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ENGINEERING

~~BNE~~ BNE - 001

DCHX WORKING FLUID RECOVERY
SYSTEM STUDY

July, 1982

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Prepared for:

United States Depart. of Energy
Geothermal Division

Contract:

DE-AC03-82-SF11700

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1.0 INTRODUCTION

The use of a direct contact heat exchanger in recovering energy from geothermal brines offers an attractive and advantageous approach to a binary power plant because it eliminates the problem of heat exchanger fouling at the heat input side of the power loop. A typical working fluid used in the direct contact approach has low miscibility in brine, however, significant amounts can still be lost from the plant unless equipment is provided to recover the working fluid from the brine. For a geothermal power plant of the 5 MW size, using isobutane as the working fluid, isobutane losses would amount to approximately 2 cents per kW-hr. A cost effective recovery system that would reduce the isobutane loss to a few mils per kW-hr would reduce operating costs and improve power plant economics.

There are many approaches available to recover isobutane from the brine before it is discharged from the plant. The available systems include physical separation as well as chemical techniques, all with various advantages and disadvantages. Recovery in most geothermal applications is complicated by the presence of non-condensable gases such as CO₂ or nitrogen in the brine. These non-condensibles have both operational and economic effects on the recovery of the working fluid.

The 500 kW DCHX pilot plant in operation at East Mesa has been able to demonstrate economic recovery of its isobutane working fluid with a simple flash extraction and compression condensation recovery system. This approach to recovery with the 500 kW pilot plant was selected based on its simplicity and the availability of hardware.

Working fluid recovery from a direct contact power plant was evaluated through a comprehensive study of the various techniques. This comparison study has been completed and the results are documented in this report. This study was performed under DOE Contract # DE-AC03-82-SF11700 as part of the 500 kW pilot plant testing pro-

gram. Using a selected approach that meets the needs of the direct contact system, a model recovery system will be designed and fabricated and installed as part of the present 500 kW pilot plant testing. The installed recovery system will be evaluated to demonstrate its capabilities to meet the design objectives both in performance and plant economics.

2.0 STUDY SCOPE

The objective of this study was to identify a recovery system approach that had the best economics for a direct contact system regardless of working fluid and the type of non-condensable gases present in the brine source. The scope of this study was constrained to utilize the conditions existing with the 500 kW demonstration pilot plant for selecting the optimum system with consideration being given for other working fluids and different non-condensable conditions than those being experienced with the 500 kW pilot plant. This limit on the scope of the study is not considered to be restrictive in that the conditions of the brine being used in the pilot plant are similar to most of the brines in existence and secondly, the isobutane working fluid is a logical selection for brine temperatures greater than 300°. The economics in the study were based on a 5 MW plant and the binary process was the same as the 500 kW pilot plant at East Mesa. The economic evaluation was simplified to the extent that operational labor costs (which should be minimal) and detailed maintenance and down time expenses were not evaluated for any of the systems compared.

3.0 SUMMARY

Separation and recovery of isobutane from brine is complicated by the presence of non-condensable gases brought in with the brine. The presence of the non-condensibles makes recovery of the isobutane for most recovery approaches a two step process. To accomodate the two step process, the study has been broken into two segments; one dealing with the separation or liberation of the isobutane from the brine, and the second dealing with separation of the isobutane from

the CO_2 or other non-condensibles liberated during the first step. Liberation of the isobutane from the brine is referred to as the stripping operation. The isolation of the isobutane from the CO_2 is referred to as the separation operation.

Four basic approaches for stripping the isobutane from the brine and four approaches for separating the isobutane from the non-condensibles were evaluated. Various combinations of the stripping and separation operations define the recovery process. The stripping and separation operations are inter-related but the separate evaluations allows comparison of the various combinations.

To strip the isobutane from the brine the processes evaluated were vacuum flash, gas stripping, salting, and absorption with a lean oil. The vacuum flashing and gas stripping processes both require the second step of separating the isobutane from the CO_2 that is also liberated. For both the salting and the lean oil absorption processes the CO_2 liberation problem is avoided and separation is not required.

The most practical approach for stripping isobutane from the brine is a vacuum flash technique. The other three stripping processes are ruled out by both practicality and economics. The gas stripping technique requires large amounts of recirculated non-condensable gas to achieve its performance with a penalty that includes large operating power levels and significant dilution of the recovered isobutane thus making later separation difficult and expensive. The lean oil approach to stripping isobutane from the brine eliminates the operating costs associated with lost isobutane but creates a new one associated with the solubility of the lean oil and the cost associated with replenishing it. The salting approach to reducing or recovering lost isobutane is impractical due to large quantities of salt required to reduce the isobutane solubility to the point where little isobutane is lost with the brine.

Four separation approaches were explored to establish the cost trade-offs and allow selection of the most economical configuration.

Where practical, several vacuum flash configurations were evaluated to establish the economic trade-offs of the total combined stripping-separation approach. The vacuum stripping approach in a multi-stage configuration reduces the isobutane lost in the discharged brine to less than 10 parts per million or a predicted equivalent flow rate less than 10 lbs/hr for a 5 MW plant.

The four separation techniques were evaluated for separation of isobutane from CO_2 and return of recovered isobutane to the power system. Separation of the two gases is desirable because the return of CO_2 to the power loop increases the CO_2 levels in the power condenser thus increasing condensing pressure. Increased condensing pressure reduces the amount of power that can be extracted from the working fluid by the power turbine thus creating an economic penalty for the plant. The four basic approaches evaluated for separation of the isobutane from the CO_2 include permeable membranes, compression and condensation, selective absorption and distillation. The distillation system is not competitive. Three of these approaches are practical and had operating costs that were competitive. These systems had a payback of less than 1 year and resulted in operating costs ranging from 1.6 mils per kW-hr to 3.3 mils per kW-hr. The costs however did not include equipment maintenance or operational man-hours required to operate them. Within the scope of this study it was not possible to optimize all three of these techniques. The simplest hardware configuration is the compression and condensation approach which only requires a compressor and condenser and appears to have the lowest potential operation cost.

During the evaluation and optimization of the compression/condensation technique it was established that the minimum operating costs for the specific conditions chosen occurred when there was no condenser vent flow. On this basis, a system in which the stripped IC_4 and CO_2 are returned directly to the power loop was evaluated. This approach of stripping the isobutane and CO_2 and returning them directly to the power condenser results in the lowest operating cost of any of the systems evaluated, i.e. 1.4 mils per kW-hr. This approach will work with any of the working fluids and any of the non-condensibles present in the incoming brine.

4.0 DISCUSSION

The evaluations of the different approaches to working fluid recovery and the ground rules used in the evaluations are summarized in the following sections.

4.1 RECOVERY SYSTEM EVALUATION GROUND RULES

The economics of isobutane recovery for commercial sized direct contact geothermal power plants was the primary objective of this study. For evaluation, a 5 MW plant was selected. A power plant this size without a recovery system would experience an operating cost penalty of approximately 2 cents per kW-hr due to the isobutane lost in the brine which is discharged from the plant. A 5 MW plant, being relatively small might experience higher relative recovery system costs than a bigger plant due to the size scaling effect. A 5 MW plant size does not affect the comparison between the different types of systems. The 500 kW pilot plant at East Mesa is considered to be a reasonable model of a commercial plant in terms of operating conditions and brine resource temperature and composition. The state points of the 500 kW plant therefore were used as a basis for evaluating and comparing the various approaches to working fluid recovery. Applications of the direct contact principle to other resources could influence the choice of recovery systems due to the use of different working fluid or variations in the non-condensable gases in the resource brine. The brine resource at the East Mesa site contains high levels of CO_2 , and, like any resource with significant amounts of non-condensibles, a pre-flash is required on the incoming brine to reduce the non-condensibles to a level acceptable for good power production. The brine resource as it reaches the 500 kW pilot plant at East Mesa is at a temperature of 340°F . Resources with higher temperatures will have increased power production per pound of brine and therefore lower costs associated with working fluid recovery.

To provide a direct cost comparison between the various systems and to establish a reasonable estimate of the operating cost penalty associated with power production the following items

were included in evaluating each approach:

1. The costs of all unrecovered or lost working fluid.
2. The power costs required to operate pumps and compressors.
3. Power cost to boost the brine pressure back to a 25 psia level for discharge from the power plant and power lost due to increase of the discharge pressure for the hydraulic turbine above the 25 psia.
4. For the optimized systems the penalties associated with lost power production due to CO₂ returned to the power system were included.
5. The cost of brine that was used to provide heat energy.
6. Equipment costs were established for each system and then converted to an equivalent operating cost based on a 40,000 hour depreciation neglecting any interest, taxes or investment cost penalties. The assumption of 40,000 hours to depreciate the hardware represents a 5 year life.

Recovery system equipment costs were estimated after the equipment was sized based on a costing guide titled "Current Costs of Process Equipment", published in Chemical Engineering, April 5, 1982. No attempt was made to evaluate the potential operating costs associated with man-power required to run the given system or with maintenance costs or the potential effect of system down time on plant capacity factors.

The following efficiencies, cost factors and plant conditions were selected as a basis for evaluating all of the recovery approaches:

1. Plant output power level	5 MW (Net)
2. Plant brine flow rate	10 ⁶ lbs/hr
3. Initial CO ₂ content of brine (after pre-flash)	300 lbs/hr

4.	IC ₄ content of brine leaving DCHX	200 lbs/hr
5.	Compressor efficiency	55%
6.	Motor efficiency	85%
7.	Pump efficiency	55%
8.	Electrical power value	\$.07/kw-hr
9.	IC ₄ cost	\$.50/pound
10.	Hydraulic turbine efficiency	85%
11.	Value of brine	\$.034/lb

4.2 TECHNIQUES FOR STRIPPING ISOBUTANE FROM THE BRINE

The four methods that were evaluated for separating the IC₄ from the brine leaving the DCHX were vacuum flash stripping, absorption of the working fluid directly from the brine, gas stripping or sparging and solubility reduction. The discussion of the various approaches will show that the vacuum flash is superior to the other methods. This approach is compatible with all of the common non-condensibles and operates at a low cost. The vacuum flash approach to stripping of working fluid was evaluated in depth to establish the most cost effective approach for various configurations and to predict their performance potential.

4.2.1 Lean Oil Absorption of IC₄

Lean oil absorption of IC₄ is a type of liquid to liquid extraction used directly with the brine. Liquid to liquid extraction is normally used when a mixture of two completely miscible liquids is to be separated into two components. It is based on the principle that a solvent not completely miscible with the mixture can be capable of selectively dissolving one of the constituents of the mixture. For this application liquid to liquid extraction was applied to a mixture of two partially miscible fluids.

For a concentration of IC₄ in the exit brine of 200 ppm the solubilities of the solvent in the brine must be less than 10-15 ppm, or a significant percentage of the IC₄ along with the solvent

will be lost. Since solubilities of the IC_4 solvents are considerably higher than the solubility of the isobutane in water (for example; kerosene - 350 ppm, paraffin oil - 220 ppm, chloroform - 750 ppm) the problem of the IC_4 recovery will only be converted to a greater problem of solvent recovery. Hence this approach would not appear to be practical and was not evaluated any further.

4.2.2 Gas Stripping/Sparging

Gas stripping of the isobutane from the brine requires bubbling a stream of non-condensable gas (CO_2 or Nitrogen could be used) through the brine. The non-condensable gas bubbles rise through the brine absorbing isobutane. The gas mixture is then directed to a separation system where the isobutane is removed from the gas mixture and recovered. The stripping gas may then be either vented or recycled to the separating equipment. Ike Sheinbaum has performed experimental work in this area and the results are summarized in his report entitled, "Stripping of Isobutane from Geothermal Brine", prepared for Lawrence Berkeley Laboratories, dated October, 1980. The report summarized data utilizing both nitrogen and CO_2 as the stripping gas and showed that approximately 100% of the isobutane could be stripped. It is felt that nitrogen might be superior because of its lower solubility in the brine and hence less stripping gas would be carried away with the brine. Referring to Sheinbaum's data, the gas flow rates used for stripping gave an average of 0.456 mole % of isobutane in the stripping gas. For a 5 MW plant having a brine flow of 1 million lbs/hr and approximately 200 ppm of dissolved isobutane, the data suggests that approximately 21,000 lbs/hr of gas would have to be processed for this operation. The equipment costs to recycle this amount of nitrogen were not estimated but were felt to present an unreasonable penalty. Based on operating experience with the 500 kW plant and a review of the process industry literature, the major problem is not removing the isobutane from the spent brine but separating and recovering the isobutane from this gas mixture. The high dilution of the isobutane that would occur with a gas stripping system would increase the difficulty of recovery of the isobutane. Therefore, gas stripping

of the spent brine to recover isobutane is not recommended because it offers significant cost and operating difficulties.

4.2.3 Reduced Solubility with Increased Salinity

Figure 1 shows solubility of isobutane in brine with various levels of salinity. The figure shows that with very high levels of salinity the solubility of isobutane is reduced to levels that result in loss rates costing less than 2 mils/kW-hr. This characteristic indicates that with higher salinity brines that the recovery problem is reduced.

The process of adding salt to increase salinity to a level that would reduce isobutane losses to an acceptable level for East Mesa brines would require 1,000 lbs of sodium chloride per lb of isobutane recovered. It is apparent that the use of salt to prevent IC_4 loss is not practical as it would require the purchase of large amounts of salt or the inclusion of a salt recovery system. This approach was not studied in further detail.

4.2.4 Vacuum Flash

The vacuum flash method of separating the working fluid from the brine involves reducing the pressure of the brine and providing a space for the working fluid to flash off as a gas. The solubility of the working fluid is proportional to its partial pressure and decreasing the total pressure of the brine reduces the amount of IC_4 that can remain in solution in the brine. By spraying the brine into a gas filled chamber a large surface area can be created allowing rapid evolution of the working fluid into the gas space. Vacuum flash stripping of the working fluid from the brine works well regardless of working fluid or type of non-condensibles involved.

A configuration in which there are multiple stages of flashing generally provides better performance than a single stage of flash. Flash configurations of up to three stages were evaluated. There was a considerable improvement in isobutane stripping with the two-stage approach over a single stage but a minimal amount of improve-

SOLUBILITY OF ISOBUTANE IN WATER AS A FUNCTION OF SALINITY

FIG. 1

ment with the three-stage over the two-stage. The economic aspects of the flash configurations were evaluated with the system used to separate and recover the isobutane from the non-condensibles. All of the flash systems were evaluated over a range of system conditions to try to establish the optimum operating parameters with either the single or multiple stages. In terms of just stripping, the two-stage flash with the first stage occurring at 35 psia and the second stage occurring at 10 psia was superior in terms of isobutane loss and operating power requirements.

4.2.4.1 Theoretical Model

The following model was used to analyze the flashing process and to establish the composition and flow rates. The temperature and pressure within the flash tank were selected, then the equilibrium phase concentrations of the liquid and vapor stream were determined.

In Figure 2, F (moles/hr) of an n -component stream are introduced as feed into the flash vaporization tank.

The resulting vapor and liquid streams are withdrawn at the rates of V and L (moles/hr) respectively. The mole fractions of the components in the feed, vapor and liquid streams are designated as Z_i , Y_i and X_i respectively.

Assuming vapor-liquid equilibrium and steady-state operation, we have the following series of algebraic relationships:

$$Z_i F = H_i L + Y_i V$$

$$Y_i = H_i K_i$$

$$\sum Y_i = 1$$

$$\sum X_i = 1$$

where K_i is the equilibrium constant for the i -th component, at the temperature and pressure in the tank. K_i values were found by using Raoult's and Henry's laws.

$$K_i = H_i / P_{\text{tot}} \quad (H = \text{Henry's constant for a very dilute solution of } i\text{-component})$$

$$K_i = P_{\text{sat}_i} / P_t \quad (P_{\text{sat}_i} = \text{vapor pressure of } i\text{-component at tank temperature})$$

These equations were used to develop the stream properties for all the flash separation configurations which then could be evaluated in terms of performance and cost. These stream properties also became the basis for the separation studies. For these studies the brine entering the flash system at 1,000,000 lbs/hr contains 300 ppm of free CO_2 and 200 ppm of IC_4 .

4.2.4.2 Single-Stage Flash

The single-stage flash is shown schematically in Figure 3.

Brine from the DCHX is run through a Pelton type hydraulic turbine, for pressure recovery. The Pelton wheel operates in a gas environment which is contained by an enclosing vessel called a tailstock. The tailstock provides the vapor space for stripping the IC_4 vapor. For some systems, (ie. pentane instead of isobutane) a recovery turbine may not be necessary and the turbine is replaced by simple spray nozzles and separation tank. The vapors are directed to a compressor that pumps them to the separation system for final recovery. Figure 4 shows the predicted effect of tailstock and hence compressor suction pressure on the flash process. As shown in the figure, decreasing the tailstock pressure increased the amount of IC_4 in the flash gas while reducing the amount of IC_4 lost in the brine. However, reducing the tailstock pressure also increased the amount of water vapor and CO_2 contained in the flash gas. These additional components can have a significant effect on the downstream separation system.

4.2.4.3 Two-Stage Flash

In general, a multi-stage flash is an improvement over a single-stage flash. A two-stage configuration is shown schematically in Figure 5.

FIG. 5

-14-

COMPRESSOR INLET COMPOSITION AND
RATE OF IC_4 LOSS IN THE BRINE AS
A FUNCTION OF THE COMPRESSOR
INLET PRESSURE FOR A SINGLE-STAGE
FLASH

FIG 4

The first stage flash was again assumed to be across a Pelton wheel hydraulic turbine while the second stage flash was across spray nozzles into a vessel called the recovery tank. As shown in Figure 5, a single compressor is used to remove the flash gas from both locations. The compressor suction pressure was assumed to be equal to the pressure of the second stage flash. A throttle valve was used to reduce the pressure of the first stage gas (tailstock) to that of the compressor inlet. This configuration was utilized in the original 500 kw pilot plant at East Mesa.

The predicted performance of the two-stage flash is shown in Figure 6. Comparing Figure 6 for the two-stage flash with Figure 4 for the single-stage flash shows the improvement in IC_4 removal from the spent brine. For example, with a compressor inlet pressure of 10 psia, the two-stage flash leaves 3.2 lbs/hr of IC_4 in the brine, while the same compressor inlet pressure (tailstock pressure) with a single stage flash leaves 5 lbs/hr of IC_4 in the spent brine. An additional advantage of the two-stage flash is the carbon dioxide and water vapor flow rates handled by the compressor are lower.

4.2.4.4 Three-Stage Flash

The performance of a two-stage flash might be improved by adding an additional flash stage. Again, as with the two-stage flash, the compressor suction pressure corresponds to the pressure in the final stage flash and the vapor flow from the previous stages is throttled to the compressor suction pressure. Figure 7 summarizes the predicted performance of this configuration. Comparing Figure 7 with Figure 6 for a two stage flash, shows the additional flash stage resulted in only a very small improvement in isobutane recovery. For example, with a 10 psia compressor inlet pressure, the two-stage flash resulted in approximately 3.2 lbs/hr isobutane flow in the spent brine after the second flash, while for the three stage flash, the isobutane flow was approximately 3.1 lbs/hr. The three stage flash did not reduce the CO_2 to be handled by the separation system.

COMPRESSOR INLET COMPOSITION AND
RATE OF IC_4 LOSS IN THE BRINE AS A
FUNCTION OF THE COMPRESSOR INLET
PRESSURE FOR A TWO-STAGE FLASH

FIG 6

COMPRESSOR INLET COMPOSITION AND
RATE OF IC₄ LOSS IN THE BRINE AS A
FUNCTION OF THE COMPRESSOR INLET
PRESSURE FOR A THREE-STAGE FLASH

FIG. 7

The pressures of the first and second stage flashes for Figure 7 were not optimized, so the three-stage system might be capable of greater performance. However, any performance increase should be slight.

4.2.4.5 Two-Stage Flash With First Flash to Power Condenser

A modification of the two-stage flash system was to have the first stage flash pressure high enough that the flash gas could be directed to the main power condenser (Figure 8).

The advantage of this configuration is that significant amounts of IC_4 may be liberated from the spent brine and recovered without requiring additional compressor work thereby improving plant economics. The carbon dioxide or other non-condensable gas liberated during the flash also returns to the condenser increasing the partial pressure of non-condensable gases in the condenser and thereby decreasing plant output.

The predicted performance of a two-stage flash system with the first flash directed to the power condenser is summarized in Figure 9. Comparing this configuration with the simple two-stage flash shows this system has greater IC_4 loss because of the non-optimum (from an isobutane recovery standpoint) first stage flash pressure. However, the reduced mass flow through the recovery compressor, lowered the compressor work and hence the compressor input power.

The value of this relationship is dependent on the rest of the separation/recovery system.

4.2.4.6 Three-Stage Flash with First Flash to Power Condenser

A three-stage flash with the first stage vented to the power condenser was evaluated to provide another baseline for the separation techniques.

The predicted performance of this configuration is summarized in Figure 10. Comparing the results of this analysis with that for the three-stage flash shown in Figure 7 shows the performance to be similar. It is concluded this method offered the same recovery as the three-stage flash, discussed in Section 4.2.4.4.

4.3 RECOVERY OF ISOBUTANE

After the working fluid has been stripped from the brine, it must be separated or recovered and returned to the Rankine cycle power loop. The ideal system would separate all the CO_2 from the working fluid, eliminate it and return the working fluid to the power loop. Four techniques for separating and recovering the working fluid were investigated: permeable membranes, compression and condensation, distillation column, and absorption. The evaluation of these techniques was based on $\text{CO}_2 + \text{H}_2\text{O} + \text{IC}_4$ mixture chemistry produced by the flash separation process developed previously.

Because of its ability to operate with both nitrogen and carbon dioxide dominated wells, its simplicity and its competitive operating costs the compression-condensation approach of recovering working fluid was selected and optimized. Within the limits of this study it was not possible to optimize each technique nor develop all the cost factors including maintenance and each system's impact on staffing or down time. Each of the recovery methods is discussed separately in detail in the following sections.

The economic evaluation of each system was based on the ground rules set forth in Section 4.1. Each configuration evaluation in-

COMPRESSOR INLET COMPOSITION AND
RATE OF IC₄ LOSS IN THE BRINE AS A
FUNCTION OF THE COMPRESSOR INLET
PRESSURE FOR A TWO-STAGE FLASH

FIG. 9

COMPRESSOR INLET²³ COMPOSITION AND
RATE OF IC₄ LOSS IN THE BRINE AS A
FUNCTION OF THE COMPRESSOR INLET PRESSURE
FOR A THREE-STAGE FLASH SYSTEM

FIG.10

cludes equipment costs and operating costs of the appropriate flash stripping configuration required to feed it. Costs associated with unrecovered pressure energy in the brine due to high first stage flash, increased power system condenser pressure, pumping to raise brine pressure back to 25 psia for discharge and specific recovery system equipment are all accounted for.

4.3.1 Membrane Permeation

When a pressure gradient is established across a specifically prepared membrane, carbon dioxide will permeate more rapidly than hydrocarbon gases. Monsanto Co. has recently introduced a new membrane system referred to as a Prism separator which makes gas separation by permeable membranes economically feasible.

The Monsanto prism separator physically resembles a shell and tube heat exchanger with a bundle of hollow fibers oriented vertically inside a tubular pressure vessel. Feed gas is injected on the shell side of the fibers and the carbon dioxide permeates the substrate, a polymer such as polysulfane, and flows through the bore of the fibers. The pressure difference between the shell and the fiber bore provides the driving force.

The Monsanto Corporation proposed the isobutane recovery system depicted in Figure 11. The process consists of two stages of membrane separation. Gases extracted from the brine in a two-stage flash make up the feedstream. Flash vapors from each stage combine for a total feed gas composition at 145°F and 10.5 psia of:

CO ₂	68.9 lbs/hr
IC ₄	196.8 lbs/hr
H ₂ O	15.4 lbs/hr

The feed gas is compressed to 260 psia and then it is mixed with effluent gas from the second stage separator. This high pressure mixture is fed to the first separation stage. Effluent gas from the first stage separator is returned to the power condenser con-

MEMBRANE SEPARATION SYSTEM

FIGURE 11

taining approximately 3.5 lbs/hr of CO_2 . The permeate gas from the first stage separator is compressed to 295 psia before entering the second stage separator. Effluent gas from the second stage separator is returned to the mixer while permeate gas containing 5.9 lbs/hr of IC_4 is vented. In the #2 compressor intercooler 37.2 lbs/hr of IC_4 and 10 lbs/hr of CO_2 are condensed and returned to the power system.

The proposed system recovers 190.9 lbs/hr of isobutane. Operating input power costs are estimated at \$12,000 annually. An additional \$5,000/yr is required for a 10% membrane replacement in three years. Monsanto's estimated capital cost which includes membrane, skid, controls, and a two-stage compressor is \$150,000. Barber-Nichols included an additional \$12,000 for the feed stream compressor and \$1.43/hr for compressor input power cost. Based on the economic ground rules this translates into \$14.00/hr operating cost including the stripping.

This system offers a payback of less than one year. The membrane is not suitable for a feed gas containing nitrogen. The rate at which a gas permeates a membrane depends on its ability to diffuse through the substrate and its affinity for the polymer, ie. to interact with the polymer. Nitrogen is relatively inert and is considered a "slow" gas as is isobutane making membrane separation impractical for nitrogen dominated brines. Membrane systems are more economical when used as a topping process or pre-separation system in conjunction with another separation technique. In a topping process, the effluent from the final membrane separation stage would contain approximately 20 mole % CO_2 . For further purification, an absorption process or compression and condensation might be used. Due to the low CO_2 mole percent in the feed stream, a topping process is not justified for this application.

The CO_2 returned with the IC_4 to the Rankine cycle increases the condenser total pressure thereby reducing the power available to the turbine and the output power. This effect was not included in this analysis.

⁻²⁵⁻
ABSORPTION SYSTEM

FIGURE 12

4.3.2 Selective Absorption & Recovery

A typical absorption system is illustrated in Figure 12. A solution selective to the component to be absorbed is introduced counter current to the feed gas stream in a column called the absorber. The solution leaving the absorber which is rich in the absorbed gas is sent to a stripping column for regeneration, i.e. separation of the gas from the solution. Regeneration in the stripping column is dependent upon favorable temperatures and pressures of the rich solution. Heat is typically added to the rich solution in a reboiler before entering the stripping column. Heat requirements are reduced by a waste heat exchanger. The regenerated solution requires cooling before introduction into the absorber. In the stripper, the solution is regenerated by stripping using a vapor or a gas stream, typically steam. In addition to the absorber and stripper columns, Hoffman advises in Phase and Flow Behavior in Petroleum Production that it is usually advantageous to employ a rectifying section using the column overhead vapors, cooled and partially condensed, to provide a reflux stream. The performance of an absorber-stripper system is dependent upon operating temperatures and pressures, feed gas composition and purity required. Economics are determined by separation requirements, recirculation rates and utility requirements to regenerate the rich solution.

To size the equipment for an absorption system the input gas was of the composition from a two-stage flash. The gas mixture for sizing the plant contained 63.9 lbs/hr of CO_2 , 196.8 lbs/hr of IC_4 , and 15.4 lbs/hr of H_2O . Absorbent recovery of the IC_4 can be accomplished either by absorbing the CO_2 from the gas stream with any one of three readily available solutions or by absorbing the IC_4 .

4.3.2.1 Selective Absorption of Non-Condensable Gas

Typical CO_2 absorption systems use sodium carbonate, potassium carbonate, and the amines as the absorbing liquid. All three mediums depend on a chemical reaction between the absorbed gas and the solution.

Industrial processes based on these solutions can be divided into two groups, those that operate the absorber at essentially ambient temperatures, 70-100°F, and those that occur at elevated temperatures, i.e. approximately the same temperature at which regeneration takes place. The latter process is primarily suitable for feed gases under pressure.

A sodium carbonate system with the absorption process taking place at ambient temperatures was considered. The solution reacts with the CO₂ as follows:

The forward reaction occurs in the absorber and the reverse reaction in the stripper. Regeneration of the solution is by vacuum distillation in the stripper column. The heat required for activation is provided by steam.

A hot potassium (Benfield) process provides an effective CO₂ removal system under pressure (approximately 300 psia). A high absorption temperature greatly increases the absorption rate and reduces the heat required to heat the rich solution to stripping temperatures. With lower absorber pressures, lean circulation rates and steam requirements increase significantly. Regeneration of the solution is by flashing to atmospheric pressure and using steam as a stripper. Operational difficulties for the high pressure system include foaming and corrosion. These problems are generally controlled by using additives.

Amines, while effective for CO₂ removal, do not offer an economic advantage to the two systems just discussed. Amines react with the CO₂ to form the amine salt of a carbonic acid. Monoethanolamine, diethanolamine and triethanolamine are commonly used in industry although the latter has dropped out due to its low reactivity and relative instability. For relatively low CO₂ concentrations and few impurities such as COS and CS₂ which form stable corrosive compounds with the primary amines the monoethanolamine solutions are generally preferred. Diethanolamines are much less

reactive with CO_2 and CS_2 and are used when gas streams contain appreciable amounts of these contaminants.

All of the above systems are viable candidates for separating carbon dioxide and isobutane. Both alkali carbonate systems offer the advantage of not contaminating the working fluid as in the case with the amines. Based on the selected gas stream composition and using the absorption-stripping factor method and assumptions presented in Hoffmans book, Phase and Flow Behavior, the absorption systems were sized. Estimated fabrication cost of the absorption systems is approximately \$230,000 not including a compressor. Compressor costs would be \$7,600 for the sodium carbonate system and \$13,000 for the potassium and amine systems. Total capital costs are equivalent to an economic penalty of \$5.88 to \$6.08/hr. Operating costs range from \$8,700/yr for the sodium carbonate system to \$13,760/yr for the amine absorption system which is equivalent to \$1.09 to \$1.72/hr. Including the costs of the vacuum extraction process and again neglecting the effect of CO_2 returned with isobutane, net system operating costs are \$13.48, \$14.15, and \$14.19 for the sodium carbonate, potassium carbonate and amine systems respectively.

The estimated payback of the CO_2 absorption recovery systems is less than one year. Performance is dependant, however, on the geothermal resource characteristics.

For a different resource, such as the brines of Raft River with nitrogen instead of carbon dioxide, alkali and amino solutions are ineffective because they will not react with nitrogen.

4.3.2.2 Selective Absorption of the Isobutane

Absorption of the isobutane from the stripped gas would require a lean-oil solvent, similar to a kerosene fraction. An isobutane absorption system has been proposed by Otto Schkade of Vatrol Co. (which designs and builds these systems) and is shown in Figure 13. Isobutane is absorbed by a chilled lean-oil in the scrubber absorber

LEAN OIL ABSORPTION SYSTEM

FIGURE 13

at an operating pressure of 25 psia. The rich oil leaving the absorber is preheated in the recovery heat exchanger by the hot lean-oil leaving the stripper. The remaining stripping heat is provided by a steam heater. The absorbed isobutane is released in the stripper by flashing in a vacuum. The lean-oil is then chilled by a refrigeration unit before returning to the absorber.

Recovery of the isobutane is estimated at 97 mass percent or 190.9 lbm/hr. Capital costs are estimated between \$241,000 and \$291,000 equivalent to \$6.23 to \$7.52/hr. Utility and steam requirements are projected to be \$3.13/hr. Including the two-stage flash costs, the net operating cost is \$16.20/hr.

The projected system has a payback of less than one year. The lean-oil system is suitable for a feed gas composed of IC_4 and CO_2 or nitrogen. There is the possibility, however, of contaminating the working fluid with the oil. Vatrol estimated contamination would reach equilibrium at 0.75 mass percent of recovered isobutane, an economic penalty of approximately \$.21/hr.

4.3.3 Compression and Condensation Separation

The IC_4 working fluid can be condensed into liquid to separate it from the non-condensable gases at reasonable pressure levels for temperatures in the 35 to 100°F range. With the IC_4 condensed out of the gas stream the remaining gases can be vented. Nominally the higher the condensing pressure the lower the mole percentage of IC_4 or other working fluid vented with the non-condensable gases. In the case of an $IC_4 - CO_2$ mixture the higher pressures result in high solubility of the CO_2 in the IC_4 . This interaction requires an evaluation of a range of conditions to establish the best economic operating point, including the flash conditions. The compression-condensation was evaluated for single and dual flash and the dual flash for both 95°F and 35°F condensing temperatures to explore this interaction. The evaluations are presented as a function of compressor power as this power was considered to be the major recovery system cost factor. Evaluation of the condensation pressures showed

that the lowest cost for all the configurations occurred at pressure levels where all of the CO_2 is dissolved in the condensed IC_4 resulting in zero CO_2 vent. This finding leads to the obvious approach of eliminating the separate condensation and returning all the stripped flow to the main condenser thus achieving minimum compressor power and eliminating the complexity of a separate condenser. In all of these configurations the CO_2 introduced into the loop causes the same performance penalty. The use of the main condenser to condense the returned IC_4 does not measurably affect its heat load. The direct return to the power loop of the stripped mixture is the lowest cost approach and provides the best scheme in terms of equipment simplicity.

4.3.3.1 Composition Modeling

The model and equations for determining composition and flow rates for the recovery condenser is given in Appendix B. System equilibrium conditions are based on concentration factors confirmed experimentally with the pilot plant and the fact that at equilibrium the input must be equal to the output. For a direct contact power loop the CO_2 entering must be equal to the CO_2 that flows out in the brine and the condenser vent. The CO_2 leaving the column with the brine must be equal to the sum of the CO_2 returned to the power loop from the separation system plus that leaving the plant in the brine. A separation system that allows CO_2 return to the power loop thus increases the CO_2 content of the gas stream it treats. Within the power loop itself the CO_2 concentration in the IC_4 is increased by a factor of eight over the level in the brine leaving the column which produces a measurable influence on the condensing pressure. The analysis of the absorption and the membrane systems ignored these recirculation effects in the first cut evaluation and only the analysis of the more attractive condensation schemes included them.

4.3.3.2 Initial Evaluation of Compression-Condensation

The single-stage flash and the two-stage flash were compared with a 95° condensing temperature. The two-stage flash was evaluated

for both an optimized first stage pressure and for first stage flash to the power condenser. Schematically the three configurations are shown in Figures 14, 15, and 16. The evaluation of these three configurations include cost of both the IC_4 left in the brine and that lost with the vented CO_2 . Pumping power is charged for boosting brine pressure from the last flash to the selected discharge pressure of 25 psia. Power lost in the hydraulic turbine due to expansion to a pressure higher than 25 psia is accounted for. Compressor power is a function of the pressure ratio and mass flow thus is determined by flash pressures, incoming brine composition and condensation pressure. These analyses did not account for any CO_2 returned to the power loop with the condensed IC_4 . The CO_2 does affect the power loop and to a lesser extent the recovery system itself but does not affect the comparison of the three configurations. The results of these evaluations are shown as the system operating cost versus compressor power in Figures 17, 18, and 19. These figures also show the contribution of the IC_4 loss, compressor power and equipment costs, and the power penalties from the hydraulic turbine and the brine return pump. The three cost figures show that the two-stage flash with a tailstock pressure of 35 psia is the best performer by 30%.

4.3.3.3 Optimization of Two-Stage Flash with Condensation

To develop the total picture of the two-stage flash with condensation recovery, an iterative computer program was set up so that the effect of CO_2 returned to the power loop could be accounted for. Both the effect on the power loop condensation pressure and the increase in CO_2 level in the brine leaving the DCHX were included. The results of the optimization, including the effects of the recirculated CO_2 , are shown in Figure 20 and comparison with the preliminary evaluation shown in Figure 19 shows an operating cost of \$7.96/hr, an increase of \$2.70/hr when the CO_2 effects are accounted for including a shift in the optimum operating point. A very interesting aspect of the condensation study that is not illustrated in Figure 19 is that the majority of the loci of minimum costs occur for a range of condensation pressures where all of the CO_2 is absorbed

SINGLE STAGE FLASH

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BRINE FROM
HYDRAULIC
TURBINE

TWO STAGE FLASH

BRINE FROM
HYDRAULIC
TURBINE

FIGURE 15

BRINE FROM
HYDRAULIC
TURBINE

TWO STAGE FLASH FIRST STAGE TO POWER CONDENSER

FIGURE 16

-34-

OPERATING COSTS FOR A SINGLE STAGE FLASH
RECOVERY SYSTEM WITH 95°F CONDENSER

TAILSTOCK PRESSURE = 5.5 TO 50 PSIA,
CO₂ = 300 PPM, BRINE FLOW = 10⁶ LB/HR
IC₄ = 200 PPM

EFFECT OF
CO₂ RETURN
TO POWER
LOOP
NEGLECTED

FIG 17

OPERATING COST OF A TWO-STAGE FLASH RECOVERY SYSTEM WITH A 95°F CONDENSER

-35-

TAILSTOCK	P = 35 PSIA
RECOVERY TANK	P = 6 TO 25.5 PSIA
TEMPERATURE	= 140°F
BRINE FLOW RATE	= 10 ⁶ LB/HR
CO ₂	= 300 PPM
IC ₄	= 200 PPM

FIG. 18

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OPERATING COST OF TWO-STAGE FLASH
RECOVERY SYSTEM WITH 95° CONDENSER
AND WITH FIRST STAGE FLASH TO
POWER CONDENSER

TAILSTOCK $P = 35$ PSIA
 RECOVERY TANK $P = 6$ TO 25.5 PSIA
 TEMPERATURE $= 140^{\circ}\text{F}$
 BRINE FLOW RATE $= 10^6$ LB/HR
 CO₂ $= 300$ PPM
 IC₄ $= 200$ PPM

EFFECT OF CO₂ RETURNED TO POWER
LOOP NEGLECTED

FIG. 19

OPERATING COSTS OF A TWO-STAGE FLASH RECOVERY SYSTEM WITH 95°F CONDENSER

FIG. 20

in the condensed IC_4 and none is vented. Figure 21 shows IC_4 loss and CO_2 returned to the power loop for different second stage flash pressures as a function of compressor power. Where the CO_2 or IC_4 total loss curves flatten off, the condensing pressure is high enough for all the CO_2 to be absorbed and returned to the power loop with the IC_4 and there is no condenser vent. The locus of points of minimum total isobutane loss is also indicated on the figure. Figure 22 shows that the minimum cost total of IC_4 loss and system power follows the points of total CO_2 absorption, or no vent, until flash pressures of 8 psia or less are encountered. Adding the compressor costs, flash tank cost, and brine pump costs to the curve labeled "Cost of IC_4 Loss and Power Loss" in Figure 22 results in the total equivalent recovery system operating cost curve of Figure 20.

4.3.3.4 Optimization of Two-Stage Flash with 35°F Condensation

Condensation at a lower temperature using refrigeration was explored to ascertain the performance of a lower temperature condenser. A water chiller is the most practical configuration to provide the low temperature condensation source and it has a lower limit of 35°F to prevent freezing the water vapor. The evaluation for the 35°F condensing source produced the results shown in Figures 23, 24, and 25. It can be seen that for the 35°F condenser that the optimum operating cost is very close to that for the 95°F condenser and that the minimum cost point also occurs with all the CO_2 absorbed and returned with the IC_4 to the power loop. The lower temperature condenser allows the optimum condensing pressures to drop for a given set of flash conditions and the power saved in compression more than offsets the cost of the refrigeration.

Two types of refrigeration cooling were evaluated: a conventional electrically powered R-12 system and an absorption unit using brine as a heat source. Either unit has a relatively constant heat load for all of the evaluated conditions since the mass of IC_4 condensed does not vary appreciably. A heat load capability of 5 tons handles system requirements and was used to derive operating

RECOVERY FLOWS FOR A TWO STAGE FLASH RECOVERY SYSTEM WITH A 95°F CONDENSER

FIG. 21

COST OF IC₄ LOSS AND POWER
LOSS OF A TWO STAGE FLASH
RECOVERY SYSTEM WITH A 95°F CONDENSER

- COST OF IC₄ LOSS AND POWER LOSS AT
 CONSTANT FINAL FLASH PRESSURE.
 - - - - - COST OF POWER LOSS DUE TO HIGHER NON-
 CONDENSIBLE PRESS. IN THE CONDENSER.
 ———— COST OF IC₄ LOSS

FIG 22

RECOVERY FLOWS FOR A TWO STAGE FLASH RECOVERY SYSTEM WITH A 35°F CONDENSER

— IC_4 LOSS (TOTAL); - - CO_2 ADDED TO WORKING LOOP

FIG 23

COST OF IC₄ LOSS AND POWER LOSS
LOSS OF A TWO STAGE FLASH
RECOVERY SYSTEM WITH A 35°F CONDENSER

FIG 24

and equipment costs. The electric powered unit required 7 kW and the heat powered absorption unit 1,000 lbs/hr of brine assuming a COP of 0.6. Based on the APRR catalog, reference 8, equipment costs were estimated at \$3,300 for each. The operating and equipment costs thus work out to an equivalent \$0.57/hr for the electric powered and \$0.34/hr for the brine powered absorption refrigeration system.

4.3.3.5 Direct Return of Two-Stage Flash to Power Condenser

Optimization of the compression and condensation systems resulted in a minimum cost operational zone wherein all the CO_2 was absorbed in the condensed IC_4 and there was no non-condensable venting. The whole point of the compression was to separate the IC_4 and non-condensibles. A two-stage flash whose gas streams are piped directly to the power loop (Figure 26) has many attractive features. Compressor power is minimized, no additional separation equipment is required and the power system losses due to the returned CO_2 are the same as for the optimum condenser system with no vent. Obviously with less equipment and extreme simplicity, maintenance, operating and downtime costs are minimal. The results of optimizing the operating conditions for the two-stage direct return flash recovery system are shown in Figure 27. System operating costs are down to \$6.90/hr versus a minimum of \$7.60/hr primarily because of reduced compressor power for a separate condenser which translates into 1.52 mils per kW-hr of produced power costs.

4.3.4 Distillation

A distillation column has the potential for providing higher purity IC_4 for return to the power loop than the other systems. A typical system configuration is shown in Figure 28. The vent gas from the flash stripper is sent to a distillation column where it is processed with the liquid reflux. The reflux liquid absorbs part of the gas stream and carries it to the bottom of the column

OPERATING COSTS OF A TWO STAGE
RECOVERY SYSTEM WITH A 35°F CONDENSER

-44-

FIG 25

"DIRECT RETURN" RECOVERY SYSTEM
FIG. 26

OPERATING COST OF TWO STAGE FLASH WITH DIRECT RETURN TO POWER CONDENSER

-46-

FIG. 27

-47-
DISTILLATION SYSTEM

FIG. 28

where it is separated by the reboiler. The effluent stream, labeled bottom products, from the reboiler can be adjusted by process conditions to provide an IC_4 stream containing a very low level of CO_2 . This high level of purity is the major asset of this process. In adjusting the system to provide the high purity IC_4 the amount of CO_2 vented is increased. With equilibrium conditions the CO_2 vented is equal to the difference in CO_2 flow of the incoming stream and that contained in the liquid leaving the system. The distillate products shown leaving the reflux accumulator contain high levels of CO_2 and for maximum performance would not be removed but would just be added to the reflux stream.

This system does provide clean IC_4 but when the CO_2 is vented, IC_4 goes with it. The higher the purity of the IC_4 the higher the loss rate of the IC_4 . Evaluating the operating limits with 1) all CO_2 being vented or 2) no CO_2 vented, it is apparent that the distillation process is not applicable for a direct contact plant. Adjusting conditions for the minimum IC_4 loss in the vent stream, a $35^{\circ}F$ condensing temperature and 200 psia, the IC_4 vent loss would be 14 lbs/hr at an equivalent cost of \$7.00/hr. The other extreme is zero vent of CO_2 and no IC_4 loss with an equivalent operating cost of \$3.40/hr due to the increased CO_2 level in the power loop. Costs for intermediate operating conditions would lie between these two extremes. These costs neglect the power required by the compressor but the result is identical to the condensation method of separation in that the most cost effective condition is with all the CO_2 returning to the loop so that the maximum amount of IC_4 can be recovered.

4.4 NON-CONDENSIBLE GAS UTILIZATION

The potential of selling the separated CO_2 was investigated by establishing its economic value. Union Chemical in Los Angeles, was contacted to establish that the wholesale value of industrial CO_2 was \$32/ton (February 1982 price). At a production rate of 20 to 100 lbs/hr, this would not provide enough income to pay for processing equipment. It was assumed that the value of N_2 would be the same or less than that of CO_2 , therefore, it was not pursued.

5.0 RECOVERY APPROACH COMPARISON AND RECOMMENDATIONS

The practical approaches for recovery of working fluid from the brine discharge of a direct contact plant include configurations with a vacuum flash to strip the working fluid from the brine and several alternate separation techniques required to remove the non-condensibles stripped with the IC_4 from the brine. The practical configurations are summarized in Table 5-1 with their equipment costs and equivalent operating costs. The vacuum flash stripping accounts for approximately \$19,800 in equipment cost less compressor for all of the system and \$1.35/hr operating cost for the brine return pump.

The lowest operating cost is shown for the two-stage flash with direct return of the stripped gases to the power loop. This system is readily configured for testing in the 500 kW pilot plant where the capability exists to verify the projected performance. It is recommended that the pilot plant and its equipment be configured for demonstration of the recovery approach and a test run to verify the engineering analysis.

TABLE 5-1

DIRECT CONTACT IC₄ RECOVERY SYSTEMS
COST COMPARISON

	<u>Equipment Costs</u>	<u>Power Costs</u>	<u>Lost IC₄ Costs</u>	<u>Total Equivalent Operating Costs</u>
Two-Stage Flash with Permeable Membrane*	\$181,800	\$4.91/hr	\$4.55/hr	2.8 mils/kW-hr
Two-Stage Flash with CO ₂ Absorption*	\$257,400	\$2.44/hr	\$4.55/hr	2.7 mils/kW-hr
Two-Stage Flash with IC ₄ Absorption (Lean Oil)*	\$285,800	\$4.69 /hr	\$4.55/hr	3.3 mils/kW-hr
Two-Stage Flash with 95°F Condenser	\$ 29,500	\$4.37/hr	\$2.90/hr	1.6 mils/kW-hr
Two-Stage Flash with 35°F Condenser & Electric Powered Refrig.	\$ 30,800	\$4.11/hr	\$2.90/hr	1.6 mils/kW-hr
Absorption Refrig.	\$ 30,800	\$3.96/hr	\$2.90/hr	1.5 mils/kW-hr
Two-Stage Flash with Direct Return to Power Loop	\$ 27,400	\$3.89/hr	\$2.25/hr	1.4 mils/kW-hr

* Systems so marked were not penalized for CO₂ returned to power loop

6.0 BIBLIOGRAPHY

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7.0 APPENDIX

APPENDIX A

THEORETICAL MODEL OF A FLASH STRIPPING SYSTEM

Consider a mixture with overall composition given by the mole fractions $Z_1, Z_2, \dots, Z_i$ at a temperature and pressure such that it consists of two phases in equilibrium, a liquid phase with mole fraction $X_1, X_2, \dots, X_i$ and a vapor phase with mole fractions $Y_1, Y_2, \dots, Y_i$:

Assume that F (moles/hr) of an n -component stream are introduced as feed into the flash vaporization tank.

The resulting vapor and liquid streams are withdrawn at the rates of V and L (moles/hr). The mole fractions of the components in the feed, vapor and liquid streams are designated as Z_i, Y_i and X_i respectively.

Assuming vapor-liquid equilibrium and steady-state operation, we have the following series of algebraic relationships:

$$Z_i F = X_i L + Y_i V \quad (\text{material balance for component } i)$$

$$Y_i = X_i K_i \quad (\text{equilibrium relation})$$

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Assuming vapor-liquid equilibrium and steady-state operation, we have the following series of algebraic relationships:

$$Z_i F = X_i L + Y_i V \quad (\text{material balance for component } i)$$

$$Y_i = X_i K_i \quad (\text{equilibrium relation})$$

$$\sum Y_i = 1 \quad (\text{by definition})$$

$$\sum X_i = 1 \quad (\text{by definition})$$

$$F = V + L \quad (\text{material balance})$$

K_i is the equilibrium constant for the i -th component, at the temperature and pressure in the tank. K_i values can be found by using Raoult's and Henry's laws.

$$K_i = H_i / P_{\text{tot}} \quad (H = \text{Henry's constant for a very dilute solution of } i\text{-component})$$

$$K_i = P_{\text{sat}_i} / p_t \quad (P_{\text{sat}} = \text{vapor pressure of } i\text{-component at tank temperature})$$

Thus there are $2_i + 2$ equations and $2_i + 2$ unknowns, and the state of the system is completely determined. That this should be the case is a consequence of Duhem's Theorem, which states that for any closed system formed initially from a given mass of particular chemical species the equilibrium state is completely determined when any two independent variables are fixed.

Although an iterative technique is required to solve this system of equations in general form, algebraic solution is possible for three component mixtures.

Assume dilute solution of CO_2 and IC_4 in water.

$$\begin{aligned} Z_{\text{CO}_2} &= Y_{\text{CO}_2} \frac{V}{F} + X_{\text{CO}_2} \frac{L}{F} \\ Z_{\text{IC}_4} &= Y_{\text{IC}_4} \frac{V}{F} + X_{\text{IC}_4} \frac{L}{F} \\ Z_{\text{H}_2\text{O}} &= Y_{\text{H}_2\text{O}} \frac{V}{F} + X_{\text{H}_2\text{O}} \frac{L}{F} \end{aligned} \quad \left. \vphantom{\begin{aligned} Z_{\text{CO}_2} \\ Z_{\text{IC}_4} \\ Z_{\text{H}_2\text{O}} \end{aligned}} \right\} \text{MATERIAL BALANCES}$$

$$Y_{\text{CO}_2} = \frac{H_{\text{CO}_2-\text{H}_2\text{O}}}{P_T} X_{\text{CO}_2} \quad \left. \vphantom{Y_{\text{CO}_2}} \right\} \text{EQUILIBRIUM RELATION}$$

$$\begin{aligned} Y_{IC_4} &= \frac{H_{IC_4-H_2O}}{P_T} X_{IC_4} \\ Y_{H_2O} &= \frac{P_{SAT H_2O}}{P_T} X_{H_2O} \end{aligned} \quad \left. \vphantom{\begin{aligned} Y_{IC_4} &= \frac{H_{IC_4-H_2O}}{P_T} X_{IC_4} \\ Y_{H_2O} &= \frac{P_{SAT H_2O}}{P_T} X_{H_2O} \end{aligned}} \right\} \text{EQUILIBRIUM RELATIONS}$$

$$\begin{aligned} Y_{CO_2} + Y_{IC_4} + Y_{H_2O} &= 1 \\ X_{CO_2} + X_{IC_4} + X_{H_2O} &= 1 \end{aligned} \quad \left. \vphantom{\begin{aligned} Y_{CO_2} + Y_{IC_4} + Y_{H_2O} &= 1 \\ X_{CO_2} + X_{IC_4} + X_{H_2O} &= 1 \end{aligned}} \right\} \text{BY DEFINITION}$$

Using algebra, the following solution for each unknown is found:

$$Z_{CO_2} = Y_{CO_2} \frac{V}{F} + X_{CO_2} \left(1 - \frac{V}{F}\right) = X_{CO_2} \left[\left(\frac{H_{CO_2-H_2O}}{P_T} - 1 \right) \frac{V}{F} + 1 \right]$$

$$Z_{IC_4} = X_{IC_4} \left[\left(\frac{H_{IC_4-H_2O}}{P_T} - 1 \right) \frac{V}{F} + 1 \right]$$

$$Z_{H_2O} = X_{H_2O} \left[\left(\frac{P_{SAT H_2O}}{P_T} - 1 \right) \frac{V}{F} + 1 \right]$$

$$\begin{aligned} X_{CO_2} \frac{H_{CO_2-H_2O}}{P_T} + X_{IC_4} \frac{H_{IC_4-H_2O}}{P_T} + X_{H_2O} \frac{P_{SAT H_2O}}{P_T} &= \\ X_{CO_2} + X_{IC_4} + X_{H_2O} \end{aligned}$$

$$X_{CO_2} \left(\frac{H_{CO_2-H_2O}}{P_T} - 1 \right) + X_{IC_4} \left(\frac{H_{IC_4-H_2O}}{P_T} - 1 \right) + X_{H_2O} \left(\frac{P_{SAT H_2O}}{P_T} - 1 \right) = 0$$

$$\frac{Z_{CO_2} \left(\frac{H_{CO_2-H_2O}}{P_T} - 1 \right)}{\frac{V}{F} \left(\frac{H_{CO_2-H_2O}}{P_T} - 1 \right) + 1} + \frac{Z_{IC_4} \left(\frac{H_{IC_4-H_2O}}{P_T} - 1 \right)}{\frac{V}{F} \left(\frac{H_{IC_4-H_2O}}{P_T} - 1 \right) + 1} + \frac{Z_{H_2O} \left(\frac{P_{SAT H_2O}}{P_T} - 1 \right)}{\frac{V}{F} \left(\frac{P_{SAT H_2O}}{P_T} - 1 \right) + 1} = 0$$

$$A = Z_{\text{CO}_2} \left(\frac{P_T}{H_{\text{IC}_4} - P_T} + \frac{P_T}{P_{\text{SATH}_2\text{O}} - P_T} \right) + Z_{\text{IC}_4} \left(\frac{P_T}{H_{\text{CO}_2} - P_T} + \frac{P_T}{P_{\text{SATH}_2\text{O}} - P_T} \right) + Z_{\text{H}_2\text{O}} \left(\frac{P_T}{H_{\text{CO}_2} - P_T} + \frac{P_T}{H_{\text{IC}_4} - P_T} \right)$$

$$B = \frac{Z_{\text{CO}_2} P_T^2}{(H_{\text{IC}_4} - P_T)(P_{\text{SATH}_2\text{O}} - P_T)} + \frac{Z_{\text{IC}_4} P_T^2}{(H_{\text{CO}_2} - P_T)(P_{\text{SATH}_2\text{O}} - P_T)} + \frac{Z_{\text{H}_2\text{O}} P_T^2}{(H_{\text{CO}_2} - P_T)(H_{\text{IC}_4} - P_T)}$$

$$\left(\frac{V}{F} \right)^2 + A \left(\frac{V}{F} \right) + B = 0$$

$$\frac{V}{F} = \frac{A}{2} + \sqrt{\frac{A^2}{4} - B}$$

$$X_{\text{CO}_2} = \frac{Z_{\text{CO}_2}}{\left[\left(\frac{H_{\text{CO}_2}}{P_T} - 1 \right) \frac{V}{F} + 1 \right]}$$

$$X_{\text{IC}_4} = \frac{Z_{\text{IC}_4}}{\left[\left(\frac{H_{\text{IC}_4}}{P_T} - 1 \right) \frac{V}{F} + 1 \right]}$$

$$X_{\text{H}_2\text{O}} = 1 - X_{\text{CO}_2} - X_{\text{IC}_4}$$

$$Y_{\text{CO}_2} = \left(\frac{H_{\text{CO}_2}}{P_T} \right) X_{\text{CO}_2}$$

$$Y_{IC4} = \left(H_{IC4} / P_T \right) X_{IC4}$$

$$Y_{HLD} = 1 - Y_{OZ} - Y_{IC4}$$

$$L/F = 1 - V/F$$

APPENDIX B

THEORETICAL MODEL OF THE RECOVERY CONDENSER

Two essentially immiscible liquid phases are present in the recovery condenser, H_2O and IC_4 . A vapor phase is common to both liquid phases. If composition of the vapor in the condenser feed stream and condensing temperature and pressure are known, the equilibrium phase concentrations in the liquid and vent stream can then be determined.

FIG. 2

From the material balance the following set of equations can be derived:

$$Z_{CO_2} = Y_{CO_2} \frac{V}{F} + X_{CO_2-H_2O} \frac{L_{H_2O}}{F} + X_{CO_2-IC_4} \frac{L_{IC_4}}{F}$$

$$Z_{IC_4} = Y_{IC_4} \frac{V}{F} + X_{IC_4} \frac{L_{IC_4}}{F}$$

$$Z_{H_2O} = Y_{H_2O} \frac{V}{F} + X_{H_2O} \frac{L_{H_2O}}{F}$$

The following set of equations comes from the equilibrium relations:

$$Y_{IC_4} = \left(\frac{P_{SAT\ IC_4}}{P_C} \right) X_{IC_4}$$

$$Y_{H_2O} = \left(\frac{P_{SAT\ H_2O}}{P_C} \right) X_{H_2O}$$

$$Y_{CO_2} = \left(\frac{H_{CO_2-H_2O}}{P_C} \right) X_{CO_2-H_2O}$$

$$Y_{CO_2} = \left(\frac{H_{IC_4-H_2O}}{P_C} \right) X_{CO_2-IC_4}$$

By definition the following equations are true:

$$Y_{CO_2} + Y_{IC_4} + Y_{H_2O} = 1$$

$$X_{CO_2-IC_4} + X_{IC_4} = 1$$

$$X_{CO_2-H_2O} + X_{H_2O} = 1$$

Now by algebraic manipulation, a solution for each unknown can be found:

$$Y_{CO_2} = 1 - \frac{P_{IC_4}}{P_C} X_{IC_4} - \frac{P_{SATH_2O}}{P_C} X_{H_2O}$$

$$= 1 - \frac{P_{IC_4}}{P_C} \left(1 - \frac{Y_{CO_2} P_C}{H_{CO_2-IC_4}} \right) - \frac{P_{SATH_2O}}{P_C} \left(1 - \frac{Y_{CO_2} P_C}{H_{CO_2-H_2O}} \right)$$

$$= 1 - \frac{P_{IC_4}}{P_C} - \frac{P_{SATH_2O}}{P_C} + Y_{CO_2} \left(\frac{P_{SATIC_4}}{H_{CO_2-IC_4}} + \frac{P_{SATH_2O}}{H_{CO_2-H_2O}} \right)$$

$$\therefore Y_{CO_2} = \frac{1 - \frac{P_{SATIC_4}}{P_C} - \frac{P_{SATH_2O}}{P_C}}{1 - \frac{P_{SATIC_4}}{H_{CO_2-IC_4}} - \frac{P_{SATH_2O}}{H_{CO_2-H_2O}}}$$

$$Z_{CO_2} = Y_{CO_2} \frac{V}{F} + \frac{Y_{CO_2} P_C}{H_{CO_2-H_2O}} \left(\frac{Z_{H_2O} - \frac{P_{SAT H_2O}}{P_C} \left(1 - \frac{Y_{CO_2} P_C}{H_{CO_2-H_2O}} \right) \frac{V}{F}}{1 - \frac{Y_{CO_2} P_C}{H_{CO_2-H_2O}}} \right) +$$

$$\frac{Y_{CO_2} P_C}{H_{CO_2-IC_4}} \left(\frac{Z_{IC_4} - \frac{P_{SAT IC_4}}{P_C} \left(1 - \frac{Y_{CO_2} P_C}{H_{CO_2-IC_4}} \right) \frac{V}{F}}{1 - \frac{Y_{CO_2} P_C}{H_{CO_2-IC_4}}} \right)$$

$$= Y_{CO_2} \frac{V}{F} + Y_{CO_2} \left(\frac{P_C Z_{H_2O}}{H_{CO_2-H_2O} - Y_{CO_2} P_C} \right) - Y_{CO_2} \frac{V}{F} \left(\frac{P_{SAT H_2O}}{H_{CO_2-H_2O}} \right) +$$

$$Y_{CO_2} \left(\frac{P_C Z_{IC_4}}{H_{CO_2-H_2O} - Y_{CO_2} P_C} \right) - Y_{CO_2} \frac{V}{F} \left(\frac{P_{SAT IC_4}}{H_{CO_2-IC_4}} \right)$$

$$\frac{V}{F} = \frac{\frac{Z_{CO_2}}{Y_{CO_2}} - \frac{Z_{IC_4} P_C}{H_{CO_2-IC_4} Y_{CO_2} P_C} - \frac{Z_{H_2O} P_C}{H_{CO_2-H_2O} Y_{CO_2} P_C}}{1 - \frac{P_{SAT IC_4}}{H_{CO_2-IC_4}} - \frac{P_{SAT H_2O}}{H_{CO_2-H_2O}}}$$

If recovery condenser pressure increases vent stream (or V/F ratio) decreases. When the vent stream (or V/F ratio) is equal to zero, further increases of the condenser pressure is impossible, therefore condenser pressure is equal to the maximum pressure P_{Cmax} .

Assume $P_C = P_{Cmax}$ and $V/F = 0$: Then recovery condenser pressure can be found by algebraic solution:

$$Z_{CO_2} = X_{CO_2-H_2O} \frac{L_{H_2O}}{F} + X_{CO_2-IC_4} \frac{L_{IC_4}}{F}$$

$$Z_{IC_4} = X_{IC_4} \frac{L_{IC_4}}{F}$$

$$Z_{H_2O} = X_{H_2O} \frac{L_{H_2O}}{F}$$

$$X_{CO_2-H_2O} + X_{H_2O} = 1$$

$$X_{CO_2-IC_4} + X_{IC_4} = 1$$

$$Y_{CO_2} = \left(\frac{H_{CO_2-IC_4}}{P_{Cmax}} \right) X_{CO_2-IC_4}$$

$$Y_{CO_2} = \left(\frac{H_{CO_2-H_2O}}{P_{Cmax}} \right) X_{CO_2-H_2O}$$

$$Y_{IC_4} = \left(\frac{P_{SAT IC_4}}{P_{Cmax}} \right) X_{IC_4}$$

$$Y_{H_2O} = \left(\frac{P_{SAT H_2O}}{P_{C MAX}} \right) X_{H_2O}$$

$$Y_{CO_2} + Y_{IC_4} + Y_{H_2O} = 1$$

$$Z_{CO_2} = X_{CO_2-H_2O} \left(\frac{Z_{CO_2}}{X_{H_2O}} \right) + X_{CO_2-IC_4} \left(\frac{Z_{IC_4}}{X_{IC_4}} \right)$$

$$= \frac{Y_{CO_2} \left(\frac{P_{C MAX}}{H_{CO_2-H_2O}} \right) Z_{H_2O}}{1 - \frac{Y_{CO_2} P_{C MAX}}{H_{CO_2-H_2O}}} + \frac{Y_{CO_2} \left(\frac{P_{C MAX}}{H_{CO_2-IC_4}} \right) Z_{IC_4}}{1 - \frac{Y_{CO_2} P_{C MAX}}{H_{CO_2-IC_4}}}$$

$$= Y_{CO_2} \left(\frac{P_{C MAX} Z_{H_2O}}{H_{CO_2-H_2O} - Y_{CO_2} P_{C MAX}} \right) + Y_{CO_2} \left(\frac{P_{C MAX} Z_{IC_4}}{H_{CO_2-IC_4} - Y_{CO_2} P_{C MAX}} \right)$$

$$Y_{CO_2} P_{C MAX} = \frac{P_{C MAX} - P_{SAT IC_4} - P_{SAT H_2O}}{1 - \frac{P_{SAT IC_4}}{H_{CO_2-IC_4}} - \frac{P_{SAT H_2O}}{H_{CO_2-H_2O}}}$$

$$Z_{CO_2} H_{CO_2-H_2O} H_{CO_2-IC_4} - Z_{CO_2} (Y_{CO_2} P_{C MAX}) H_{CO_2-IC_4} -$$

$$Z_{CO_2} (Y_{CO_2} P_{C MAX}) H_{CO_2-H_2O} + Z_{CO_2} (Y_{CO_2} P_C)^2 + Z_{H_2O} (Y_{CO_2} P_{C MAX})^2 -$$

$$Z_{H_2O} (Y_{CO_2} P_{C MAX}) H_{CO_2-IC_4} - Z_{IC_4} (Y_{CO_2} P_{C MAX}) H_{CO_2-H_2O} + Z_{IC_4} (Y_{CO_2} P_C)^2 = 0$$

$$(Y_{CO_2} P_C)^2 + (Z_{CO_2} H_{CO_2-H_2O} H_{CO_2-IC_4}) -$$

$$(Z_{CO_2} H_{CO_2-IC_4} + Z_{CO_2} H_{CO_2-H_2O} + Z_{IC_4} H_{CO_2-H_2O} + Z_{H_2O} H_{CO_2-IC_4})(Y_{CO_2} P_C) = 0$$

$$A = \frac{1}{2} [Z_{CO_2} (H_{CO_2-IC_4} + H_{CO_2-H_2O}) + Z_{IC_4} H_{CO_2-H_2O} + Z_{H_2O} H_{CO_2-IC_4}]$$

$$Y_{CO_2} P_{C_{MAX}} = A - \sqrt{A^2 - Z_{CO_2} H_{CO_2-IC_4} H_{CO_2-H_2O}}$$

$$P_{C_{MAX}} = (Y_{CO_2} P_{C_{MAX}}) \left(1 - \frac{P_{SAT IC_4}}{H_{CO_2-IC_4}} - \frac{P_{SAT H_2O}}{H_{CO_2-H_2O}} \right) + P_{SAT IC_4} + P_{SAT H_2O}$$