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Applied Research Laboratory

FINAL REPORT

Near Critical / Supercritical Carbon Dioxide Extraction for Treating Contaminated Bilgewater

PHASE 2

Investigation of Counterflow Extraction Column Operation

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13. ABSTRACT (Maximum 200 words) This study investigated the use of near critical carbon dioxide (NCCO2) extraction as a method for removing oily and greasy contaminants from bilge water on deployed US Navy ships. The investigation involved the following tasks: A. Qualitative and quantitative evaluation of the operation of a packed bed counterflow extraction column with near critical carbon dioxide as the extraction phase. B. Measurement of desorption rates to determine appropriate retention times for recovery of CO2 from treated bilgewater. C. Evaluation of separator designs for removal of contaminants from carbon dioxide gas prior to recycling.				
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EXECUTIVE SUMMARY

This report summarizes work performed at the Applied Research Laboratory of the Pennsylvania State University under Office of Naval Research Grant N00014-99-1-0421 covering the period from March 1 through December 31, 1999. This study investigated the use of near critical carbon dioxide (NCCO₂) extraction as a method for removing oily and greasy contaminants from bilge water on deployed US Navy ships.

This report should be considered to be a continuation of the paper *Final Report: Near Critical / Supercritical Carbon Dioxide Extraction for Treating Contaminated Bilgewater. Phase 1: Partition Studies and Extraction Column Design*, by J. A. Peters (February 24, 2000). The earlier document includes an extensive introductory section and literature review.

The current investigation involved the following tasks;

- A. Qualitative and quantitative evaluation of the operation of a packed bed counterflow extraction column with near critical carbon dioxide as the extraction phase.
- B. Measurement of desorption rates to determine appropriate retention times for recovery of CO₂ from treated bilgewater.
- C. Evaluation of separator designs for removal of contaminants from carbon dioxide gas prior to recycling.

It proved impossible to operate the counterflow column in a steady fashion (Task A). The height of the continuous (aqueous) phase could not be maintained at a constant level despite large changes in flowrate and raffinate valve size.

It appears that the column was in a flooded condition, although standard liquid/liquid and gas stripping analyses indicate that the column should have been operating within the unflooded regime. Another explanation for this behavior is the potential formation of a dense carbon dioxide phase, either in the column itself or within the throat(s) of the raffinate valve(s).

Desorption experiments (Task B) indicate that heating the raffinate to 90 – 100 °F results in a residence time requirement of approximately 8 minutes for efficient carbon dioxide recovery.

Because steady state operation could not be maintained, no extraction efficiency data was obtained, and it was not possible to evaluate separator performance (Task C).

Despite the difficulties encountered in operating the packed-bed counterflow extraction apparatus, the partition data described in the earlier report remains valid. This indicates that NCCO₂ extraction process may still be a viable solution for treating contaminated bilgewater. A semi continuous process might be a more appropriate way to implement this technology.

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1. INTRODUCTION

This report summarizes work done at the Applied Research Laboratory of the Pennsylvania State University under Office of Naval Research Grant N00014-99-1-0421. The period of performance of this investigation was March 1 through December 31, 1999.

This program evaluated the use of Near Critical Carbon Dioxide (NCCO₂) extraction for treating contaminated bilgewater.

This work followed an earlier investigation, completed in February, 1999. The final report for the previous study (in addition to presenting empirical results) includes detailed discussions of the need for bilgewater treatment, current bilgewater treatment systems, the technology of near critical/ supercritical carbon dioxide extraction and its use in water treatment, and an extensive literature review. The present document should be considered to be a continuation of the earlier report (Peters, 2000). Only a very brief summary of the technology will be given, below.

Figure 1 is a schematic of a typical counterflow extraction apparatus for water treatment. In this device, contaminated wastewater flows downward through the extraction column, while the less dense NCCO₂ phase flows upward. Mechanical agitation and/or packing material distributed through the column ensures adequate contact between the two phases.

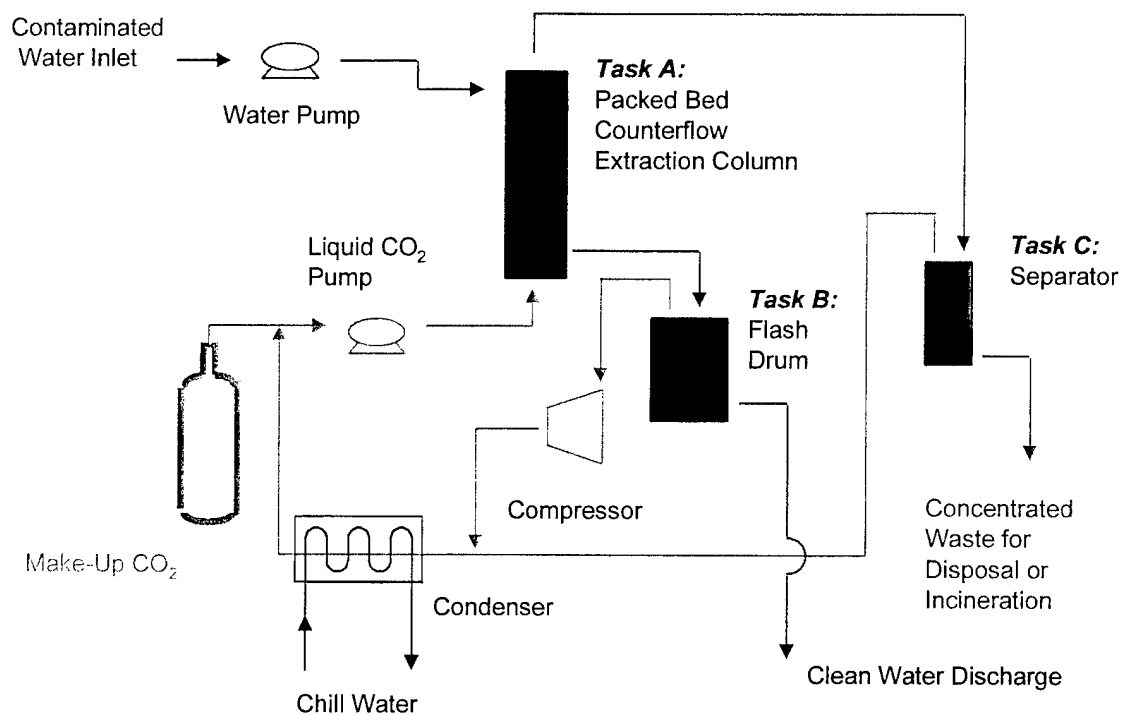


Figure 1: Schematic of Typical NC/SCCO₂ Water Treatment System

Organic contaminants tend to concentrate in the carbon dioxide phase, and are carried out of the column by the CO_2 . The carbon dioxide flows into a separator, where the pressure is reduced, causing the CO_2 to vaporize. The contaminant species, which are not soluble in the gas phase, fall out of solution and are collected in a highly concentrated form. The pure carbon dioxide is condensed to a liquid and recycled. A supply of CO_2 is carried to make up for losses, including carbon dioxide that dissolves in the aqueous phase.

The contaminants are recovered in a highly concentrated form, suitable for incineration or handling as hazardous waste. Note that this waste stream is similar to the concentrated oil that is currently recovered from existing separators. NC/SCCO₂ extraction does not destroy contaminants.

1.1 Program Outline

The current study was broken down into three tasks. Each portion of the program focused on a particular portion of the apparatus, as indicated in Figure 1.

Task A demonstrated operation of a laboratory scale NCCO₂ counterflow extraction column. The goals of this portion of the study were to completely characterize the extraction operation. In a qualitative sense, the overall behavior of a packed-bed NCCO₂ treatment column was evaluated and problems and pitfalls identified.

Quantitatively, Task A was intended to compare the efficiency of the extraction process against models developed using quasi-empirical unit process design methodologies from the chemical engineering literature (see Peters, 2000). It was hoped that the end result of this portion of the study would have been a set of guidelines for scaling the counterflow design to larger systems. As will be discussed below, it proved impossible to achieve steady state operating conditions, and no useful treatment efficiency data was obtained.

Task B focused on recovery of carbon dioxide from the treated aqueous stream. The goal of this task was to characterize the rate of desorption of carbon dioxide from a saturated or super-saturated solution at various temperatures, allowing a practical flash drum to be designed.

Task C involved demonstration of a separator for removal of recovered contaminants from the CO_2 stream. As will be discussed below, no quantitative data was obtained because of difficulties encountered in achieving steady state column operation.

Each task will be discussed separately, below.

2. TASK A: CHARACTERIZATION OF NCCO₂ COUNTERFLOW EXTRACTION COLUMN OPERATION

As discussed above, the first task evaluated operation of a counterflow extraction column. In addition to a qualitative demonstration of an NCCO₂ packed-bed counterflow extraction column, it was anticipated that analysis of treated samples would yield extraction efficiency data that could be compared to predictions to "calibrate" the tools originally used for column design.

2.1: Apparatus, Task A

A near critical carbon dioxide extraction column was developed at the Applied Research Laboratory to support water treatment studies. Figure 2 is a schematic of this apparatus, while Figures 3 through 8 are various views showing column components.

The column itself is assembled from two 48" sections of 3" schedule 40 pipe. Bolted flanged closures are used to secure 1" thick lids to the column ends. A 1" thick transition junction connects the two sections of column, resulting in an internal height of 97". Elastomer O-rings (Buna-N rubber, size 2-340) are used to seal the joints between the column sections and lids / transition junction. All column components are fabricated from 316 stainless steel. Eight 1/2"-13 UNC alloy steel socket head cap screws (grade 8), with matching nuts and hardened washers are used at each joint.

As shown in Figure 2, water is supplied to the top of the column by a positive displacement pump (CAT Triplex Plunger Pump, Model 3CP1130). The pump is driven by a 2 Hp Baldor electric motor, controlled by a variable speed electronic drive, AC Tech model 012002B. Calibration of this pump was performed over a wide range of pressures and flowrates. As anticipated, for a given drive speed, the flowrate is directly proportional to the drive speed setting, and is relatively independent of delivery pressure. A check valve (Nupro model SS-4C) is installed between the pump and column to prevent backflow of CO₂ when the pump is stopped.

Carbon dioxide is delivered by a Haskell air-driven booster pump, model DSTV-25. The standard pump is modified with the addition of the "three-way cycling spool" option, which uses the carbon dioxide inlet pressure to drive the piston on the return stroke, thus reducing drive air consumption. The pump stroke rate, and hence the CO₂ flowrate, is controlled by the drive-air pressure, which is set using a hand loaded regulator and gauge. The stroke rate also depends on difference between the carbon dioxide supply pressure and the column pressure. At lower delivery pressures, the pump strokes faster, delivering a higher CO₂ flowrate. Calibration of this pump indicates that a fairly reliable estimate of CO₂ flowrate can be determined by monitoring the pump stroke rate and multiplying by the displacement volume (26.6 ml/stroke). The Haskell pump incorporates an integral check valve.

Flow of raffinate (treated water) from the bottom of the column is controlled by one or more metering valves. As shown in Figure 2 (and as will be discussed in a later section), the current configuration incorporate two control valves. Valve "A" is a Hoke model 1335G27, and is generally left in the fully opened ($C_v = 0.01$) position. Valve "B" is a Hoke model 1325G2Y. Since metering valves should generally not be used for shutoff purposes, a separate shutoff valve is located downstream of each. Valve "A" is associated with a Whitey SS-1VS4 needle valve, while a SS-6UW-4C air actuated shutoff valve is located downstream of metering valve "B." This allows flow through valve "B" to be turned on or off remotely.

Carbon dioxide flows from the top of the column through a dome loaded back pressure regulator, Grove "Mity Mite" model S-91W. This regulator features stainless steel construction with a PTFE (Teflon) diaphragm. The regulator is wrapped with electrical heater tape and layer of Fibrefrax insulation. A thermocouple is spot welded to the outside of the regulator. An electronic temperature controller is used to drive the heater tape in order to maintain the regulator at approximately 175 °F (79 °C). This is necessary to counteract the cooling that occurs as liquid carbon dioxide flashes into a gas as its pressure is reduced inside the regulator.

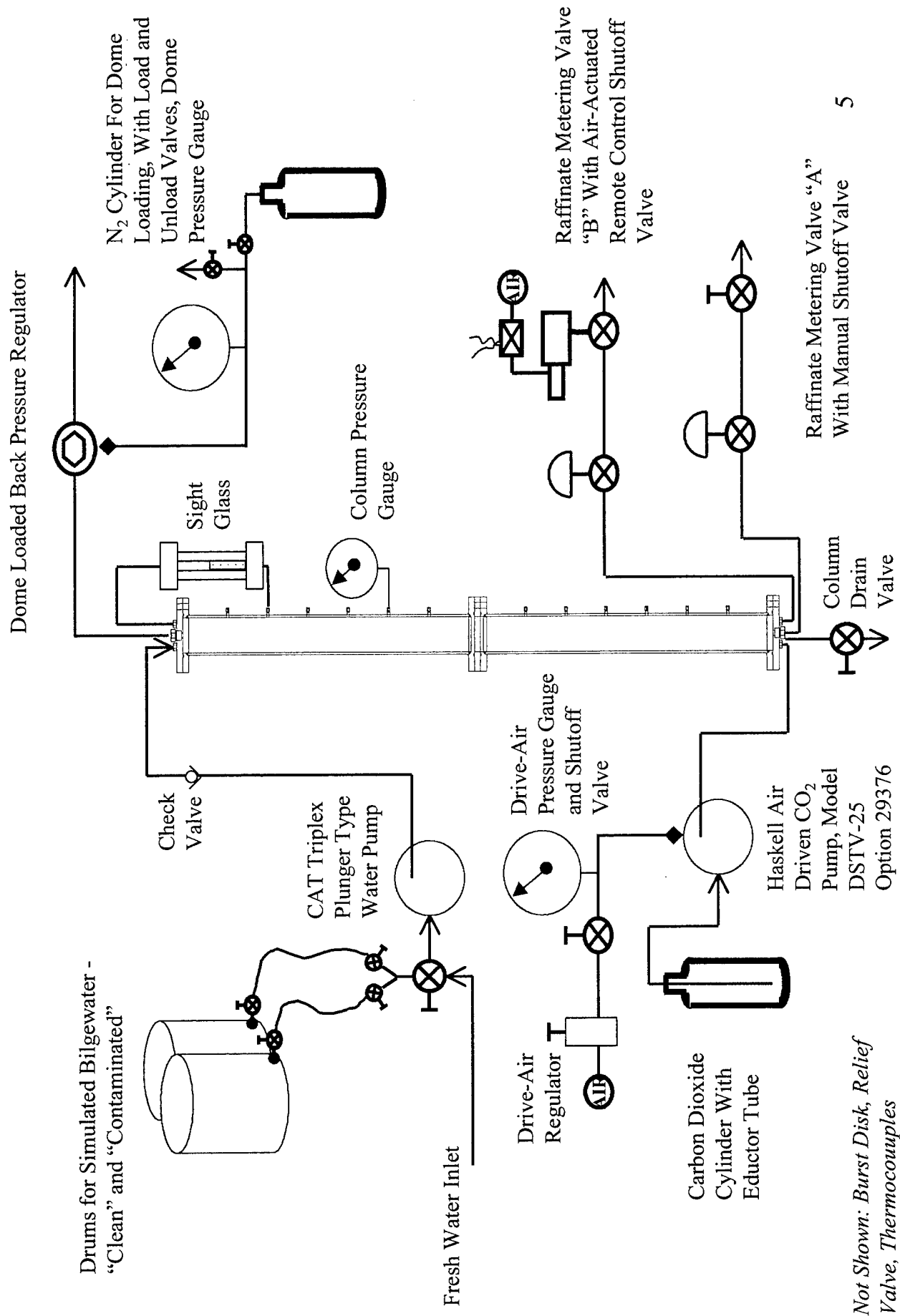
As shown in Figure 4, a high pressure sight glass manufactured by Jurguson (model 11 TL 10) is located near the top of the column. This allows the level of the continuous phase (water) to be monitored by the operator.

Table 1 summarizes the operating limits and safety conditions of various critical column components.

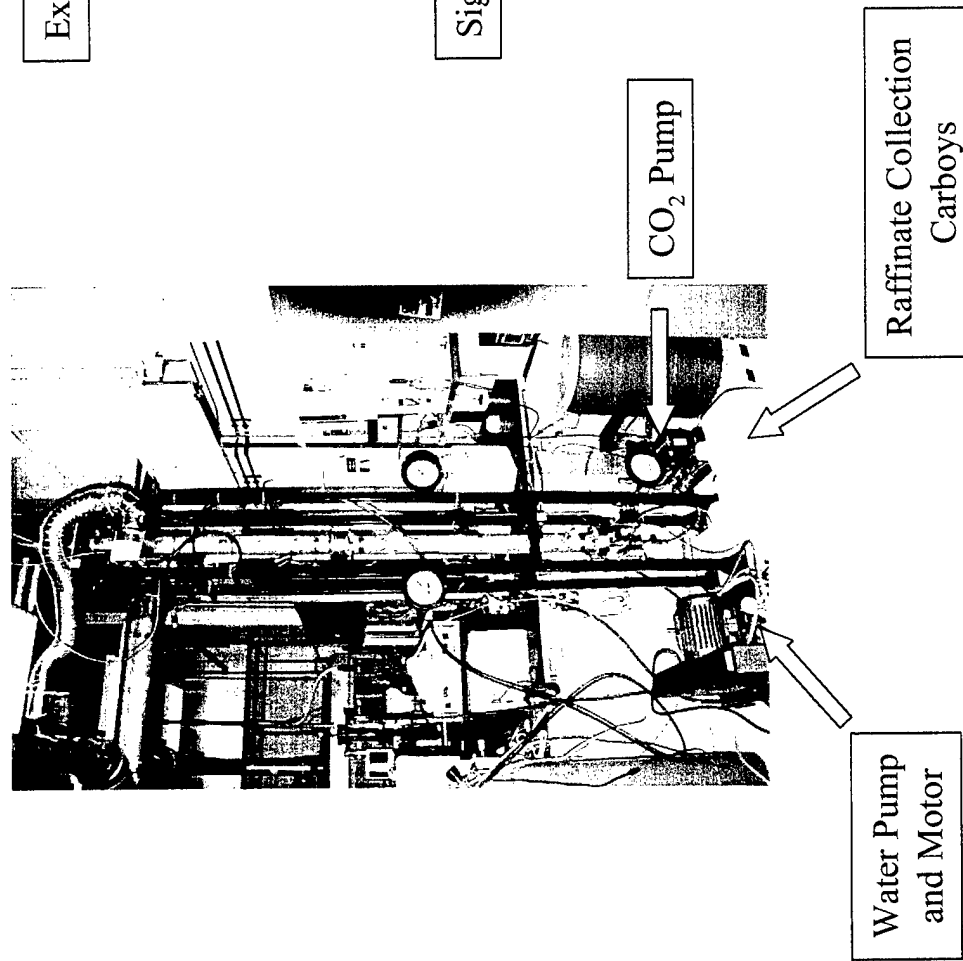
Table 1: ARL NC/SCCO₂ Extraction Column Pressure Limits and Safety Devices

Component	Design Pressure Limit	Comments
Column	1500 psi with factor of safety of 2.0 to yield stress (considerably higher to failure).	
Sight Glass	Design operating conditions 1200 psi at 100 °F	
Water Pump	Pop-Off valve set to approximately 1100 psi	Valve begins opening at 1100 psi, fully open by 1200 psi to prevent damage to pump should it become dead-headed. Also limits the flow of water into the column should it become overpressurized.
CO ₂ Pump	Dead-head pressure $\leq$ 1125 psi	Air drive pressure set to 45 psi or less, pressure ratio of 25 results in 1125 max output pressure. Gross overpressure is avoided by a Nupro relief valve SS-4R3A-A, set at approximately 50 psi.
Relief Valve Nupro Model SS-4R3A-C	Set at 1100 psi	Opens first in event of overpressurization
Burst Disk Oseco Type: STD, Size: 1/4 A Model: R-3884-01	1240 psi at 74 °F	Blows in the event that relief valve cannot handle sudden pressure surge.
All other components (valves, regulators, gauges, etc. capable of operation at 2000 psi or higher).		

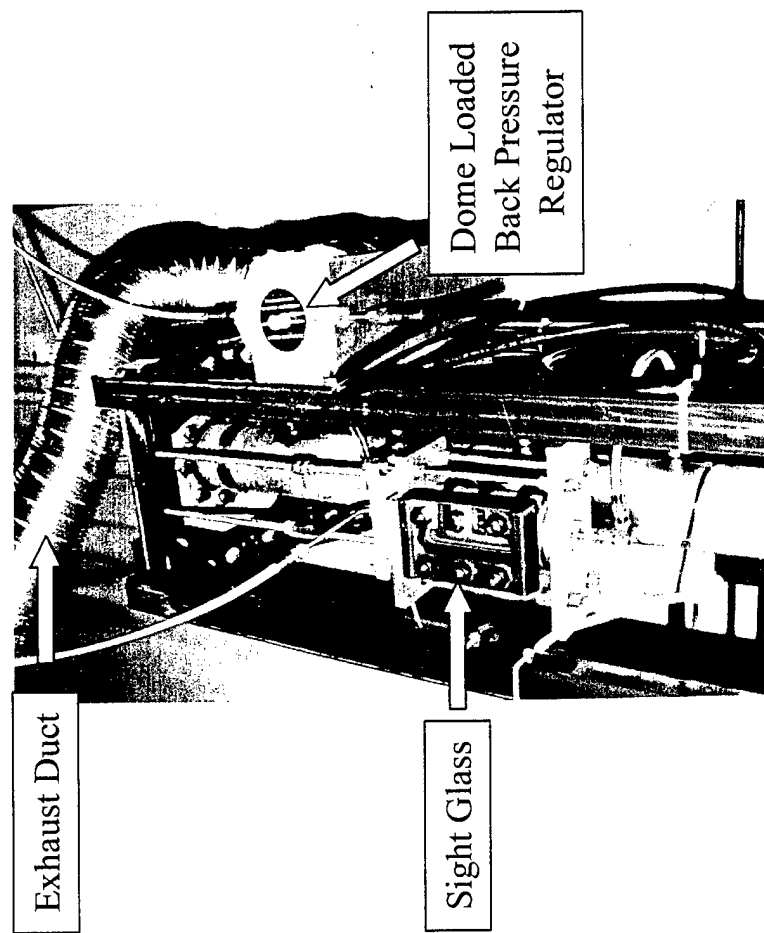
Figure 2: Schematic of ARL/PSU NC/SCCO₂ Extraction Column



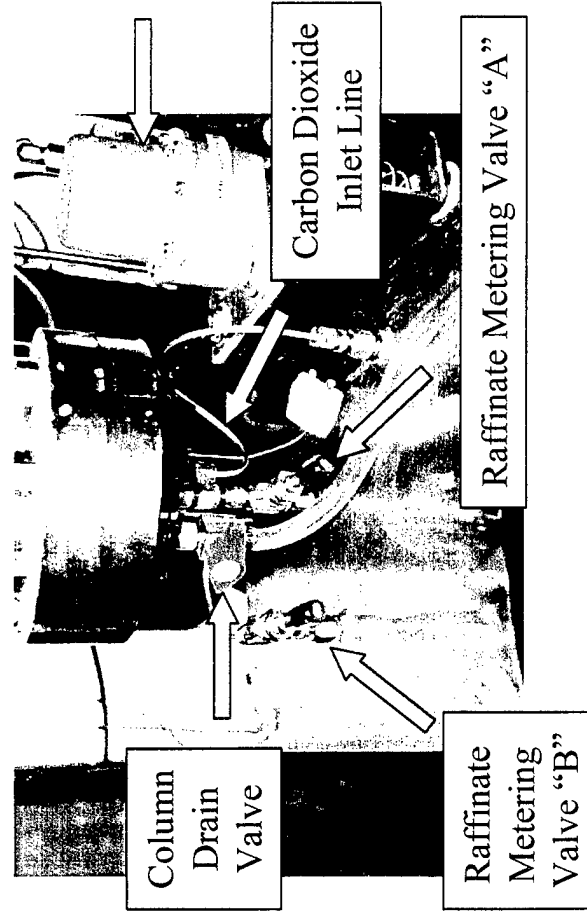
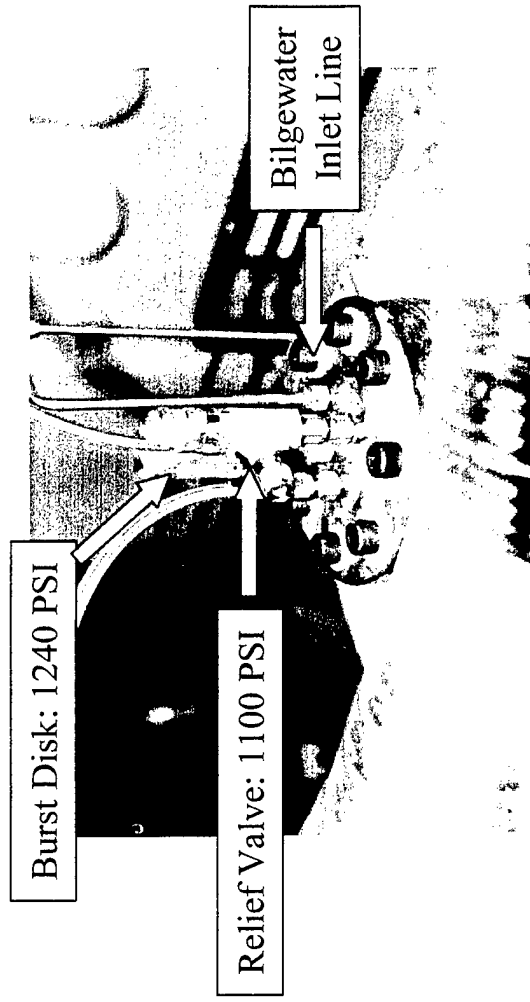
**Figure 3: Overall View of
NC/SCCO₂ Counterflow Extraction
Column**



**Figure 4: Top Portion of
NC/SCCO₂ Counterflow Extraction
Column**



**Figure 5: (Right) Top of NC/SCCO₂
Extraction Column**



Air Actuator for Remote
Control Shutoff Valve

**Figure 6: (Left) Bottom
of NC/SCCO₂
Extraction Column**

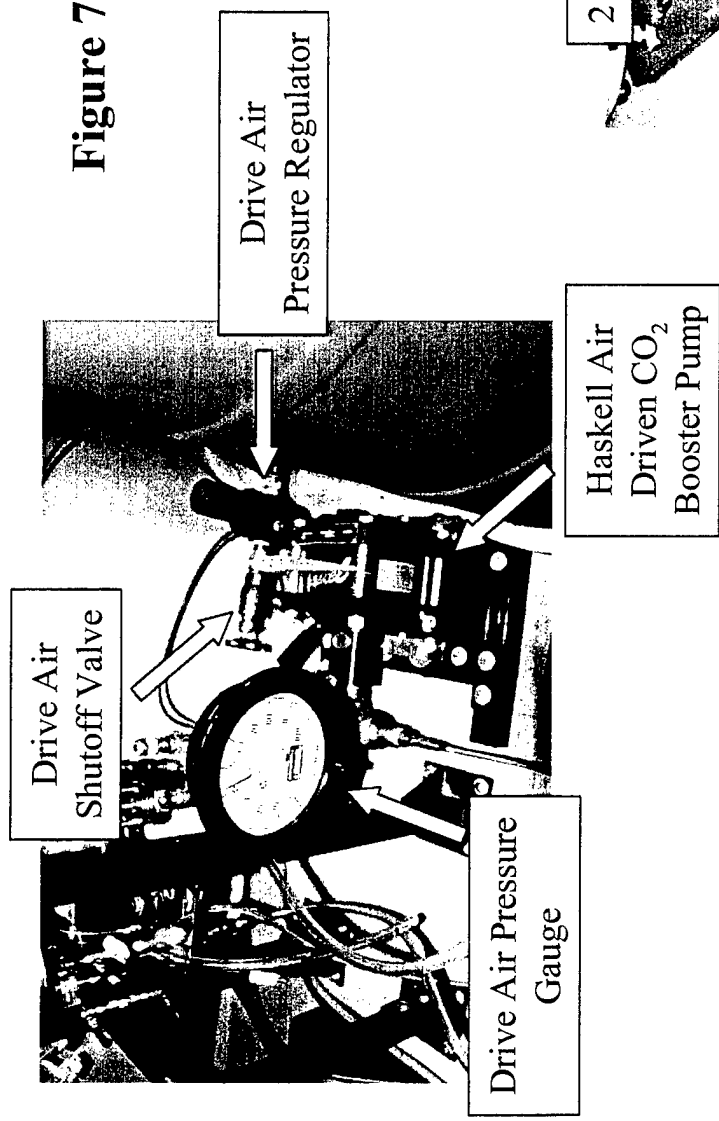


Figure 7: (Left) Air Actuated CO₂ Pump

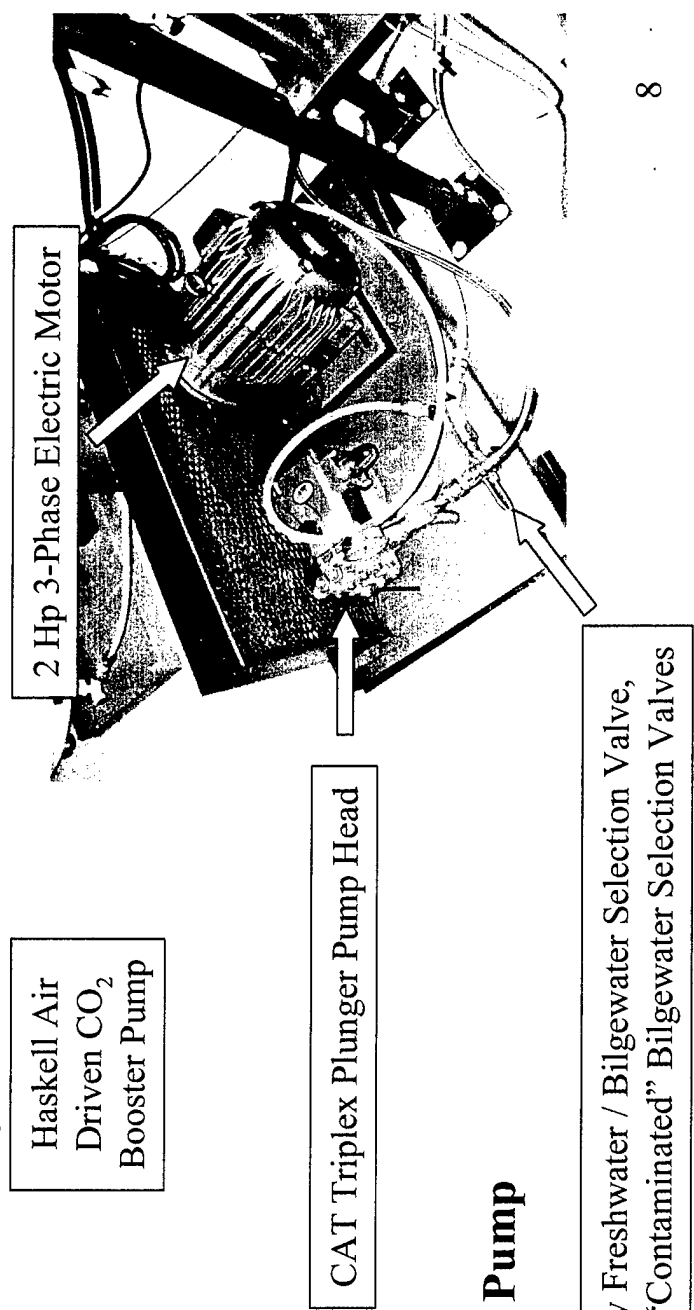


Figure 8: (Right) Water Pump

2.2: Counterflow Extraction Studies

The ARL NCCO₂ extraction column discussed above was used to investigate counterflow extraction for removing contaminants from simulated bilgewater. For this study, the column was filled with 1/2" ceramic Berl saddles (dumped).

As discussed in the previous report, it was determined that a 1% (by weight) solution of sodium chloride was sufficient to largely counteract the effects of surfactants. Seawater has a salinity of approximately 3.5% (Weiss et. al., 1974). If we assume for the sake of simplicity that this salinity is due solely to the presence of sodium chloride, it is necessary to add 39.5% seawater to non-saline bilgewater to produce an equivalent sodium chloride concentration of 1%. This is higher than the 30% addition used in some batch extraction tests, and should therefore be conservative with regard to the desired effect on the partition coefficient K_{CO_2} . (Peters, 2000).

A simulated bilgewater mixture was synthesized as shown in Table 2. This "recipe" makes 30 gallons (113.6 L) of feedstock, equivalent to 21.5 gallons (81.4 L) of non-saline bilgewater contaminated with 300 ppm oil and 25 ppm detergent, mixed with 8.5 gallons (31.2 L) of seawater. The slight differences (1-3%) in specific gravity between seawater, bilgewater, and the mixture were ignored in deriving this feed formulation.

Table 2: Composition of Feedstock for Counterflow Extraction Tests

Component	Quantity
Tap Water	30 Gallons (113.6 L)
Standard Sea-Salt Mixture (Lake Products Co.; ASTM D-1141-52, Formula A, Table 1, Section 4)	1325 gm
DTRC Detergent Mix #4 (see Table 6)	2.035 gm
DTRC Oil Mix #4 (see Table 6)	24.42 gm

The ingredients were mixed (in the order of Table 2) in a 55 gallon drum. An electrically driven impeller was used to continuously stir the "bilgewater," starting at least an hour before the test and continuing throughout the experiment. Because there was some question about the ability of this mixture to form a stable emulsion, an test was conducted in which 30 gallons of the mixture was pumped from one drum to another, with samples taken periodically. Analysis (by FTIR) of these samples showed a relatively constant oil level, indicating that a stable feed composition could be maintained for the duration of an extraction experiment.

In addition to this mixture, which simulated contaminated bilgewater, a "clean" bilgewater formulation, consisting of all ingredients except the Oil Mix, was used as a priming solution during the startup period.

A step-by-step operating procedure is given in Appendix A. A series of eight extraction tests were attempted. A narrative description of each experiment is given in Appendix B.

2.3 Results, Task A

In general, the results of this investigation were not promising. It proved impossible to maintain a steady-state operating condition in the NCCO₂ extraction column. Three features in particular stand out.

- It is difficult to maintain a constant raffinate flow. Since the column operates at essentially constant pressure and temperature, it should in theory be possible to set the raffinate valves to deliver the appropriate flowrate of water (with dissolved CO₂) and never have to adjust them over the course of an experiment. In practice, nearly continuous adjustments are required.

Sizing the valves is also problematic. In the first experiment, a valve with a C_v of 0.01 seemed nearly sufficient to deliver the appropriate water / CO₂ flow. In contrast, in experiments #6, #7 and #8, there were periods during which two valves with a combined C_v of 0.034 were unable to deliver the required water flow, even when the flowrate was significantly reduced by slowing the pump.

- The phases present in the column are not as straightforward as originally anticipated. In addition to the water-with-dissolved-CO₂ and liquid CO₂ phases, there appears to be a third phase, probably consisting of liquid CO₂ with dissolved water.
- It appears that the column is operating in a “flooded” condition. LaGrega et. al. (1994) define flooding in air-stripping operations as the conditions in which the air flow is great enough to “.. hold back the free downward flow of water..” It appears that an analogous situation is occurring in the extraction column.

Although the column appears to be operating in flooded mode, comparing nominal operating conditions against the graphical flooding correlations discussed in the previous report (Peters, 2000) indicate that the column should not be flooded. The very high density of NC/SCCO₂ relative to air may make parameters (such as those given by Perry and Green, 1984 and LaGrega et. al., 1994) poor indicators of flooding when NC/SCCO₂ is used as the stripping medium. Similar considerations apply to the flooding data given by McCabe (1985) for liquid/liquid extraction. Although McCabe’s correlations do not explicitly account for physical properties of the dispersed phase, the properties of NC/SCCO₂ that distinguish it from a typical liquid (such as low viscosity) may render these correlations invalid.

The formation of a layer of denser than anticipated carbon dioxide near the bottom of the column would explain many of the unusual effects noted in this series of experiments. In order for liquid carbon dioxide to have a density greater than the bilgewater-with-dissolved-CO₂ solution at the nominal operating pressure of these tests, it would have to be cooled to below the normal freezing point of water (Teng and Yamasaki, 1998). As discussed in Appendix C, thermocouples added to the bottom of the column did not register any such dramatic temperature effects.

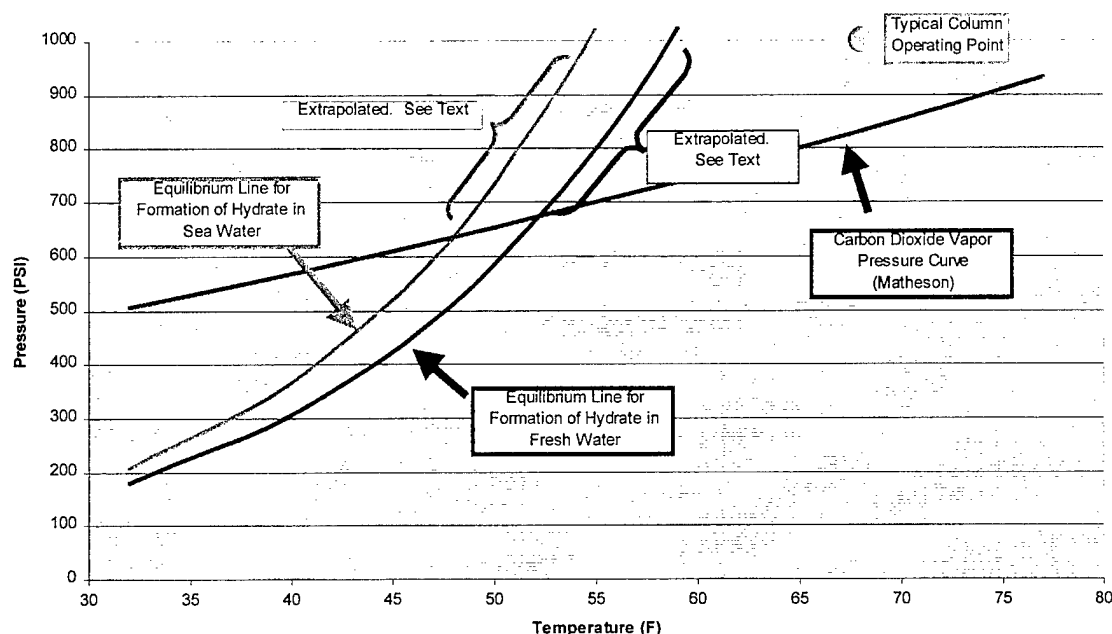
Another possibility became apparent in the course of investigating the density of water/ CO_2 /salt solutions. Carbon dioxide forms a hydrate $\text{CO}_2 \cdot x\text{H}_2\text{O}$, where “x” for the fully hydrated material is 5.75. According to Teng, Yamasaki and Shindo (1996), “ CO_2 hydrate is a clathrate compound, in which water and CO_2 are associated without ordinary chemical bonding but through complete enclosure of a set of CO_2 molecules in the cavities of the clathrate formed by water molecules.” The density of the hydrate was determined to be 1065 kg/m^3 ; greater than that of the seawater/ CO_2 /ice mixture at temperatures above the freezing point.

This material is an “icelike crystalline compound,” according to Dholabhai, et. al, (1993), who point out its important consequences for the natural gas industry, since many gas deposits have high CO_2 content, and the “formation of hydrates in gas pipelines and processing equipment could lead to catastrophic consequences.” Natural gas (methane) also forms solid hydrates.

A number of studies (Tse and Bishnoi, 1994; Engelos and Hall, 1994; Dholabhai et. al., 1996) have investigated the formation of the carbon dioxide hydrate in pure water and in electrolyte solutions. Figure 9 is taken from Dholabhai et. al (1996) and shows equilibrium lines for CO_2 hydrate in pure water and in synthetic sea water.

As shown in Figure 9, the presence of salts in the seawater tends to inhibit the formation of the clathrate hydrate to some extent. In our application, the feed is only about one-third as saline as seawater, so the equilibrium line should lie between the two curves of Figure 9.

Figure 9. Phase Diagram for Formation of CO_2 Clathrate Hydrate



As indicated in Figure 9, the equilibrium lines are extrapolated above the vapor pressure curve. None of the phase studies performed to date appear to have considered formation of the hydrate at pressures greater than saturation. This may indicate that hydrates do not form in this region, but the author believes that this is more likely a reflection of an inherent equipment limitation. In each investigation cited above, the pressure was regulated by the amount of CO₂ admitted to the view cell. Thus, the maximum pressure available at a given temperature was the saturation pressure of CO₂. It is not clear what happens at pressures greater than saturation. The equilibrium curves may be continuous (as shown in Figure 9) or may be discontinuous, with the presence of liquid CO₂ favoring or inhibiting the formation of the hydrate.

Interestingly, Teng and Yamasaki indicate that the hydrate is "...crystalline (if $T \leq 283$ K) or a quasi crystalline (if $T > 283$ K) structure." This temperature ($\approx 50^\circ$ F) is slightly greater than that at which the hydrate-in-sea-water line crosses the vapor pressure curve, lending support for the existence of the hydrate in the liquid CO₂ region.

As shown in Figure 9, normal column operation occurs in a region to the right of the equilibrium lines – i.e. in a region that is too warm for the hydrate to form. Although measurements taken during the last two extraction tests did not register any significant cooling of the bottom portion of the column, it is possible that hydrate formation may still be a factor in operation of the NCCO₂ bilgewater column since;

- A) As the thermocouples were installed after the packing, it was impossible to insert them into the center of the column. Temperature measurements therefore represent conditions near the outside edge of the fluid. It is possible that some cooling may take place near the center of the column.
- B) Even if no hydrate forms in the column itself, there is likely to be significant cooling in the raffinate valves as the dissolved CO₂ flashes into a gas. In the last two extraction tests, temperatures measured downstream of raffinate valve "A" were approximately ten degrees Fahrenheit (5.6 degrees Celsius) cooler than the feedwater temperature. Although the water was still warmer than the anticipated hydrate formation temperature, conditions at the throat of the valve, where the phase change took place, may have been significantly colder, allowing a solid plug to form in the valve itself.
- C) It is entirely possible that at pressures higher than saturation the clathrate hydrate exists at a higher temperature than indicated by the equilibrium curves, which were measured only below saturation pressure.

In their study of the solubility of liquid CO₂ in seawater, Teng and Yamasaki (1998) dismiss the importance of the hydrate layer on their measurements, noting that the hydrate does not restrict mass transfer between phases and forms only at the interface between the CO₂ and water (see also Teng, Kinoshita and Masutani, 1995). Since the interface in their apparatus was very small, only a small amount of hydrate was present at

any given time. In our apparatus, of course, the interface between the CO₂ and aqueous phases was deliberately dispersed throughout the column, possibly leading to more significant hydride formation.

2.4 Conclusions, Task A

As detailed in the narrative reports of individual extraction tests, steady state column operation was only achieved for very brief periods of time. In general, the column appeared to operate in a flooded condition. It is not clear if the column was flooded in the usually sense of the term, or if some other factor such as an unanticipated dense CO₂ phase was present in the bottom of the column.

Because steady state operation was not achieved, no quantitative extraction efficiency results were obtained.

3. TASK B: EVALUATION OF FLASH DRUM OPERATION

As discussed above and shown in Figure 1, raffinate (treated bilgewater) flows from the bottom of the column, carrying dissolved and entrained carbon dioxide. As the pressure drops, most of this CO_2 desorbs and bubbles out of solution. The flash drum serves to separate as much of this CO_2 as possible, reducing the amount of make-up carbon dioxide that must be carried.

Note that the clean water discharge will always contain some amount of dissolved CO_2 . In the limit, the carbon dioxide concentration in the discharge will be the equilibrium concentration at the flash drum operating temperature and pressure.

Task B of this study focused on flash drum operation, notably the effects of temperature on the rate of carbon dioxide recovery.

3.1 Apparatus, Task B

Figure 10 is a photograph of the apparatus used for this portion of the investigation, while Figure 11 (next page) is a schematic diagram of this equipment.

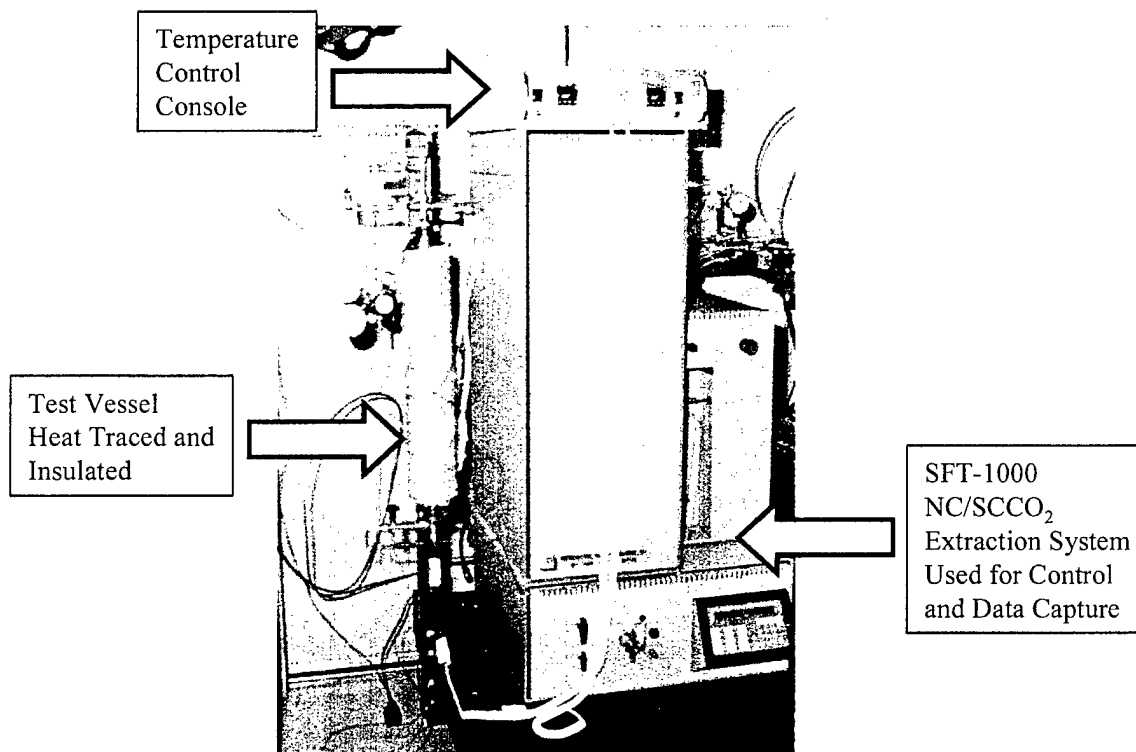
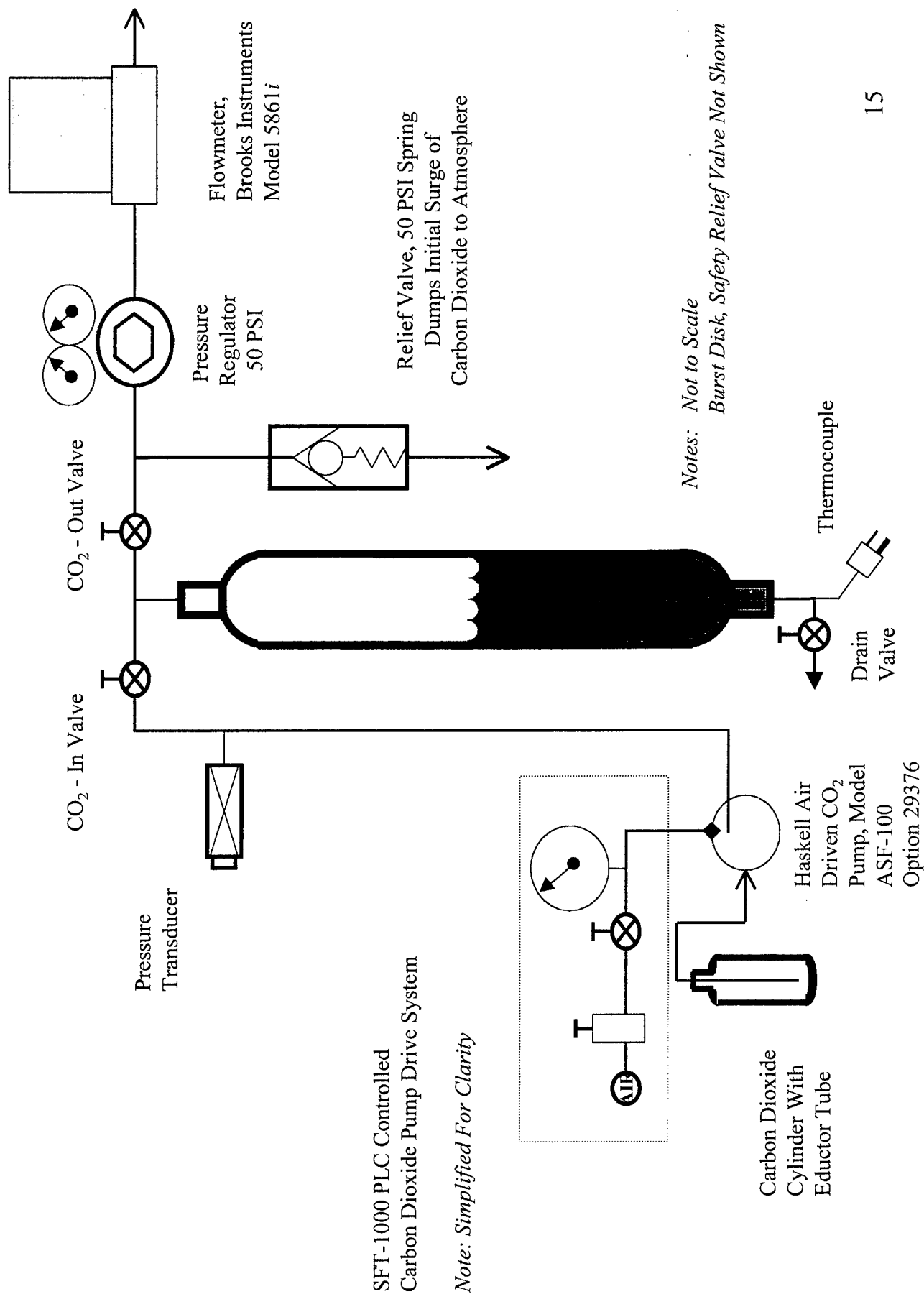


Figure 10: Apparatus for Task B

Figure 11: Schematic of Apparatus for Task B



As shown in Figures 10 and 11, the apparatus consists of a simulated flash drum made from a 1-gallon Whitey sample cylinder. This vessel is attached to ARL's SFT-1000 general-purpose NC/SCCO₂ system in place of the normal extraction vessel. The carbon dioxide delivery system, pressure transducer, and CO₂ flowmeter components of the SFT-1000 therefore become part of the Task B apparatus.

In operation, the "flash drum" is filled half-way with water, heated to a desired level, then pressurized with CO₂ using the SFT-1000 computer controlled CO₂ pump. When the system has reached equilibrium, the CO₂ inlet is closed and the outlet valve opened quickly to vent gas. Carbon dioxide flows through a pressure regulator, followed by a mass flowmeter, then is vented to the atmosphere. The signal from the flowmeter is measured by a data acquisition program running on a Pentium class PC.

In an actual flash drum, it is anticipated that the bulk of the carbon dioxide will flash off very quickly as the water flows out of the column through the raffinate valves (see Figures 2 and 6). This initial burst of gas will be followed by a slower desorption process as the supersaturated carbon dioxide solution gradually degasses, eventually reaching equilibrium. In the experimental apparatus, the rapid offgassing of carbon dioxide is simulated by a check valve, which dumps the initial burst of gas to the atmosphere. The flowrate of this gas is not measured, as the only the gradual desorption process is of interest.

Appendix C contains a detailed operating procedure and data sheet.

3.2 Results, Task B

The data collected during the desorption experiments consists of carbon dioxide mass flowrates measured over time. This data was integrated to convert from flowrate to mass flowed. Figure 12 shows this mass flowed data as a function of time for 12 individual experiments, graphed on a common axis and adjusted so that all desorption curves share the same starting point.

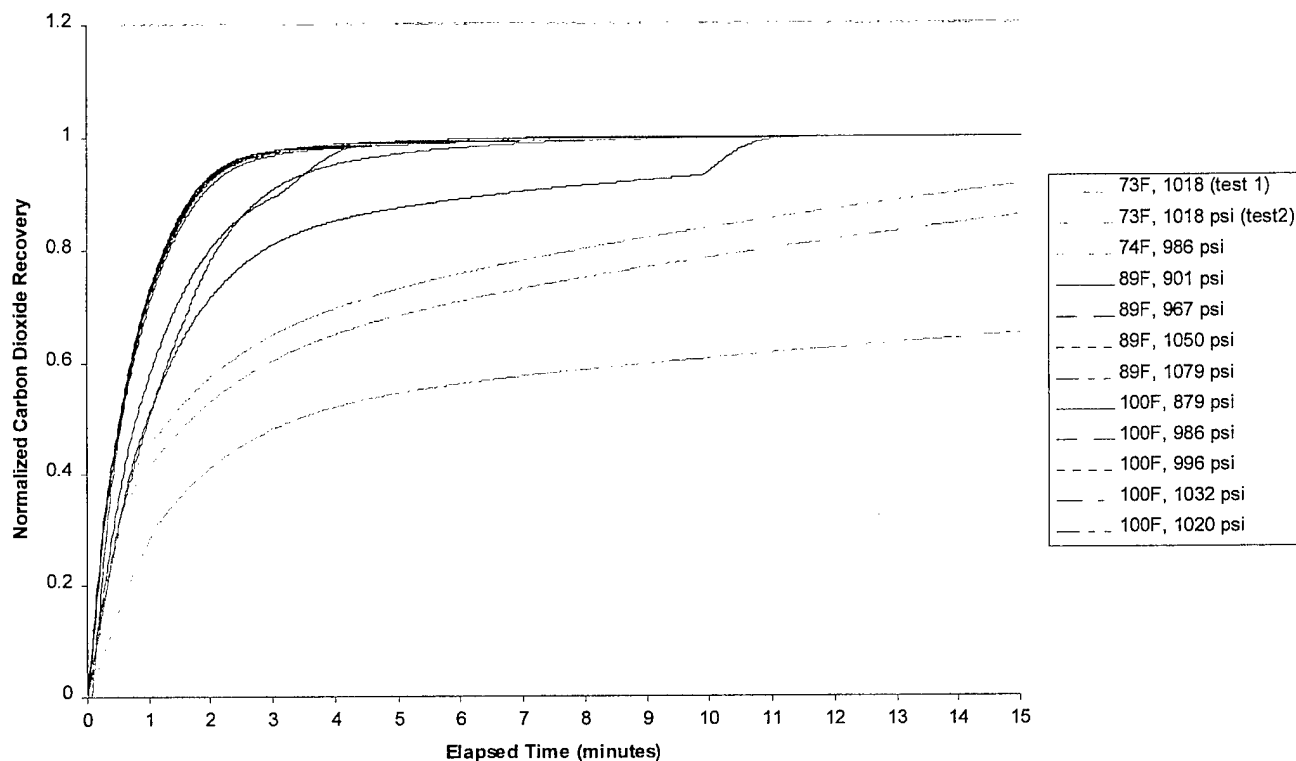
Note that the curves of Figure 12 were normalized by dividing the mass flowed data by the value at the end of the run. Thus, each curve starts at zero and asymptotically approaches 1.0 over time.

As shown in Figure 12, warmer temperatures enhance the rate at which carbon dioxide desorbs from the water column in the flash drum. This result was not unexpected, as most chemical and transport processes occur faster at higher temperatures. Note that at 100 °F, all experiments indicated a 99.9% desorption at an elapsed time of 8.0 minutes, while desorptions carried out at 73 °F were only 59% to 80% complete at this time.

Normalization of the Figure 12 data accounts for the fact that the warmer solutions hold less CO₂ at the start of the desorption process. In other words, the steep rise of the 100 °F

desorption curves represents a more rapid approach to equilibrium, not just the fact that less CO₂ was evolved from these samples.

Figure 12: Task B Results- Recovery of CO₂ vs. Time



3.3 Conclusions, Task B

Clearly, carbon dioxide desorbs more quickly from warmer solutions. To a first approximation, the results of this investigation show that if the raffinate were heated to 100 °F, an eight minute residence time should be sufficient to ensure essentially complete desorption of carbon dioxide. For a 10 gallon per minute system, an 80 gallon flash drum would therefore be required. Assuming a bilge temperature of 50 °F, approximately 300 pounds (45 gallons) of JP5 would be consumed on a daily basis to provide the heat needed to bring the raffinate to 100 °F for a steady 10 gallon per minute flow.

In practice, the advantages of heating the raffinate (i.e. reduced flash drum size and recovery of more carbon dioxide) would have to be weighed against the added complexity of the system, the size and weight of heat exchanger components, and the additional fuel consumed.

4. TASK C: INVESTIGATE SEPARATOR OPERATION

As shown in Figure 1, near critical carbon dioxide flows from the top of the counterflow column and into a separator. As its pressure is reduced, the CO₂ vaporizes. The contaminants, which are not soluble in the gas phase, are collected in the separator.

4.1 Apparatus, Task C

In our apparatus, the pressure in the column was controlled with a dome loaded back pressure regulator, Grove “Mity Mite” model S-91W. This device incorporates a PTFE diaphragm. Initial attempts to use a nitrile diaphragm failed – NCCO₂ apparently permeated this material, resulting in an explosive decompression failure when the pressure was reduced.

The pressure drop from column to atmospheric conditions occurred across this regulator. In order to compensate for the heat of vaporization and Joule-Thompson cooling associated with the resulting phase change, the regulator was electrically heated. A 312 watt tape (Thermolyne model number BWH051-040) was employed, in conjunction with a K-type thermocouple and electronic temperature controller. The entire apparatus was wrapped with a 1” thick layer of alumina/zirconia insulation, as is evident in Figure 4. A temperature setpoint of 175 °F was used.

A “Stairmand Type” reverse flow cyclone separator, originally developed for another project, was slightly modified and installed downstream of the back pressure regulator. This device is shown in Figure 13. Note that the inlet line and upper portion of the separator were electrically heated.

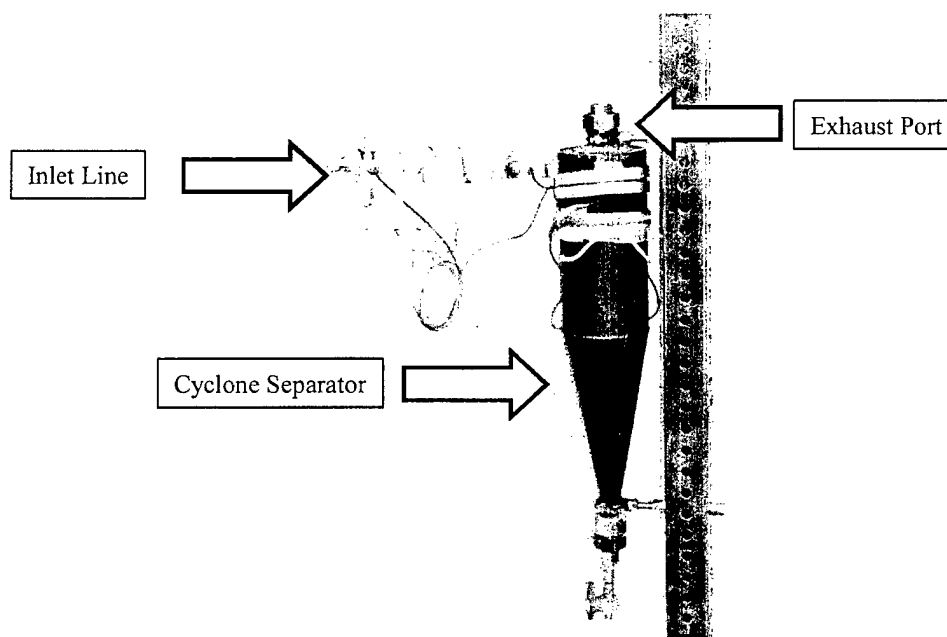


Figure 13: Cyclone Separator (Insulation Removed for Clarity)

4.2 Results, Task C

As discussed in Appendix B, steady flow was not achieved. Since the separator (Task C) was evaluated along with column operation (Task A), no meaningful results were achieved.

5. CONCLUSIONS, RECOMMENDATIONS FOR FURTHER RESEARCH

To the author's knowledge, this program was the first study to evaluate NCCO₂ extraction for water treatment utilizing a packed-bed counterflow column. In a qualitative sense, the results of this investigation indicate that there is a fundamental problem with operation of this type of device. As a result of this failure to maintain steady-state operation, the major goal of this investigation (i.e. to quantitatively evaluate column operation and compare treatment efficiencies against predictions), was not achieved.

The reason for the failure of the column to operate in a stable steady state fashion is not entirely clear. It is possible that the column was flooded in the conventional sense, meaning that design correlations developed for liquid-liquid and gas stripping operations are not suitable for NCCO₂ extraction column design.

Another possibility is that a dense carbon dioxide phase (e.g. a clathrate hydrate) may have formed in the lower portion of the column and/or raffinate valves, resulting in unstable operation.

These issues are probably best addressed by a small-scale project, using a transparent column section to observe the phase behavior of the CO₂ in the lower half of the column. Unfortunately, the problems encountered in our investigation may be a function of column diameter, meaning that a practical transparent section (e.g. with a diameter of 1" or less) may not capture the behavior that caused unsteady operation in our system.

It should be emphasized that the problems encountered with counterflow extraction column operation in no way contradict the results of the earlier stages of this research (Peters, 2000). Near critical carbon dioxide has been shown to be effective for extracting oily contaminants from simulated bilgewater, and addition of seawater is still a valid method for defeating surfactant effects. Implementation of an NCCO₂ – based treatment system is still possible, even though the approach used in this investigation appears to be problematic.

Another option is a "semi continuous" system, in which a series of batch extraction operations occur simultaneously. Operation of the batch extractors would be timed so that one vessel would always accept new bilgewater while another discharges treated raffinate. While optimization of this system and design of a production unit would require a significant research and development investment, initial tests could be performed on a relatively small scale.

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APPENDIX A: OPERATION OF NC/SCCO₂ COUNTERFLOW EXTRACTION COLUMN

Guidelines for Safe Operation

1. Always wear safety glasses and hearing protection while working around the column.
2. Be familiar with the location and function of all instruments (such as pressure gauges) and controls (such as manual and remote-control valves and regulators).
3. Never defeat any safety devices such as burst disks or relief valves.
4. The dead-head pressure of the air driven CO₂ pump is 25 times that of the drive air pressure. It is capable of reaching pressures as high as 4000 psi. The drive air pressure must be kept below 45 psi to avoid overpressurization of the column ($25 \times 45 \text{ psi} = 1125 \text{ psi}$).
5. Spills of water (e.g. when changing collection vessels) occasionally occur. Mop up spills promptly. Do not handle electrical equipment when standing in a wet location or when your hands are wet.
6. All feed solutions that contain oil, and all treated raffinate collected during experiments, must be handled as chemical waste in accordance with standard ARL and Penn State policies. Contact PSU Environmental Health and Safety to request pick-up of this material. Note that waste manifest forms should be submitted after each test.

Shutdown Steps

In case of an unexpected pressure rise, a burst disk failure, the relief valve opening, or other unanticipated event, follow these steps as quickly as possible, in this order.

1. Open the remote control air-actuated shutoff valve downstream of raffinate valve "B."
2. Close the valve on top of the CO₂ bottle.
3. Shut off the water pump (push "stop" button on drive).
4. Shut off drive-air to the CO₂ pump.

At this point, it is safe to begin lowering the pressure of the column by slowly bleeding off pressure from the back pressure regulator dome. Reduce the pressure gradually, in stages. Carbon dioxide should flow through the regulator each time the dome pressure is reduced. As the dome and column pressures equalize, CO₂ flow will slow, then stop.

If the column pressure is reduced too quickly, water-ice and/or solid CO₂ may form in the column. This should be avoided if possible, as further operations (flushing column with clean water) will be delayed until the ice melts.

Normal Column Operation

1. Prepare 30 gallons of the "bilgewater" mixture (consisting of water, oil mix, detergent mix and sea-salt) in the 55-gallon contaminated feedstock drum.
2. Prepare a second 30 gallon drum of "clean bilgewater" (containing water, detergent and sea-salt, but no oil) in the 30 gallon priming solution drum.
3. Install a new CO₂ cylinder, tare-ing the scale beforehand. Note cylinder weight.
4. Close both raffinate shutoff valves and the column drain valve.
5. Energize heater tape on back pressure regulator. Use a temperature controller setpoint of 175 °F.
6. Make sure that the freshwater/bilgewater valve is in the bilgewater feed position. Set drum valves and clean/contaminated selection valve to feed the "clean" priming solution to the pump.
7. Energize the variable speed drive. Set drive frequency to 18.50 Hz (push 1850 then the "enter" key). Push the "start" button to start water flow.
8. As soon as water appears in the sight glass, shut down the water pump (push "stop" on the drive).
9. If necessary, open the column drain valve to lower the water level to the very bottom of the sight glass. Close this valve.
10. Pressurize the dome to 1000 psi with nitrogen gas using the dome fill and vent valves.
11. While monitoring the liquid level in the sight glass, crack the CO₂ cylinder valve to admit liquid carbon dioxide to the bottom of the column. The sound of carbon dioxide bubbling into the column will be heard. As liquid CO₂ enters the column, the water level will rise. Shut the cylinder valve when the level reaches the top of the sight glass.

Eventually, the liquid will flash into a gas and rise to the top of the column, while some CO₂ will dissolve in the water. The water level will fall back to near its original level, and the column gauge pressure should drop back to zero.
12. Repeat step 11 several times, adding liquid CO₂ to the column. Each time, once the CO₂ and water have equilibrated, the column pressure will be higher. Eventually, the column will reach bottle pressure (800 – 900 psi) and the cylinder valve can be left in the fully open position.
13. Turn on the water pump and immediately open manual raffinate shutoff valve "A."

14. Observe the sight glass to monitor the height of water in the column. If the level climbs above the 75% level in the glass, open remote control raffinate shutoff valve "B." Once the level returns to the 25% level, close this shutoff valve.
15. When relatively steady operation has been achieved, open the drive-air valve to start CO₂ pump flow. The pump should begin stroking.
16. Monitor column conditions. The goal is to achieve steady state operation at the following conditions;
 - Column pressure = 1000 psi.
 - Water level at midpoint of sight glass.
 - Water flowrate of 0.35 gallons/minute (1.32 L/min). This is equivalent to a drive setpoint of 18.50 Hz.
 - Carbon dioxide flowrate of approximately 16.1 pounds/hour. At normal temperatures and pressures, this is obtained by keeping the pump stroke-rate at 10-11 strokes per minute.
17. When a relatively steady-state operating condition has been achieved, change the drum valves and clean/contaminated selection valves to feed the "contaminated" bilgewater solution to the pump. Note time and weight of carbon dioxide cylinder.
18. After 13 minutes (two column volumes of bilgewater will have flowed through the column) draw a sample of the feedstock and collect a sample of raffinate. Note weight of carbon dioxide cylinder.
19. Collect eight more samples at 6.5 minute intervals. Note carbon dioxide cylinder weight at each sample.
20. After the last sample has been collected, shut down and vent the system as described in "Shutdown Steps," above.
21. Close drum valves and switch freshwater/bilgewater selection valve to the freshwater position. Energize the water pump and allow clean tap water to flow through the pump into the column. When the water level reaches the top of the sight glass, shut down the pump, turn the 3-way valve to the center (off) position and drain the column using the column drain valve. Repeat this operation two more times.
22. De-energize the back pressure regulator heater.

APPENDIX B: SUMMARY OF COLUMN OPERATION TESTS AND DISCUSSION OF RESULTS

Test #1

This was the first column shakedown run. The goal was to test operation of all components, including both the water and carbon dioxide pumps. Only tap water was used - no oil, detergent or sea-salt was added.

It was relatively easy to see the meniscus (delineating the level of water in the column) in the sight glass. Maintaining a constant level appeared to be possible, but required nearly continuous adjustment of the raffinate (treated water) flow-control valve. Note that only a single metering valve, with a C_v ¹ of 0.01, was used for control of raffinate in this test.

Test #2

A second raffinate control valve was added to the bottom of the column. This valve was considerably larger ($C_v = 0.3$) than the original metering valve (which also remained in place). A remote control shutoff valve was installed downstream of this second metering valve. The shutoff function was implemented by an air-actuated pintle valve, driven by shop air delivered through a 3-way solenoid valve. A control switch was located so that the sight glass could be observed by the valve operator. It was anticipated that the new on/off valve combination could be opened and closed manually to exert "fine" control of the liquid level, allowing the original control valve to be left in an essentially fixed position.

This experiment was attempted by a single operator.

This test demonstrated that the new combination of valves could, in fact, be used to improve control of liquid level. Unfortunately, it still proved necessary to frequently adjust the (two) metering valves. This, coupled with the need to monitor column pressure, made it clear that subsequent tests would require two operators - one to control liquid level with the new on/off valve, and one to adjust control valves while observing column pressure and pump operation.

An interesting phenomenon was noted during this experiment. While opening the new remotely controlled valve caused more water (with dissolved CO_2) to flow out of the bottom of the column as expected, an unanticipated effect was also apparent. When the valve was opened, the water in the sight glass became cloudy as bubbles of carbon dioxide came out of solution. As this happened, the liquid level actually increased for some time, before beginning to fall.

¹ The C_v is a commonly used measure of the flow capacity of a valve or orifice. A valve with a C_v of 1.0 will flow 1.0 gallon of room temperature water at a 1.0 psi pressure drop. Although it is inappropriate to use C_v specifications for design purposes in unusual circumstances (such as the two-phase flow conditions of these experiments), these values do provide a useful means of comparing the relative sizes of valves.

Apparently, opening this new (larger) control valve had enough of an impact on column pressure to significantly change the volume of the CO₂ phase. This effect may have been the result of several factors; first, more CO₂ was present as a pure phase as it escaped from aqueous solution. Second, since the column operates so close to the critical point, even a very slight change in pressure may have significantly decreased the density of liquid CO₂. In addition, escape of carbon dioxide from the aqueous phase may have lowered the temperature of the column contents, which would also have had the effect of increasing the CO₂ density.

Despite this unanticipated effect, the new on/off valve did appear to have the intended effect of eventually reducing the level of water in the column.

Test #3

This was the first shakedown test in which simulated bilgewater was used. A drum of "clean bilgewater," consisting of water, detergent and sea-salt, was mixed for use during the startup period. A second drum of "contaminated bilgewater," containing oil as well as salt and detergent, was also made up.

The run started using the "clean bilgewater" or priming solution. As the run progressed, an interesting effect was noted. A second meniscus formed in the sight glass, indicating that there were three phases present in the column. At this time it appears that the lower meniscus separates the water (with dissolved CO₂) from a phase consisting of liquid CO₂ with dissolved water, while the upper meniscus separated the CO₂ / dissolved water phase from the pure liquid CO₂ phase.

As the run progressed, carbon dioxide began escaping from the top of the column through the back-pressure regulator. The flow never seemed to reach a steady state condition, although it was difficult to judge solely on the basis of the sound of escaping gas.

After a period of operation in which it proved very difficult to maintain steady state conditions, the pressure in the column began to climb slowly. In response, the CO₂ pump stroke-rate slowed, eventually the pump became dead-headed. Almost simultaneously, a brief very loud noise was heard emanating from the top of the column. Although the indicated column pressure never climbed above 1100 psi, it was assumed that the burst disk had blown. An emergency shutdown was implemented by turning off the water and CO₂ pumps, and opening both control valves and the column-drain ball valve.

As water and CO₂ escaped rapidly through the column drain valve, a plug of ice formed in the nylon drain line - pressure built up behind this plug and the line burst. The drain valve was closed and the column was allowed to vent slowly to atmospheric pressure.

When the burst disk was examined, it was found to be intact. The back-pressure regulator was disassembled and checked, and its internal components appeared to be

undamaged. The relief valve was checked and appeared to function nominally - opening at 1100 psi as expected. The column pressure gauge was also calibrated and found to be accurate.

It appears that a plug of ice (and/or solid CO₂) had formed in the flexible exhaust line downstream of the back pressure regulator, and that the loud noise was the result of this plug blowing free as pressure built behind it.

The exhaust assembly was re-plumbed to eliminate this long length of unheated hose. The external separator was connected directly to the exhaust of the back-pressure regulator with a length of 3/8" stainless steel tubing. This exhaust line and the top of the separator were wrapped with heater tape and insulation - thermocouples were installed at appropriate locations for control of the heaters.

It was assumed that inadvertent flow of water through the CO₂ line contributed to the test failure. In an attempt to reduce this in future runs, the sight glass was lowered by 13 inches. This effectively increased the headspace (while, of course, reducing the active height of the column).

Test #4

This run was again started using the priming mixture (or "clean bilgewater"). After a run-in period the column appeared to be operating in a fairly steady fashion. The water feed was switched to deliver "oily bilgewater" to the column and the system was operated for nearly half an hour.

Throughout this period of operation it was difficult to maintain control of the liquid level. The level fell below the sight glass, and although the on/off valve was in the closed position the water never climbed back to its desired level. At the same time, the CO₂ pump stroke rate varied widely, indicating that the column pressure was not constant. Fearing that the exhaust line might plug and that this could result in rupture of the external separator, the run was aborted.

Although four raffinate samples were taken, they are of dubious value since the liquid level was unknown throughout most of the test, and it is not clear if a steady CO₂ flowrate was ever really achieved.

To simplify the system, it was decided to remove the external separator. This reduced concerns about plugging, since all of the remaining components are capable of withstanding the maximum pressure that could theoretically be achieved (an air drive pressure of to 45 psi results in a dead-head pressure of 1125 psi from the CO₂ pump). It was hoped that this would allow at least some useful data to be gathered in subsequent experiments.

Test #5

This test started normally, using the non-oily priming mixture. Although all components appeared to be operating normally at the start of the experiment, eventually the water level fell inexplicably. Despite the fact that the on/off valve was closed, the level never climbed.

It was observed that bubbles were appearing in the feed drum. Apparently, the Viton o-ring seals in the water check valve had failed, allowing CO₂ to flow back through the CAT pump, causing it to lose its prime so that no water was delivered to the column. The system was shut down.

O-rings were obtained and the check valve was rebuilt.

The phase change associated with opening the on/off valve (see Test #2 discussion) had proved troubling for some time. It was believed that this was at least partially a consequence of a too-large valve ($C_v = 0.30$). Although this valve had been barely cracked for most of these experiments, the coarse nature of the adjustment made it difficult to obtain a suitable flowrate. For this reason, the large valve was replaced by a smaller control valve with a C_v of 0.024. It was felt that this should be sufficient, since the original (always open) valve, which of course remained in the system, had appeared to be nearly sufficient by itself in the first experiment.

Test #6

This test started normally. It proved very difficult to maintain a constant liquid level. Despite the fact that both of the control valves (total $C_v = 0.034$) were fully open, the water level continued to climb. The water pump rate had to be reduced several times to keep the meniscus within the sight glass.

Throughout this process, the CO₂ pump continued to stroke. During much of this test, a significant amount of gas was heard escaping from the top of the column. Since this was so apparent during this run and had not been particularly noticeable during earlier tests, it appears likely that most of the previous experiments featured only sporadic carbon dioxide flow.

Eventually, the water pump had to be stopped completely to avoid a too-high water level. Even though the raffinate valves remained open, and water was seen to be flowing from the bottom of the column, the meniscus level remained constant. The CO₂ pump continued to stroke, but little or no CO₂ was heard flowing from though the back pressure regulator.

The run was aborted by shutting off the CO₂ pump and slowly bleeding down the column pressure.

Test #7

This test was similar to the previous experiments except that four additional thermocouples were added, three on the column itself and one on raffinate line "A" downstream of the metering and shutoff valves.

The run followed the pattern established in previous experiments. It proved impossible to maintain a constant water level in the sight glass. The water flowrate had to be adjusted downward several times in order to keep the level from climbing uncontrollably. There was only sporadic flow of carbon dioxide through the back pressure regulator.

After approximately 45 minutes of flow, the relief valve opened, even though the column pressure was registering just slightly above the nominal 1000 psi level, approximately 100 psi below the anticipated relief valve cracking pressure. The run was immediately aborted.

When the relief valve was tested after the run, the cracking pressure was found to be closer to 1050 psi. Disassembly revealed swelling and hardening of the poppet seal o-ring. As with the check valve o-ring discussed above, it will be necessary to replace this seal between tests. For long-term use, a Teflon or Teflon-coated o-ring would be needed.

Temperatures were monitored throughout the experiment. The feed tank temperature was measured at 73 °F (23 °C) before and after the run.

The top thermocouple (located just above the column midpoint) remained between 77 °F and 79 °F (25 °C and 26.1 °C) for most of the test. The mid-column temperature appeared to be significantly affected by flow of from the top of the column. During the periods in which carbon dioxide flowed through the back-pressure regulator, the temperature dropped to approximately 73 °F (22.7 °C). When the relief valve opened, this thermocouple registered 71 °F (21.7 °C).

The remaining column thermocouples registered fairly constant temperatures throughout the experiment.

The thermocouple on raffinate drain line "A" indicated a temperature of approximately 65 °F (18.3 °C) for most of the experiment. As anticipated, there appears to be considerable cooling associated with the escape of carbon dioxide from the bottom of the column.

It should be noted that the thermocouple temperature readings were only accurate to within one or two degrees Fahrenheit (0.6 to 1.2 degrees Celsius) and were intended to capture gross deviations from normal temperatures, none of which were apparent during this experiment.

Test #8

This test used the same configuration as the previous experiments.

This run was a last attempt to obtain some useful data by flowing "contaminated" bilgewater for the entire test, rather than starting with the non-oily priming solution and waiting, probably in vain, for the system to reach a steady-state condition before starting the flow of oily water.

The test featured behavior similar to previous experiments. A fairly steady state condition was obtained for a time, but eventually the water flowrate had to be reduced in order to avoid overfilling the column. Despite a very high CO₂ pump stroke rate, very little (if any) carbon dioxide flowed out of the top of the column, most or all escaping through the raffinate valves.

Two column volumes of contaminated bilgewater were run through the system before a sample was taken. An additional sample was taken 6.5 minutes (one nominal residence time) later. At 26 minutes into the experiment, it was necessary to stop water flow altogether in order to avoid overfilling the column. Several minutes later, it became apparent that the raffinate valves were becoming clogged. The raffinate thermocouple measured 31 °F (-0.6 °C) at this point – probably indicating that water ice had formed in the metering valve. The system was shut down and allowed to vent.

APPENDIX C: PROCEDURE FOR TASK B (FLASH DRUM) PORTION OF EXPERIMENTAL STUDY

Test Number _____

Pressurizing Procedure Date: _____

1. Set heater controllers to desired temperature. Allow vessel to reach temperature.
2. Turn on all valves to the SCCO₂ unit and turn it on. Set rest pressure to 800 psi.
3. Make sure the CO₂-IN valve to the vessel is open, and the CO₂-OUT valve is closed.
4. Toggle to save rest parameters. Allow vessel to reach 800 psi (bottle pressure).
5. Set rest pressure to desired value. Toggle to save rest pressure. The integrator will have to be re-set after the first pressurization. Afterwards, system will routinely pressurize to approximately 50 psi above setpoint, but otherwise should be OK. Write down time vessel pressurized here _____.
6. Place the high pressure/heat caution sign on the vessel.

Test Procedure Date: _____

1. Make sure SCCO₂ system power is on. CO₂-IN valve on test vessel should be open, CO₂-OUT closed.
2. System should have remained pressurized for at least 10 hours prior to test. Check system pressure as indicated by PLC display, and note here. _____ Write down temperatures displayed on the two temperature controllers and note here _____ (Top Heater Tape) and _____ (Bottom Heater Tape). Change rest pressure setpoint to 0 (zero) psi.
3. Start PC data acquisition program (MONCHAN). Turn off all channels except D/A channel 0 (zero) and Channel 6 (thermocouple). Hit "Start" button – data should be displayed on Channels 0 and 6.
4. Don safety glasses and hearing protection if not already in place
5. Turn on power to relief valve heater tape. Monitor temperature on handheld display. When temperature reaches 150°F, turn off power. Monitor pressure displayed on PLC – if pressure begins to rise rapidly, open exhaust valve to dump CO₂ and leave area.
6. Start data logging. Select a file name and write it down here _____.
7. Turn off inlet valve to test vessel. Reset rest pressure to 0 psi.
8. Warn others in area of impending loud noise. Open door to lab to increase airflow.
9. Open exhaust valve. CO₂ will flow out of relief valve until pressure drops below 50 psi. CO₂ will continue to flow through flowmeter for some time. Monitor reading on MONCHAN screen. When flow stops (voltage reaches a steady level for some time), stop data logging.
10. System is ready to be recharged overnight for next experiment.