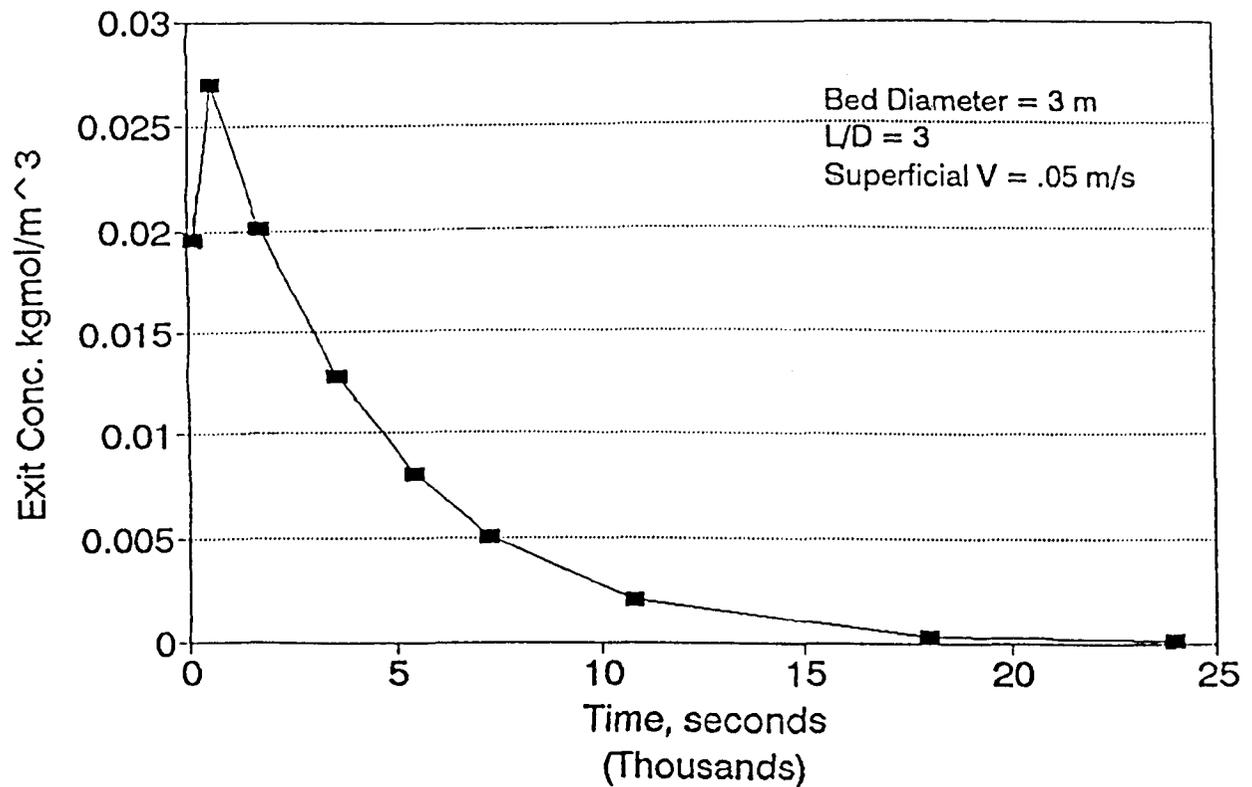


Figure 10. Calculated Exit Concentration Profile for Scaled-up Desorber

Desorbed Fraction vs. Time

Plant Design Case

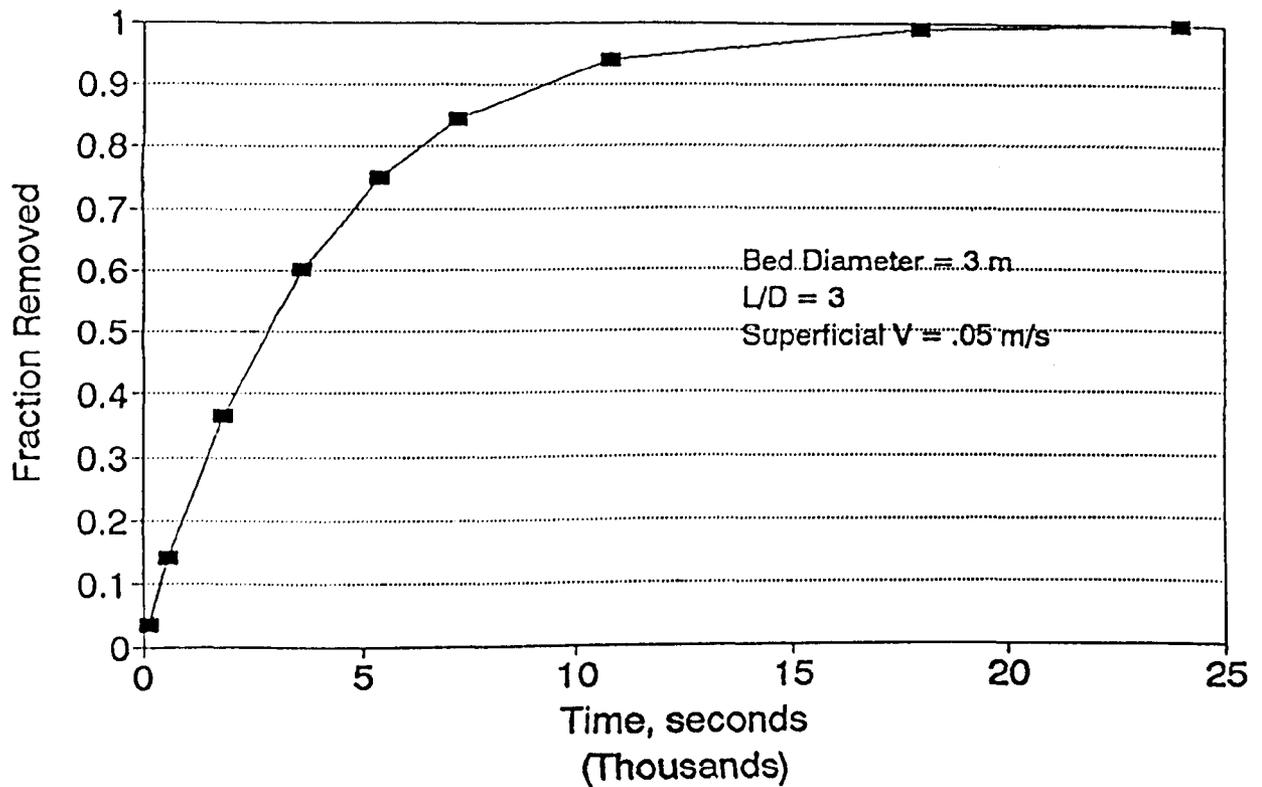


Figure 11. Calculated Desorbed Fraction Profile for Scaled-up Desorber

E. CONCLUSIONS

A pilot plant for the regeneration of GAC using supercritical fluids was constructed and operated demonstrating the feasibility of this application. Several contaminants were investigated including 2-chlorophenol which was deemed to represent a difficult desorption and provide a conservative basis for design. Phase equilibria measurements were made on the systems 2-chlorophenol/CO₂ and 2-chlorophenol/methanol/CO₂ and equation of state parameters likely to affect the regeneration process.

IV. APPLICATION TO DESIGN OF TREATMENT FACILITIES

A. SUMMARY

The results of the pilot plant studies have been applied to the design of a fixed-site GAC regeneration unit consisting of a three element desorber with two stage flash separation. Optimization of the process centers around minimizing the cost of recycling the SCF through an efficient recompression scheme and cycle configuration in the desorber unit. An economic evaluation shows a processing cost of 10.6¢/lb GAC. This non-destructive process allows re-use of the GAC reducing carbon replacement costs and significantly decreases carbon disposal by landfill or incineration.

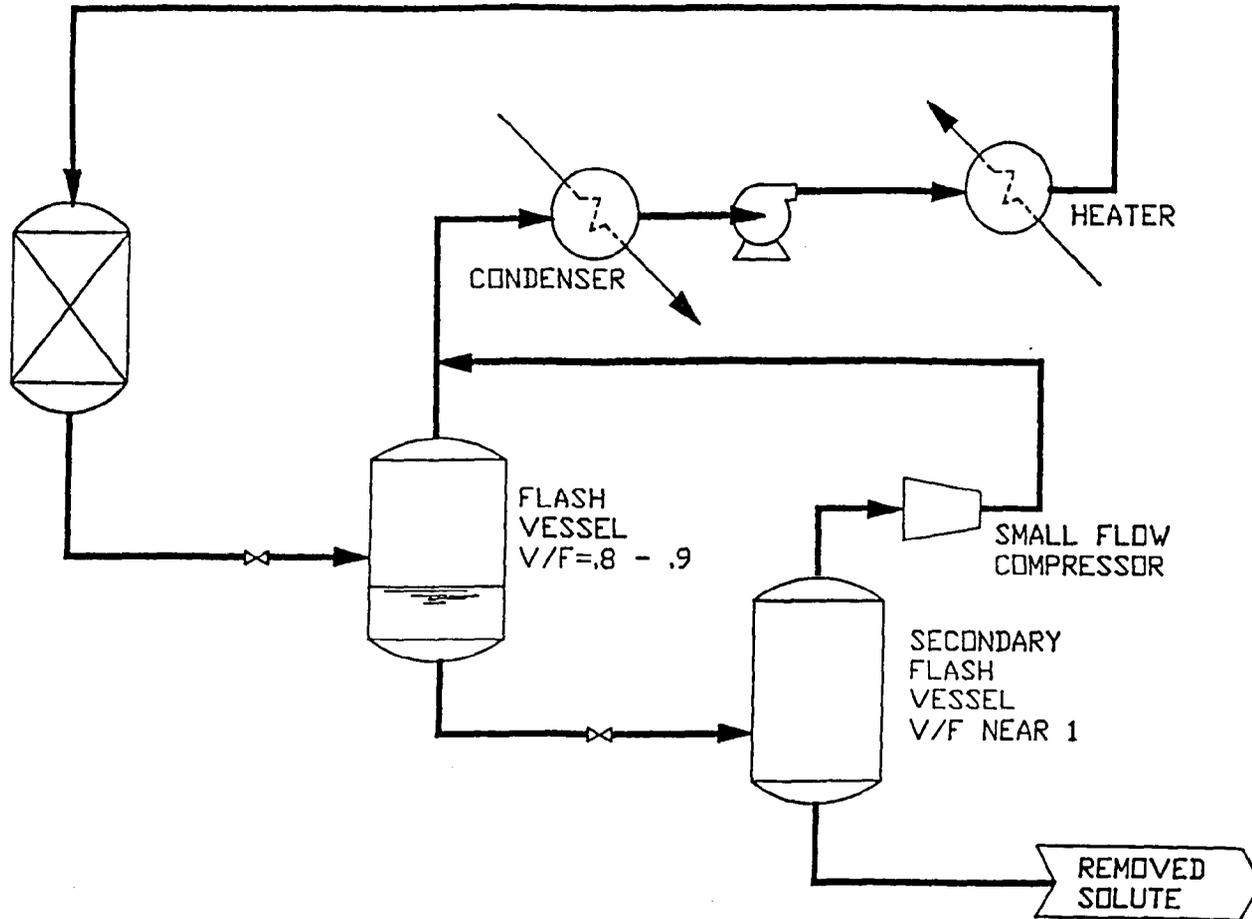
B. DESIGN METHODOLOGY AND ASSUMPTIONS

1. Flowsheet Development

Previous studies and industrial practice has shown that direct recycling of vapors (via recompression to supercritical pressure) is problematic in that demisting of the entrained solute is difficult and costly due to high compression of large vapor flows. An alternative which is often lower cost and is operationally superior is to condense the flashed vapors, pump the liquid phase to the desired pressure, and then heat to operating temperature. These concepts denoted as Options 1 and 2, respectively, are shown in Figs. 12 and 13. Each of these options has been simulated with ChemCAD version 2.41 process simulation software.

2. Regeneration Cycle Configuration

The regeneration data for 2-chlorophenol indicates the mass transfer kinetics are limiting. Thus the exit concentrations are not approaching the SCF solubility limits at any time, most particularly during the last half of the desorption cycle time. Consequently, it is advantageous to use a progressive sequence in which the SCF from a bed in the last half of its cycle is used to



OPTION 2: IMPROVED FLOWSHEET

Figure 13. SCF Recycling Option 2

accomplish the first half of the cycle of another bed. With three beds as a unit, the cycle sequence is shown in Fig. 14.

The final flowsheet adopts this approach, minimizing cost of recycling the fluid and keeping the exit concentration fairly stable as a function of time. It is an assumption of this configuration that the individual regeneration vessels are being emptied of regenerated carbon and refilled during the off-line time. One half of a complete regeneration cycle should be adequate for the solids handling steps.

The model developed via analysis of the experimental data was used to examine the effects of bed height and fluid velocity over practical ranges. The optimal superficial velocity was determined by increasing the flow until further increments no longer result in decreased cycle time. This limit exists because the mass transfer rate is the desorption rate limiting step. A superficial velocity of 4.0 ft/min was found to be optimal and was adopted for the final flowsheet and economic analysis.

The cost calculations and analyses were performed on a computer spreadsheet (Quattro Pro). Cost/capacity relationships for major equipment inserted in the spreadsheet have been derived from cost data presented in Peters and Timmerhaus (1980) and Guthrie (1974).

The chemical engineering cost index for CPI industry was used to convert purchased costs to a 1991 basis. The Guthrie (1974) data includes ratios for total installed costs to purchased costs for each type of equipment, and these are used to develop the Direct Capital Investment. Ratios for Indirect Capital are taken from Peters and Timmerhaus (1980).

C. FINAL DESIGN AND ECONOMIC ESTIMATES

1. Flowsheet

The predominant factor determining operating feasibility and overall economy is the SCF recycle efficiency. As discussed previously, the condensation of vapors from the first flash with a liquid pump for recompression and a gas compressor from the secondary flash vapors is much more economical than recompressing a vapor stream from a single flash. This scheme is more energy efficient primarily because the operating temperature of the facility is not far removed from ambient. This recycle scheme has been incorporated into a process simulation flowsheet along with the 3-unit desorber described above. The flowsheet is shown in Fig. 15.

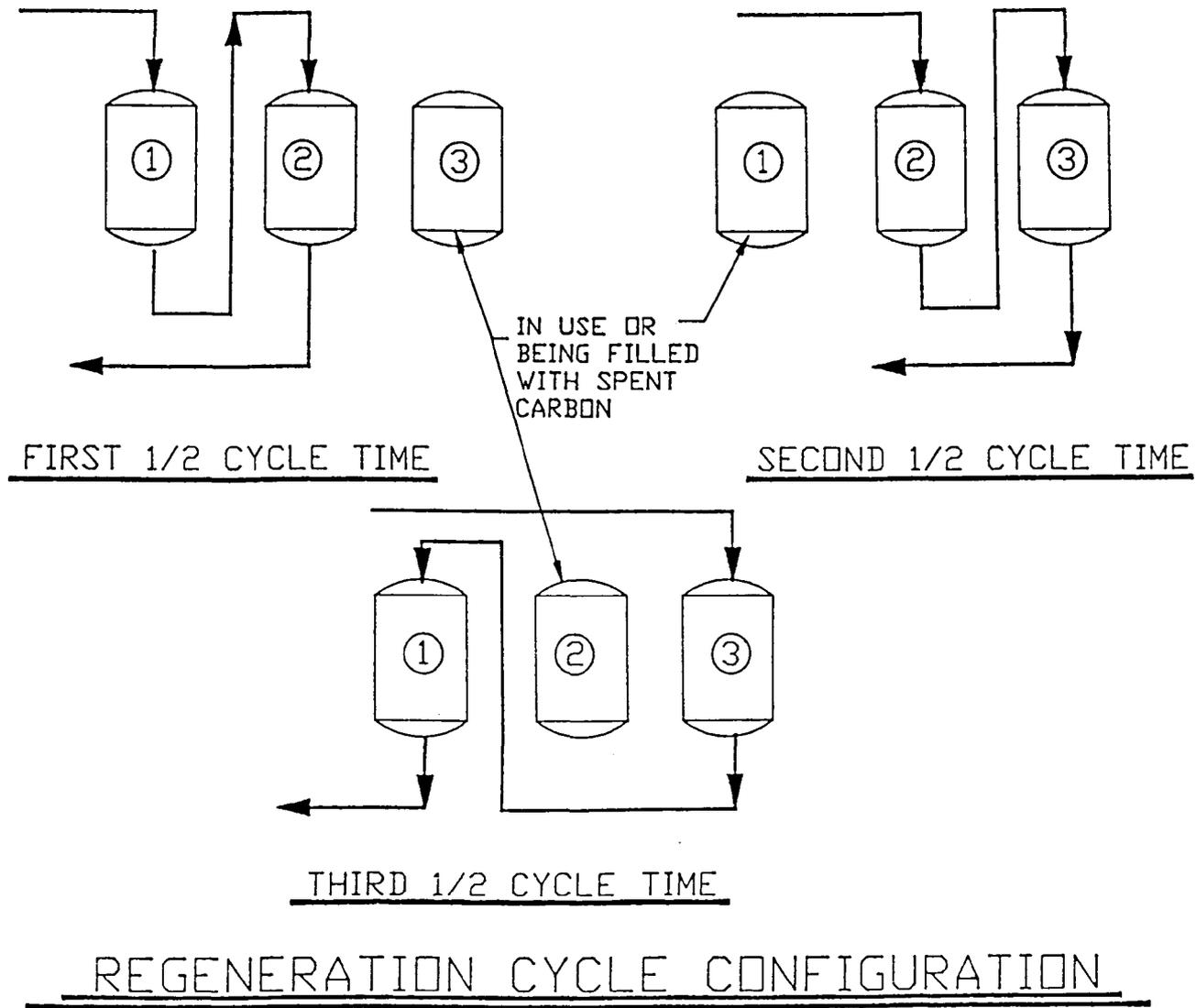


Figure 14. Desorber Regeneration Cycle Sequence

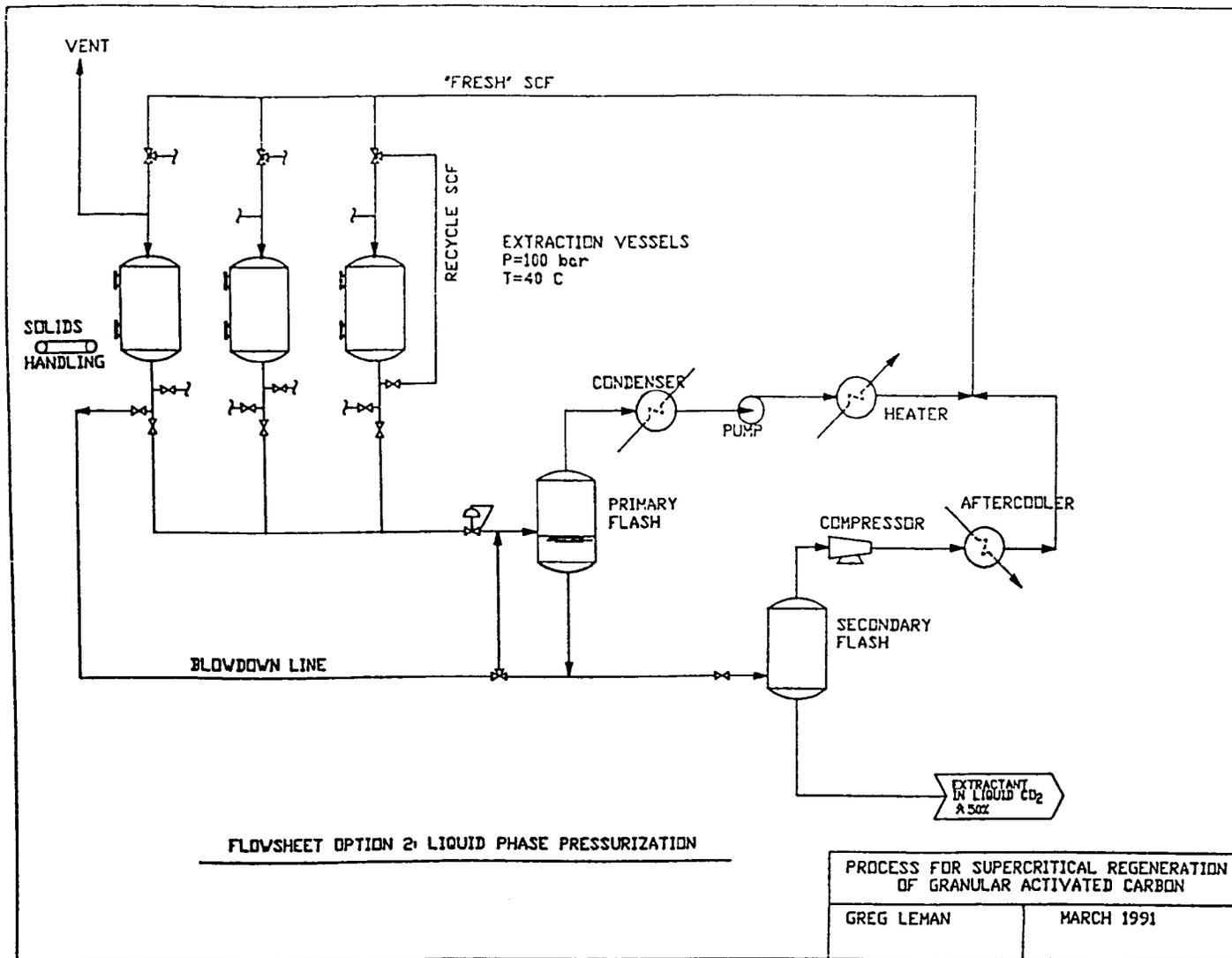


Figure 15. SCF Regeneration Process Simulation Flowsheet

2. Design Calculations

For ease of use in the spreadsheet, all graphical data from various sources have been fit to equations. Base cost is in the year given by Guthrie (1974) or Peters and Timmerhaus (1980) with appropriate cost indices applied to determine costs in 1991 dollars.

A. PRESSURE VESSELS (EXTRACTION UNITS AND FLASH SEPARATORS)

Base cost in 1970 dollars for a vessel of diameter D (ft) operating at pressure P(psig):

$$C_{\text{vsl}}^{70} = 294 D^{1.825} \quad (8)$$

Cost factors for pressure (F_p) and internal support (C_{int}) are given by:

$$\begin{aligned} F_p &= 0.057 P^{0.625} \\ C_{\text{int}}^{70} &= 35.2 D^{1.37} \end{aligned} \quad (9)$$

For pressure vessels, the ratio of direct capital to purchased cost is 3.0 (Guthrie, 1974); thus, the total direct capital (DC_{vsl}) in 1991 dollars is:

$$DC_{\text{vsl}}^{91} = \frac{450}{126} F_p [C_{\text{vsl}}^{70} + C_{\text{int}}^{70}] * 3.0 \quad (10)$$

No allowances were made for stainless steel or better alloys. If specific applications require alloy construction, capital costs will increase accordingly.

B. HEAT EXCHANGERS

Base cost in 1979 dollars for an exchanger with surface area A (ft²):

$$C_{\text{HX}}^{79} = 547 A^{0.543} \quad (11)$$

The cost factor for pressure in excess of 1000 psig is given by:

$$F_p = 0.575 + 4.14 \times 10^{-4} P \quad (12)$$

The ratio of direct capital to purchased cost is 2.30 for heat exchangers giving a total direct capital of:

$$DC_{HX}^{91} = \frac{450}{230} F_p C_{HX}^{79} * 2.30 \quad (13)$$

C. INDUSTRIAL GAS COMPRESSORS

Costs for compressors, up to 3-stage with intercooling, are given by:

$$C_{comp}^{79} = 2.59 q^{0.517} \quad (14)$$

where q is the intake flow in actual cubic feet per minute. The direct capital ratio is 1.57 and total direct capital is then:

$$DC_{comp}^{91} = \frac{450}{230} C_{comp}^{79} * 1.57 \quad (15)$$

D. INDUSTRIAL REFRIGERATION

The flowsheet includes condensation of CO_2 at $51^\circ F$, thus requiring an ammonia refrigeration loop. The cost for this system and its operation costs are calculated as follows: the unit cost, in 1979 dollars, for a Q_{RF} ton (1 ton = 12,000 BTU/hr) unit operating at $20^\circ F$, is:

$$C_{RF}^{79} = 3.098 Q_{RF}^{0.742} \quad (16)$$

Operating costs are approximately \$1.20/ton-day and the direct capital ratio is 3.46, therefore, the total direct capital is:

$$DC_{RF}^{91} = \frac{450}{230} C_{RF}^{79} * 3.46 \quad (17)$$

3. Economic Analysis

The design presented is a fixed-site unit with a regeneration capacity of 24 tons of GAC per day. The capital cost does not include equipment for steam generation and so assumes that the plant is part of a larger industrial unit from which steam is supplied at \$1.50/1000 lb and cooling water at \$1.00/10,000 gal. A summary of the direct capital investment costs is given in Table 3. Indirect costs are estimated as 38% of direct costs, then fees and contingencies are 25% of direct

Table 3. Summary of Investment Costs (M\$, 1991)	
Direct Capital Costs:	
Extraction Vessels	345.7
Primary Flash Vessel	19.8
Reboiler for Primary Flash	42.1
Secondary Flash Vessel	3.8
Condenser	84.2
Refrigerated Condensate Loop	93.1
High P Liquid Pump	43.4
Heater for High P Liquid	49.2
Secondary Flash Recycle Compressor	93.1
After Cooler	72.6
Blowdown Recycle Compressor	49.2
After Cooler	1.8
Process Control/Instrumentation	250.0
Unlisted Equipment (35% of Total Dir.)	483.5
Total Direct Capital	1,631.5
Indirect Costs (0.38 × Direct Costs)	620.0
Fees and Contingency (0.25 × Dir. + Ind.)	562.9
Working Capital (15% of Total Capital)	496.6
Total Capital Investment	3,310.9

plus indirect costs. The total capital investment for the unit is 3.3 million dollars. Table 4 is a summary of operating costs for the regeneration unit on the basis of one operator per shift (24 hr operation), 0.5% loss rate for the SCF, and 4¢/lb replacement costs for CO₂, yielding a regeneration cost of 10.6¢/lb.

Table 5 lists our costs along with those reported by DeFilippi and co-workers (1980,1983) for phenol, dinitrobutylphenol, atrazine, and an estimate for thermal regeneration. Comparisons of treatment costs with thermal regeneration are favorable. In addition to maintaining a stable capacity, SCF regeneration is consistently less expensive than thermal treatment. The final alternatives are incineration or disposal by landfill. Incineration of soils containing hazardous wastes is at least 20¢/lb for a similar scale unit (EPA Engineering Bulletin, 1990). This process compares favorably both economically and ecologically with the alternatives.

D. CONCLUSIONS

A 24 ton/day fixed-site regeneration plant has been designed and examined for economic feasibility. The estimated capital and operating costs are valid within approximately 30%. If a small, mobile unit were to be built, the operating costs would be somewhat higher due to an economy of scaling which favors larger units and, the infeasibility of including a refrigeration system, forcing the use of the high cost flowsheet option which requires only cooling water.

The cost of this process compares favorably with thermal regeneration, the most often chosen alternative, but has the distinct advantage of maintaining a stable adsorbate capacity. This many-cycle regenerative use reduces carbon replacement costs and avoids disposal of spent material.

Table 4. Summary of Operating Costs (M\$/YR, 1991)		
Direct Production Costs:		
Make-up CO ₂	271.4	
Operating Labor	200.0	
Direct Supervision	40.0	
Utilities:	Electricity	162.4
	Steam	142.1
	Cooling Water	2.5
Maintenance (7% of T.C.I.)	231.8	
Operating Supplies (15% of Maint.)	34.8	
Laboratory Charges (15% of Op. Labor)	30.0	
Fixed Charges:		
Depreciation	163.1	
Taxes and Insurance (3% of Fixed Cap.)	67.5	
Plant Overhead (60% of Op. Lab. + Sup. + Maint.)	283.1	
Administrative Costs (15% of Op. Lab. + Sup. + Maint.)	70.8	
Total Treatment Cost	1,699.4	
Unit Treatment Cost	10.6 ¢/lb	

Table 5. Comparison of Operating Costs for Regeneration of GAC			
Contaminant	Capacity/Throughput (Ton/Day)	Reported Unit Cost (¢/lb)	Adjusted Unit Cost^a (¢/lb)
2-Chlorophenol	24	10.6	10.6
Atrazine	2.5	14 ^b	29
Dinitrobutylphenol	1	29 ^b	46.2
Phenol	5	8.5 ^c	16.1
Thermal Regeneration		29-36 ^b	46-57
Incineration (From Data on Soils)		18-48 ^d	20-53

^aAdjusted to 1991 dollars assuming 6% inflation

^b1983 dollars

^c1980 dollars

^d1989 dollars

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NOMENCLATURE

Symbols

- A - Heat transfer area
- $A_m(w)$ - Incomplete gamma function
- b, b' - Dimensionless groups defined in Eq. 4a
- C - Concentration in SCF phase
- C^{70} - Cost in 1970 dollars
- C^{79} - Cost in 1979 dollars
- D - Diameter
- DC^{91} - Direct capital costs in 1991 dollars
- E - Enhancement factor
- F - Fraction desorbed
- F_p - Cost factor for pressure
- K - Adsorption equilibrium constant
- k - Desorption rate constant
- k_p - Overall mass transfer coefficient
- L - Length of carbon bed
- P - Pressure
- Q - Refrigeration system capacity
- q - Compressor intake flow rate
- r_o - GAC particle radius
- t - Time
- u - Superficial velocity of fluid at T and P of bed
- w - Dummy variable in incomplete gamma function

Superscripts

- sat - Saturation (VLE or SVE boundary)

Subscripts

- a - Adsorbed phase
- cmp - Compressor
- hx - Heat exchanger
- int - Internal support
- o - Initial
- pore - Fluid in pore
- rf - Refrigeration system
- vsl - Pressure vessel

Greek Symbols

- α - Void fraction of GAC bed
- β - Porosity of GAC particles
- Θ - Dimensionless time defined in Eq. 4a
- ρ - Density of GAC particles