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**THE SUPPLY OF CARBON DIOXIDE FOR ENHANCED OIL RECOVERY**

Final Report, October 15, 1976—September 1, 1977

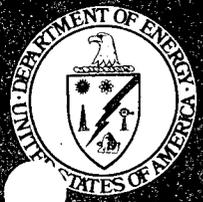
William M. Rump  
Mike Hare  
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December 1977  
(TIC Issuance Date)

Work Performed Under Contract No. EX-76-C-01-2515

Pullman Kellogg  
Houston, Texas

**MASTER**



**U. S. DEPARTMENT OF ENERGY**

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Final Report For The  
Period October 15, 1976 – September 1, 1977

William M. Rump  
Mike Hare  
Raymond E. Porter

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## TABLE OF CONTENTS

	<u>Page No.</u>
List of Abbreviations	iii
List of Figures	iv
List of Tables	v
Abstract	vi
I. <u>SUMMARY</u>	1
II. <u>INTRODUCTION</u>	
A. Enhanced Oil Recovery - Background	4
B. Carbon Dioxide Miscible Flooding for EOR	5
C. Scope of this Report	7
D. Definition of Cases	8
III. <u>CARBON DIOXIDE SUPPLY SITUATION</u>	
A. Introduction	11
B. Above-Ground Sources	14
C. Naturally Occurring Carbon Dioxide Wells	23
IV. <u>CANDIDATE OIL FIELDS/RESERVOIRS</u>	26
V. <u>CARBON DIOXIDE FROM HIGH PURITY PROCESS VENTS</u>	
A. Introduction	30
B. Proposed System for South Louisiana	31
C. Economic Summary	36
VI. <u>CARBON DIOXIDE FROM LOW PURITY STACK GASES</u>	
A. Introduction	39
B. Process Description	41
C. Process Flow Diagram	48
D. Material Balance	50
E. Chemical, Utility, Economic Summaries	52
VII. <u>CARBON DIOXIDE FROM NATURALLY OCCURRING SOURCES</u>	
A. Introduction	58
B. Case I	
1. Process Description	60
2. Process Flow Diagram	62
3. Material Balance	64
4. Chemical, Utility, Economic Summaries	66

TABLE OF CONTENTS (CONTD.)

	<u>Page No.</u>
VII. <u>CARBON DIOXIDE FROM NATURALLY OCCURRING SOURCES</u> (CONTD.)	
C. Case III	
1. Process Description	70
2. Process Flow Diagram	74
3. Material Balance	76
4. Chemical, Utility, Economic Summaries	78
D. Case IV	
1. Process Description	83
2. Process Flow Diagram	92
3. Material Balance	94
4. Chemical, Utility, Economic Summaries	96
VIII. <u>CONCLUSIONS AND RECOMMENDATIONS</u>	
A. Conclusions	103
B. Recommendations	107
IX. <u>APPENDIX</u>	
A. Physical and Equilibrium Properties of Carbon Dioxide	109
B. U. S. Bureau of Mines Data for Naturally Occurring Carbon Dioxide	113
C. Candidate Carbon Dioxide Enhanced Oil Recovery Fields	114
X. <u>BIBLIOGRAPHY</u>	119

## LIST OF ABBREVIATIONS

B - Billion  
BBL - Barrel (42 U.S. Gal.)  
Cp - Heat capacity at constant pressure  
DCFROR - Discounted cash flow rate of return  
EOR - Enhanced oil recovery  
ERDA - U.S. Energy Research and Development Administration  
°F - Degrees Fahrenheit  
Gal. - U.S. Gallon  
GPM - Gallons per minute  
Gr - Grains  
GURC - Gulf Universities Research Consortium  
KWH - Kilowatt-hour  
lb - Pound  
LB MOL - Pound mole  
LHV - Lower Heating Valve  
M - Thousand  
MM - Million  
MEA - Monoethanol amine  
Mega - 10  
NGL - Natural Gas Liquids  
PPM - Parts per million; V - by volume; W - by weight  
PSI - Pounds per square inch; A - absolute; G - gauge (base 14.7 psia)  
SACROC - Scurry Area Canyon Reef Operations Committee  
SCF - Standard cubic feet (60°F, 14.7 psia)  
SCFD - Standard cubic feet per stream day  
SNG - Synthetic (or substitute) natural gas  
STPD - Short tons per day  
TEG - Triethylene glycol  
Wt. - Weight  
> - Greater than  
< - Less than

## LIST OF FIGURES

	<u>Page No.</u>
III-1 Expected Oil Recovery and CO <sub>2</sub> Consumption by CO <sub>2</sub> EOR Techniques	13
III-2 Aggregate CO <sub>2</sub> Supply from Aboveground Sources	16
III-3 CO <sub>2</sub> Available from Power Plant Stack Gases and Cement Plants	18
III-4 CO <sub>2</sub> from Process Vents	22
III-5 Areas Known to have Naturally Occurring CO <sub>2</sub> Wells	24
IV-1 Locations of CO <sub>2</sub> Enhanced Oil Recovery Candidate Fields	28
V-1 Proposed CO <sub>2</sub> Pipeline from Process Vents	33
V-2 Schematic of Pipeline from Process Vents Showing Line Sizes, Lengths, and Feed Rates	34
VI-1 Continuous MEA Recovery with Sodium Carbonate	45
VI-2 125 MMSCFD CO <sub>2</sub> from Flue Gas (Process Flow Dwg. P-4636-D)	49
VII-1 125 MMSCFD CO <sub>2</sub> from Natural Sources - Case I 98% CO <sub>2</sub> , 2% CH <sub>4</sub> (Process Flow Dwg. P-825-A)	63
VII-2 125 MMSCFD CO <sub>2</sub> from Natural Sources - Case III 50% CO <sub>2</sub> , 50% CH <sub>4</sub> (Process Flow Dwg. P-4693-D)	75
VII-3 Block Flow Diagram Stretford Process	91
VII-4 125 MMSCFD CO <sub>2</sub> from Natural Sources - Case IV 48% CO <sub>2</sub> , 50% CH <sub>4</sub> , 2% H <sub>2</sub> S (Process Flow Dwg. P4691-D)	93
IX-1 Carbon Dioxide Phase Diagram	112

LIST OF TABLES

	<u>Page No.</u>
I-1 Investment and Cost Summary	3
III-1 Aboveground Source of CO <sub>2</sub>	15
III-2 CO <sub>2</sub> Sources from Process Vents	20
V-1 Economic Summary - CO <sub>2</sub> from Ammonia Plant Vents	37
VI-1 Chemicals Summary - CO <sub>2</sub> from Plant Flue Gases	53
VI-2 Utility Summary - CO <sub>2</sub> from Power Plant Flue Gases	54
VI-3 Economic Summary - CO <sub>2</sub> from Power Plant Flue Gases	55
VII-1 Chemicals Summary for Recovery of CO <sub>2</sub> from Natural Sources Containing 98% CO <sub>2</sub> , 2% Hydrocarbon	67
VII-2 Utility Summary for Recovery of CO <sub>2</sub> from Natural Sources Containing 98% CO <sub>2</sub> , 2% Hydrocarbon	68
VII-3 Economic Summary - CO <sub>2</sub> from Natural Sources Containing 98% CO <sub>2</sub> , 2% Hydrocarbon	69
VII-4 Chemicals Summary for Recovery of Carbon Dioxide from Natural Sources Containing 50% CO <sub>2</sub> , 50% Hydrocarbon	79
VII-5 Utility Summary for Recovery of Carbon Dioxide from Natural Sources Containing 50% CO <sub>2</sub> , 50% Hydrocarbon	80
VII-6 Economic Summary - Recovery of CO <sub>2</sub> from Natural Sources Containing 50% CO <sub>2</sub> , 50% Hydrocarbon	81
VII-7 Chemicals Summary for Recovery of CO <sub>2</sub> from Natural Sources Containing 50% Hydrocarbon, 48% CO <sub>2</sub> , 2% H <sub>2</sub> S	97
VII-8 Utility Summary for Recovery of CO <sub>2</sub> from Natural Sources Containing 50% Hydrocarbon, 48% CO <sub>2</sub> , 2% H <sub>2</sub> S	98
VII-9 Economic Summary - Recovery of CO <sub>2</sub> from Natural Sources Containing 50% Hydrocarbon, 48% CO <sub>2</sub> , 2% H <sub>2</sub> S	99
VIII-1 Investment and Cost Summary	106
IX-1 Candidate Fields with Reservoirs that Meet GURC Critical Parameters for Miscible CO <sub>2</sub>	115
IX-2 Carbon Dioxide Miscible Flooding - Candidate Fields/ Reservoirs Located in Producing Trends or Areas	118

## ABSTRACT

Results are presented from a study by Pullman Kellogg, with assistance from Gulf Universities Research Consortium (GURC), of the carbon dioxide supply situation for miscible flooding operations to enhance oil recovery.

Candidate oil reservoirs have been identified, and the carbon dioxide requirements and the potential recoverable oil for some of these have been estimated.

A survey of carbon dioxide sources has been conducted within the geographic areas where candidate oil reservoirs exist. Sources considered were both high and low quality gases from combustion vents, chemical process stacks, and naturally occurring gas deposits.

The survey shows more than enough carbon dioxide is available from above-ground sources alone to meet expected demands.

Systems to purify and deliver the carbon dioxide have been designed and the costs of the delivered carbon dioxide estimated. Lowest cost is carbon dioxide from natural source with credit for by-product methane.

A more comprehensive survey of above-ground and natural sources is recommended.

## I. SUMMARY

This report concludes the first phase of a study by Pullman Kellogg, assisted by Gulf Universities Research Consortium, of enhanced oil recovery through carbon dioxide miscible flooding. During this phase of the study, the location of major above-ground and some naturally occurring sources of carbon dioxide have been identified within a thirteen state region known to have fields/reservoirs suitable for EOR by carbon dioxide miscible flooding (information presented for natural sources is limited by incomplete geological data and by the proprietary nature of ownership). In addition, separation and transportation cost for several hypothetical cases including both above-ground and natural sources were developed.

Time and funding has limited this phase of study to a broad scope orientation type of report. For example, sensitivity studies are not included for the affect on cost of carbon dioxide purity or pipeline distances, nor is any attempt made to match carbon dioxide sources to the best candidate fields/reservoirs. It was also not possible during this phase of study to include certain portions of the cost picture such as cost of purchasing carbon dioxide or drilling wells for natural sources. It is expected that a report in greater depth will be concluded within twelve months during a second phase of study.

Although limited in scope, several conclusions can be drawn from this phase of study. For example, above-ground sources of carbon dioxide in the thirteen state region (estimated at 33 billion SCFD presently) are sufficient to satisfy the projected future demand for EOR applications even without discovery of substantial new sources of natural supply. It also appears that each state surveyed could be self supporting in carbon dioxide from above-ground sources; however, much of this carbon dioxide (roughly 80%) is presently available as a by-product from cement plant or power plant stack gases and is of low quality. Recovery of carbon dioxide from these abundant sources will thus be expensive due to high separation costs, which could prevent extensive use of these abundant sources.

The highest quality above-ground sources of carbon dioxide are process vents from fertilizer and chemical plants. Presently, uncommitted by-product carbon dioxide from ammonia manufacture (typically 98% CO<sub>2</sub>) is the most promising process vent source since about 70 percent is located in areas of high potential for EOR by CO<sub>2</sub> miscible flood - namely, Louisiana, South Texas, and Oklahoma. By-product carbon dioxide from Synthetic Natural Gas plants (SNG) has great potential as a future source of carbon dioxide for EOR especially if a significant amount of SNG is produced by gasification of coal. The amount of high purity carbon dioxide from process vents is expected to fall short of total requirements if EOR by carbon dioxide miscible flood proves to be commercially successful.

Natural gas wells rich in carbon dioxide have perhaps the greatest potential as a future source of carbon dioxide for EOR; however, the exact quantities available are not known since no exhaustive survey of this source has been made. Areas believed to have great potential for high purity naturally occurring carbon dioxide wells are the Four Corners area (Utah, Colorado, Arizona, New Mexico), Southeast Colorado, Northeast New Mexico, and Central Mississippi. Based on historical data for the natural gas industry, it is generally concluded that natural sources alone (like process vents) cannot supply all the carbon dioxide requirements for EOR efforts if carbon dioxide miscible flooding is commercially successful.

Based on cost data developed during this phase of study (Table I-1), the lowest cost carbon dioxide would be from a natural source containing by-product natural gas to offset the cost of producing the carbon dioxide. Realistically, it seems that the natural sources studied in this report would most likely be developed independently of EOR efforts for the natural gas content alone. Thus the carbon dioxide rather than the natural gas would be available as by-product. The cost of the carbon dioxide in this case would depend on many considerations including to what extent the cost of developing the natural gas source is charged against the carbon dioxide.

Above-ground sources, especially from stack gases such as power plants will be expensive. In the latter case, close proximity to the candidate field/reservoir will be highly desirable for utilization of this abundant source.

TABLE I-1

Investment and Cost Summary

<u>Carbon Dioxide Source Aboveground</u>	<u>Carbon Dioxide Capacity MMSCFD</u>	<u>Investment MM\$ U.S.</u>	<u>Cost \$/MSCF CO<sub>2</sub></u>	
Ammonia Plant Vents	184	Transmission System	134.8	1.15
Power Plant Fluegas	125	Recovery Plant	34.1	1.04
		Transmission System	19.2	0.21
		Total	53.3	1.25
<u>Natural Sources</u>				
Case I (98% CO <sub>2</sub> -2% CH <sub>4</sub> )	125	Transmission System	62.9	0.72
Case III (50% CO <sub>2</sub> -50% CH <sub>4</sub> )	125	Recovery Plant	11.4	-1.62
		Transmission System	67.9	0.87
		Total	79.3	-0.75
Case IV (48% CO <sub>2</sub> -50% CH <sub>4</sub> -2% H <sub>2</sub> S)	125	Recovery Plant	48.0	-1.19
		Transmission System	68.3	0.89
		Total	116.3	-0.30

Notes -

- U.S. Gulf Coast Location is assumed
- Investment Costs 2nd Quarter 1977
- All investment + 25%
- Transmission systems pipelines
  - Ammonia Plant Vents - 145 mile trunkline
  - Power Plant - 25 mile
  - Natural Sources - 100 mile

## II. INTRODUCTION

### A. ENHANCED OIL RECOVERY - BACKGROUND

By 1975, the petroleum industry in the United States had discovered an estimated 418 billion barrels of domestic oil. Of this amount, approximately 200 billion barrels - roughly one half - was discovered by the mid 1930's, and about 75 percent was discovered by 1950. Production from these proven reserves as of 1975 totaled about 109 billion barrels, and it is estimated that current recovery techniques will add an additional 28 billion barrels of production. Recovery from current proven reserves using existing techniques will average about 33 percent.[1,2]

As recently as 1962, the expected recovery efficiency from proven domestic reserves was about 28 percent. The increases in expected recovery efficiency since that time can be attributed to the application of secondary recovery techniques (as compared to primary recovery using natural reservoir energy).[2]

Until recently, secondary recovery techniques have focused on injection of water, the so called waterflood, to recover additional oil from the reservoir. Waterflood is still the predominant technique used in secondary oil recovery, and about half the current domestic crude oil is produced by this technique.

Natural gas has sometimes been injected into reservoirs to maintain reservoir pressure, but this technique, never widely practiced, is only rarely used now because of inherent inefficiencies and high gas costs.

In view of declining domestic discoveries and rising demand, the United States oil industry in recent years has focused increasing attention on developing new methods of improving oil recovery efficiency. These methods generally called enhanced oil recovery (EOR) involve techniques somewhat more advanced than those used previously. This higher degree of sophistication is required since existing techniques have already recovered the oil which is easily recovered.

Methods for EOR under development in recent years employ a variety of techniques to increase oil recovery efficiency. These include so called "thermal" methods in which steam or air to support combustion is injected into the reservoir (generally used on heavy oils), chemical flooding in which various polymers or surfactants are injected, and miscible flooding with carbon dioxide injection.

Thermal processes are presently the most developed of the EOR methods. (It is estimated that 200 thousand barrels per day are presently recovered using thermal techniques.) Carbon dioxide miscible flooding and chemical methods, despite continuing research and field testing, have yet to achieve widespread commercial use.

## B. CARBON DIOXIDE MISCIBLE FLOODING FOR EOR

The concept of injecting gas into oil reservoirs to improve recovery is not new. In the traditional manner (referred to here as an immiscible process) the injected gas delays pressure decline, and helps displace the oil to the producing wells.

A concept which has gained wider acceptance in recent years is the so called miscible flooding technique for EOR. In a miscible displacement process, the fluid injected into the reservoir acts as a solvent for the oil, and under the conditions of miscibility essentially eliminates the interfaces and capillary forces between the oil and the fluid.

Various hydrocarbon gases (and liquids) have been used as miscible and immiscible agents in the past; however, their use has been essentially discontinued due to the rising costs for hydrocarbons in relation to the additional oil recovered.

A favorable alternate to hydrocarbons as miscible agents is carbon dioxide. Upon initial injection the carbon dioxide is not miscible with the oil. Because of its ability to vaporize hydrocarbon components in the oil, a miscible mixture between the reservoir oil and the carbon dioxide may be formed. In addition, the dissolved carbon dioxide volumetrically expands the oil and reduces its viscosity, which allows the oil to flow more readily and can result in better recovery.

Carbon dioxide miscible flooding is still considered an experimental process, and its effectiveness as an EOR process remains largely unproven. For example, little is known about which methods of practicing carbon dioxide miscible flooding are most effective, and a great deal of variation exists among the proposed methods of application. Some designs call for alternating carbon dioxide with water injection, while others involve use of an additional gas such as methane or flue gas in combination with carbon dioxide flooding. Also highly uncertain at present is the amount of incremental oil recovery which can be obtained from a given volume of carbon dioxide injected. Identification of reservoirs which are potential candidates for carbon dioxide miscible flooding is yet another area of uncertainty.

Little is known about the effect on the process of previous recovery techniques or individual reservoir properties such as rock formation or reservoir temperature.

In addition to questions relating to technical aspects of the process, the cost and availability of potential carbon dioxide supplies are important considerations affecting the potential application of carbon dioxide miscible flood for EOR. Information in these critical areas is somewhat uncertain at present.

Despite these uncertainties, the potential for oil recovery by carbon dioxide miscible flooding is large. Depending on the economic parameters one chooses, estimates range up to 10 billion barrels ultimate recovery by this process.[3] A best guess for the amount of oil expected to be recovered by carbon dioxide miscible flood is in the range of four billion barrels. Whether such production will ever be realized depends to a great extent on whether sufficient low cost carbon dioxide can be found.

Although, still considered an experimental process, carbon dioxide miscible flooding for EOR is being tried on a commercial scale. Beginning in early 1972, the SACROC unit in Scurry County, Texas started injection of carbon dioxide in the Canyon Reef field of West Texas. The carbon dioxide miscible flood in combination with waterflood was selected after study of various flooding techniques. These studies showed that a water driven carbon dioxide miscible flood would yield the highest increased recovery, and was potentially the most economically attractive.

Carbon dioxide for the SACROC project is obtained from natural gas wells located some 200 miles south of the Canyon Reef field. After purification the carbon dioxide is transported by pipeline to the field.<sup>1</sup> It is estimated that an additional 100-200 million barrels of oil will be produced from the Canyon Reef field by the carbon dioxide miscible flood.

A number of additional tests of carbon dioxide miscible flooding are currently underway. These tests are located primarily in West Texas, South Louisiana, Mississippi, and West Virginia.

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<sup>1</sup>Part of the carbon dioxide is used for a carbon dioxide flood at the North Crossett field located along the pipeline.

### C. SCOPE OF THIS REPORT

This report is the result of efforts by Pullman Kellogg, with assistance from Gulf Universities Research Consortium (GURC), to study for the United States Energy Research and Development Administration (ERDA) the availability and cost of supplying carbon dioxide for miscible flooding operations.

This study, conducted under Contract EX-76-C-01-2515, began with the identification of candidate oil reservoirs thought to be suitable for EOR by use of carbon dioxide miscible flooding techniques. These oil reservoirs, located in thirteen states, established the approximate geographic locations where carbon dioxide is needed. Reservoirs in the thirteen states were selected by GURC on the basis of criteria pertaining to rock and fluid properties and reservoir conditions which make them candidates for EOR using carbon dioxide miscible flooding. Further refinement of this initial screening by GURC for some of these reservoirs has resulted in estimates of the potential recoverable oil and the quantity of carbon dioxide required for miscible flooding.

Within this geographic area all above ground sources of carbon dioxide have been determined and classified according to source and available quantities. Underground sources of naturally occurring carbon dioxide are identified only as to approximate geographic location within the thirteen state region. Development of additional information pertaining to natural sources of carbon dioxide is left to future study, and is beyond the scope of this report.

One of the aims of this study is to determine a cost for carbon dioxide delivered to the operator of the oil reservoir. Portions of this cost, however, cannot be developed within the confines of this study. For example, the costs of purchasing carbon dioxide from the owner or drilling gas wells for naturally occurring carbon dioxide are not established. Drilling costs per unit of carbon dioxide are a function of many factors such as depth, purity and location of the deposit. These costs will be established during a second phase of this investigation (See Summary and Recommendations sections). As an alternate approach, systems have been hypothesized for the delivery of carbon dioxide from selected sources to candidate reservoirs and the costs, including recovery plants and transportation systems, have been developed for the cases selected for study (see definition of cases).

In addition to these tasks, this study includes an investigation of sources of physical and equilibrium properties of carbon dioxide. Results of this investigation are included in the appendix to this report.

D. DEFINITION OF CASES [4]

The cases selected for study in this report include the following sources of carbon dioxide:

1. Power plant flue gas
2. Ammonia plant vent gases
3. Naturally occurring gas deposits

During the course of this study further definition was developed for each of the above cases. For example, the power plant source has been defined as flue gas from a coal-fired plant. A coal fired power plant was selected as this seems most realistic in light of future energy policies.

The ammonia plant process vent case was selected early in the study after investigation of carbon dioxide sources and GURC information on candidate reservoirs. This investigation indicated that for the South Louisiana area, ammonia plant process vents could probably supply sufficient carbon dioxide for an EOR project. It was also noted that the South Pass area, an area containing several fields with reservoirs satisfying the GURC critical parameters for potential carbon dioxide miscible flood EOR applications, was located nearby.

Hypothetical cases are used to evaluate naturally occurring sources of carbon dioxide. This approach is adopted because detailed information on natural carbon dioxide sources is not widely available and in many cases still under investigation. These cases consist of a high quality source - 98 percent carbon dioxide, and low quality source - 50 percent carbon dioxide. For each of these, possible contamination of the source is allowed for by assuming a two percent hydrogen sulfide level.

Assumptions

In developing costs for this study, certain ground rules and assumptions have to be made. Primary to these are that this study is concerned with commercial installations, rather than pilot installations. Commercial installations are defined here as those requiring at least 100 million standard cubic feet per day of carbon dioxide.

In keeping with the definition of commercial installations adopted for this study, systems are designed for the delivery of 125 MM SCFD of carbon dioxide from the power plant and naturally occurring sources. As a result of the study of carbon dioxide available from ammonia plant vents in the South Louisiana area, this system is designed to deliver 184 MMSCFD of carbon dioxide.

An equally important assumption is the quality of carbon dioxide required for miscible flooding. Although much discussion currently exists about this topic, the quality selected is a nominal 98 percent. For sources containing hydrogen sulfide, this is reduced to 1/4 grain H<sub>2</sub>S per 100 standard cubic feet of carbon dioxide produced.

Assumptions have been made to develop transportation costs. Lacking specific source-candidate reservoir locations, arbitrary pipeline lengths have been adopted for each case (except for process vents case) on the basis of best guesses of possible economic length.<sup>1</sup> The carbon dioxide is assumed to be delivered to the candidate reservoir at 2,000 psig, and a 200 psig pressure loss has been assumed for all pipelines. For the naturally occurring sources, the gas is assumed to be available at 250 psig and 75°F, water saturated.

---

<sup>1</sup>See Notes, Table I-1, for a summary of pipeline distances.

NOTES FOR SECTION II - INTRODUCTION

- [1] Enhanced Oil Recovery, National Petroleum Council, Dec. 1976, pg. 11.
- [2] Doscher, T. M., Wise, F. A. "Enhanced Crude Oil Recovery Potential - An Estimate," Journal of Petroleum Technology, May 1976, pp. 578-579.
- [3] Enhanced Oil Recovery, National Petroleum Council, Dec. 1976, pp. 33-38.
- [4] Definition of cases and assumptions adopted at progress meeting in Houston between Kellogg, GURC, and ERDA representatives - Jan. 26, 1977.

### III. CARBON DIOXIDE SUPPLY SITUATION

#### A. INTRODUCTION

An assumption fundamental to the concept of enhanced oil recovery by carbon dioxide miscible flooding is the availability of sufficient low cost carbon dioxide to make the recovery technique economically viable. This section will discuss the sources of carbon dioxide considered for possible use in EOR, and will attempt to define the quantities expected to be available from each. Succeeding sections in this report focus attention on the economic aspects associated with the sources selected for study.

The theoretical volume of supercritical carbon dioxide required to recover a barrel of oil at anticipated reservoir conditions is 2.5-3.0 MSCF [1,6]. The actual volume required can be 5-7 MSCF or more.<sup>1</sup> Since the best guess target for CO<sub>2</sub> EOR is approximately 4 billion barrels of oil [2], upwards of 30 trillion cubic feet of CO<sub>2</sub> could be required.<sup>2</sup>

It should be emphasized that equally as important as the total CO<sub>2</sub> available (as is most often reported) is the rate at which the CO<sub>2</sub> can be supplied. It is not enough to have so many trillion cubic feet of CO<sub>2</sub> available over the long run if only a few million cubic feet per day can be produced.

From projections by Lewin and Associates [2], the expected oil production by CO<sub>2</sub> EOR in 1995 is 930,000 bbl/day. If a worst case of 7 MSCF CO<sub>2</sub> per barrel of oil recovered is assumed, then peak CO<sub>2</sub> demand will be expected to reach 6.5 billion SCFD. Using the expected production figures from the Lewin study and 3-7 MSCF CO<sub>2</sub>/bbl oil, Figure III-1 represents what could be considered a boundary for the future demand of carbon dioxide.

This study has considered the following potential sources of carbon dioxide [3,4]:

1. Power plant stack gases
2. Flue gases from cement plants and limestone calcination
3. By-product of fertilizer and chemical plants
4. Naturally occurring gas wells high in CO<sub>2</sub>
5. By-product from coal gasification plants (SNG plants)
6. Fermentation industries
7. Phosphate manufacturing.

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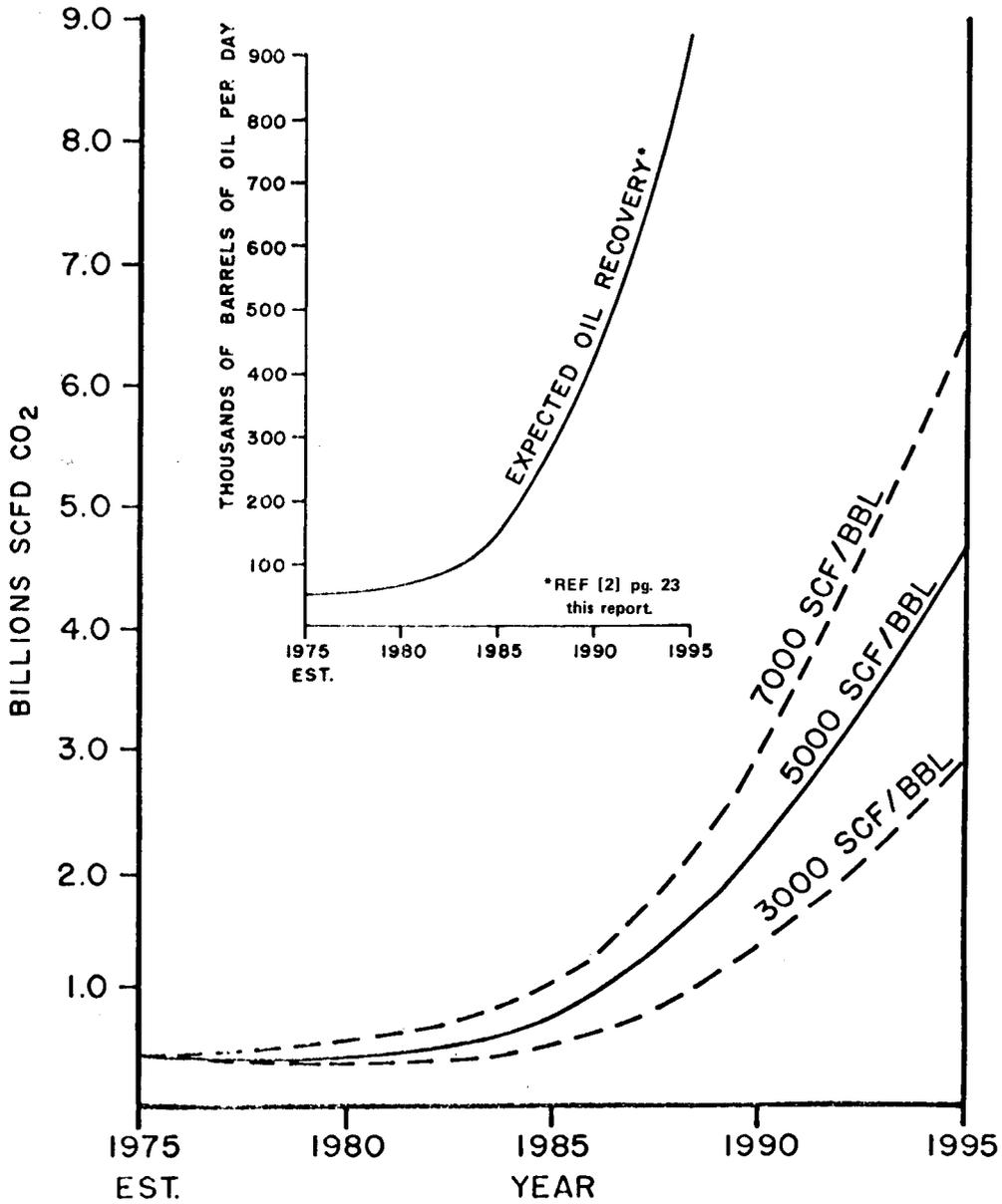
<sup>1</sup>Net CO<sub>2</sub> - total injected minus CO<sub>2</sub> recycled.

<sup>2</sup>Under the most favorable economic conditions (10% DCFROR, \$25/bbl oil) the limit of incremental oil recovery by CO<sub>2</sub> EOR is estimated at 7.5 billion barrels[2,5]. This, then could require as much as 50 trillion SCF of CO<sub>2</sub>.

Initial screening efforts have shown that the first four sources of CO<sub>2</sub> listed are the more likely ones for EOR applications; therefore, these form the basis for the CO<sub>2</sub> supply picture presented in this section. The elimination of the last two is justified because of low availability coupled with high CO<sub>2</sub> separation costs. For the fifth source, coal gasification plants, the potential CO<sub>2</sub> production is large; however, the prospect for construction of facilities in the near future is uncertain.

Discussion of the carbon dioxide supply situation in this section is limited to the thirteen states indicated to have oil fields suitable for carbon dioxide miscible flooding. Results of the survey for the first three sources (classified as above-ground sources) are discussed first followed by a discussion of the naturally occurring sources. Figures are currently limited for the amount of carbon dioxide available from natural sources; therefore, this discussion is largely qualitative (see also Appendix, Part B).

Figure III-1



EXPECTED OIL RECOVERY AND CO<sub>2</sub> CONSUMPTION  
BY CO<sub>2</sub> EOR TECHNIQUES

B. ABOVE GROUND SOURCES

Aggregate Supply Picture

Within the thirteen-state area, the total available CO<sub>2</sub> from all above-ground sources is 33 billion SCFD (Table III-1), the bulk of which is low concentration, low purity stack gases. This total is more than adequate to satisfy the expected peak requirements; however, the available supply of the more desirable, high purity CO<sub>2</sub> from chemical plants will be far short of requirements if carbon dioxide miscible flooding for EOR proves to be a successful commercial process.

The distribution of all available above-ground carbon dioxide is depicted in Figure III-2, prepared from the data in Table III-1. From preliminary compilations of CO<sub>2</sub> EOR candidate fields and the associated CO<sub>2</sub> requirements<sup>3</sup>, it appears that each area can be self-supporting in CO<sub>2</sub>; however, local CO<sub>2</sub> is going to cost much more in some areas than in others. The supply of naturally occurring CO<sub>2</sub> has not been well defined, but it is definitely conceivable that for certain areas, notably West Texas, the importing of natural CO<sub>2</sub> could have an economic advantage over local supply.

It is evident from Figure III-2 that the most abundant supplies of above-ground CO<sub>2</sub> are located in Illinois, South Texas, and California. Louisiana has only 30 percent as much CO<sub>2</sub> as Illinois; however, it is felt that South Louisiana could have one of the better matches between high purity CO<sub>2</sub> supply and reservoir requirements. This possibility is explored in further detail in Section V.

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<sup>3</sup> See Section IV

TABLE III-1  
 ABOVE GROUND SOURCES OF CO<sub>2</sub> - MMSCFD

<u>State</u>	<u>Total</u>	<u>Power Plant*</u>	<u>Cement Plant</u>	<u>Chemical Plant</u>
Ark.	520.1	386.5 (1)	122.0 (1)	11.6 (3,4)
Colo.	2,165.2	2,088.2 (1)	77.0 (1)	-0-
La.	2,118.7	1,733.6 (1)	85.0 (1)	300.1 (3,4)
Miss.	719.8	555.8 (1)	106.0 (1)	58.0 (3,4)
N. M.	2,372.4	2,314.7 (1)	38.0 (1)	19.7 (3,4)
Ok.	1,176.6	867.3 (1)	203.0 (1)	106.3 (3,4)
W. Tx.	2,000.0	1,529.4 (1)	416.0 (1)	54.6 (3,4)
S. Tx.	4,700.0	3,983.6 (1)	609.0 (1)	107.4 (3,4)
Fla.	3,907.0	3,251.0 (2)	648.0 (6)	8.0 (3,4)
Cal.	4,663.0	2,347.0 (2)	2,246.0 (6)	70.0 (3,4)
Mont.	294.0	117.0 (2)	177.0 (5)	-0-
Utah	441.3	260.0 (2)	177.0 (5)	4.3
Ill.	6,713.5	6,192.0 (2)	436.0 (6)	85.5**(3,4)
Wyo.	<u>1,008.5</u>	<u>825.0</u> (2)	<u>177.0</u> (5)	<u>6.5</u> (3,4)
	32,800.1	26,451.1	5,517.0	832.0

- (1) Finney & Heath - "Oilfields & Sources of CO<sub>2</sub> in a Nine-State Area of the Southwest U.S." - Feb. 1977.
- (2) "Steam-Electric Plant Factors" - 1975 National Coal Association.
- (3) World Nitrogen - 1976 Stanford Research Institute.
- (4) Chemical Economics Handbook - 1973.
- (5) Bureau of Mines & Arthur D. Little - 1972 - regional values apportioned equally (no breakdown given).
- (6) Statistical Abstracts of U.S. - 1976 for cement plants. Use factor 0.1 MMSCF CO<sub>2</sub>/Ton Cement.

\*Values from ref. 1 are apparently based on installed capacity whereas those from ref. 2 are based on actual KWH generation for the year.

\*\*Includes two SNG plants totaling 80.6 MMSCFD.

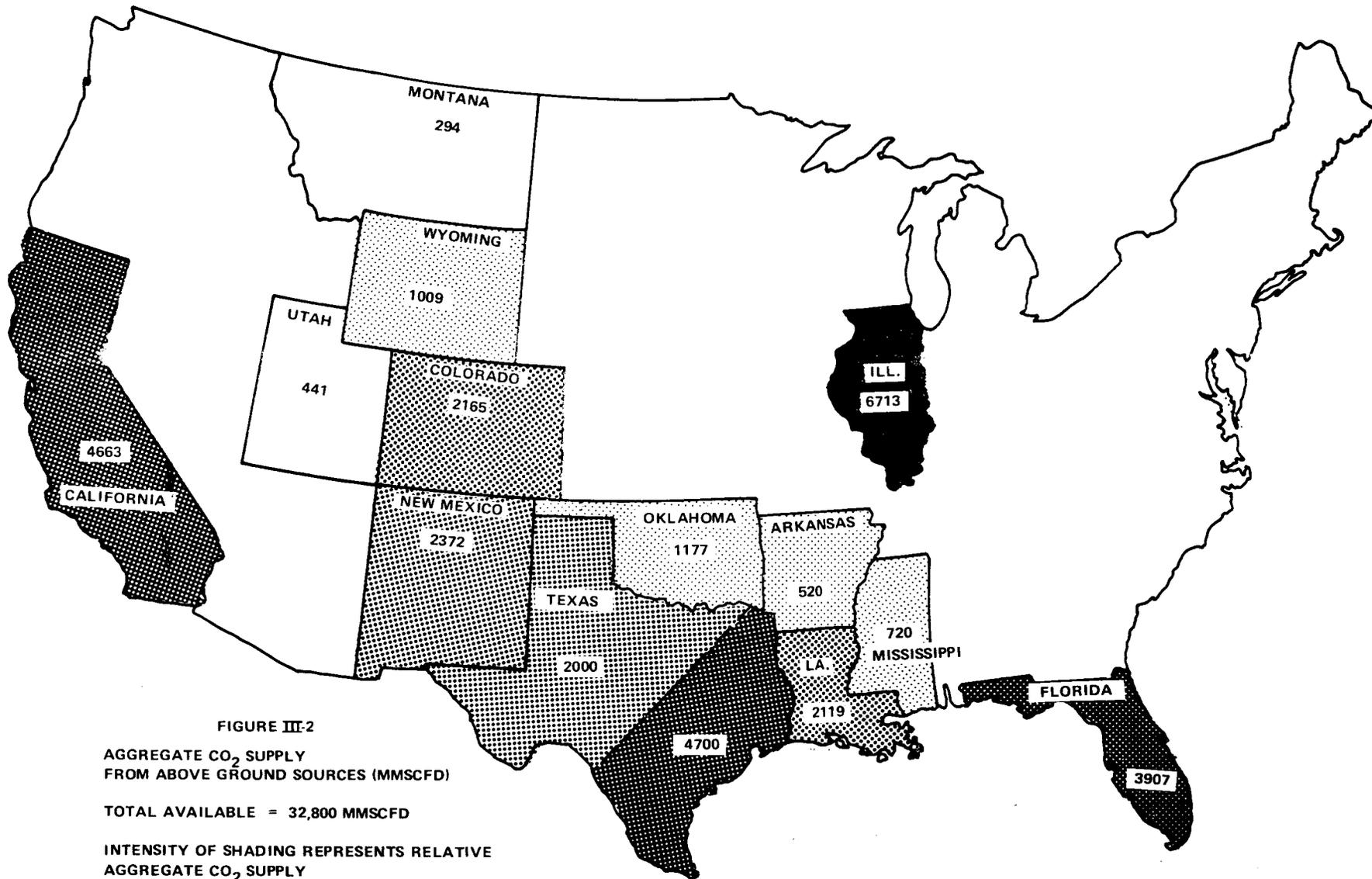


FIGURE III-2

AGGREGATE CO<sub>2</sub> SUPPLY  
FROM ABOVE GROUND SOURCES (MMSCFD)

TOTAL AVAILABLE = 32,800 MMSCFD

INTENSITY OF SHADING REPRESENTS RELATIVE  
AGGREGATE CO<sub>2</sub> SUPPLY

## Stack Gas Sources of Carbon Dioxide

By far the largest known and most widespread single source of CO<sub>2</sub> is stack gases from power plants (Table III-1), accounting for over 26 billion scfd, or 80 percent of the CO<sub>2</sub> available. Typically power plant CO<sub>2</sub> output falls within the range of 1 to 300 million SCFD for gas fired plants and can be as much as 2 billion SCFD for coal fired plants[3]; however, the concentration of CO<sub>2</sub> in the stack gases is low (6-16 percent) and the available pressure is low (< 5 inches water positive pressure). As a consequence the expense of purification and compression can push the cost to \$1.04/MSCF CO<sub>2</sub> before delivery.<sup>4</sup> At the rate of 5 MSCF CO<sub>2</sub>/bbl oil the cost of oil will rise by \$5.20/bbl.<sup>5</sup> To further aggravate the situation, currently existing, high output coal-fired plants are generally located at an unfavorable distance from the oil reservoirs, whereas the low output gas-fired plants are generally found nearby. The use of coal produced CO<sub>2</sub> could, therefore, involve significant transportation costs. It is felt that power plant sources of CO<sub>2</sub> will be attractive only if the high costs associated with recovery are offset by low transportation costs, thereby eliminating all power plants except those in close proximity to candidate fields.

The distribution of power plant plus cement plant produced CO<sub>2</sub> is depicted in Figure III-3. This map has been prepared from electric power generation capacity and fuel consumption data as provided by Finney[3] and the National Coal Association[9]. For the purposes of this report CO<sub>2</sub> output (MMSCFD) from power plants is calculated by multiplying megawatt generation capacity by 0.14 for gas-fired units, 0.393 for oil fired units, and 0.84 for coal fired units. Cement plant CO<sub>2</sub> output has been calculated from plant capacity data by Finney[3], Little[5], and from Statistical Abstracts of the U.S.[6]. CO<sub>2</sub> output (MSCFD) is calculated by multiplying tons/day capacity by 90 for gas fired units, 178 for coal fired units, and 100 for unspecified units. The quantities of CO<sub>2</sub> from cement plants are combined with power plant values for purpose of distribution mapping. As would be expected, the power plant generated CO<sub>2</sub> distribution closely parallels the aggregate supply picture with California, South Texas, and Illinois supplying the bulk of the CO<sub>2</sub>.

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4 See Section VI

5 Net CO<sub>2</sub> - total injected minus CO<sub>2</sub> recycled.

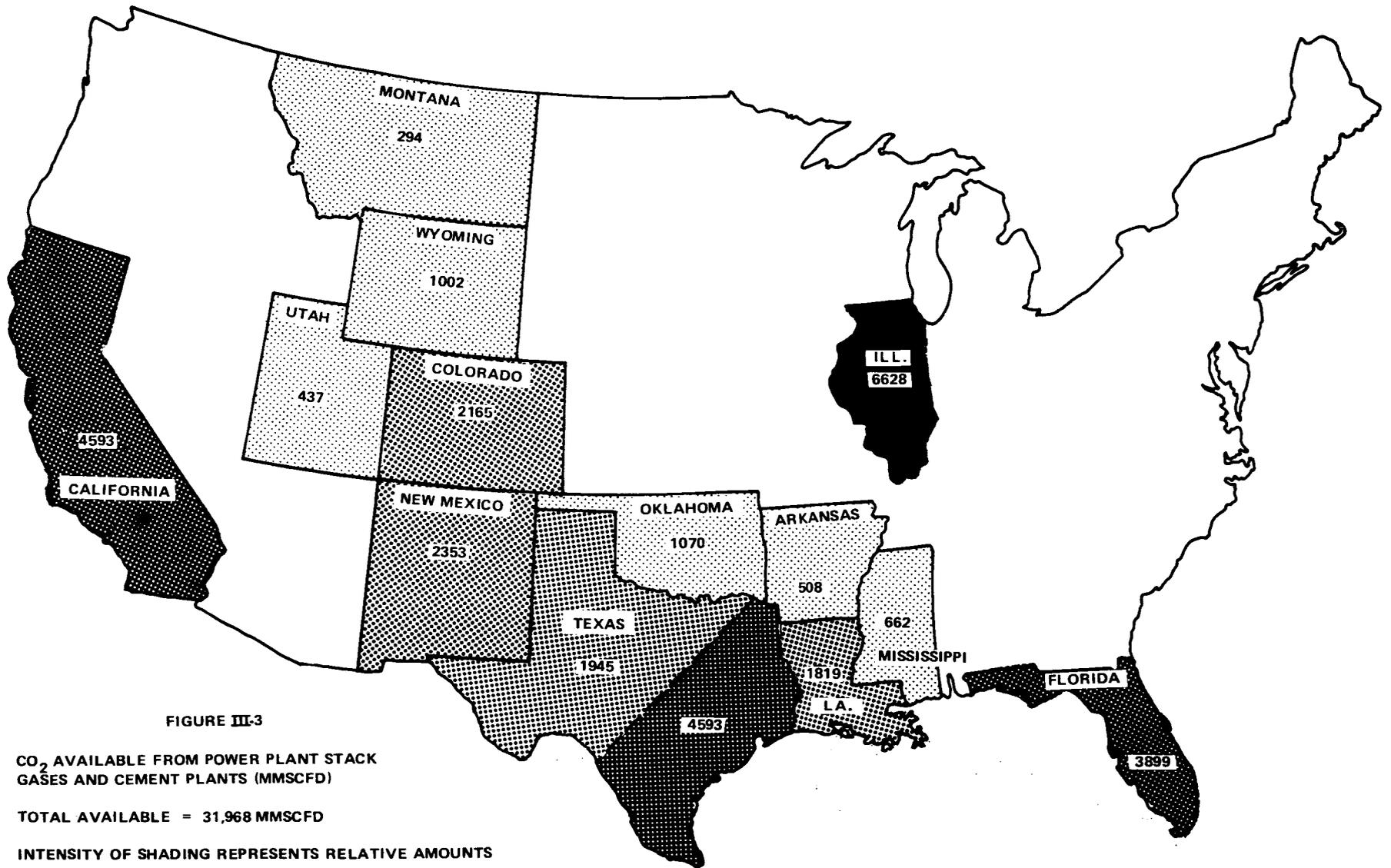


FIGURE III-3

CO<sub>2</sub> AVAILABLE FROM POWER PLANT STACK GASES AND CEMENT PLANTS (MMSCFD)

TOTAL AVAILABLE = 31,968 MMSCFD

INTENSITY OF SHADING REPRESENTS RELATIVE AMOUNTS

## Carbon Dioxide from Process Vents

One of the more promising and highly desirable CO<sub>2</sub> sources is high purity by-product CO<sub>2</sub> from process plant vents. There is approximately 830 MMSCF of recoverable CO<sub>2</sub> being vented daily (Table III-2 and Fig. III-4), and of this over half is suitable for generalized collection schemes.<sup>6</sup>

There are a number of processes venting CO<sub>2</sub> and among these the more commonly considered are:

1. Synthesis gas manufacture in ammonia and hydrogen plants
2. SNG production
3. Ethylene oxide synthesis
4. Acrylonitrile synthesis

The total CO<sub>2</sub> output from all acrylonitrile plants is small ( 13 MMSCFD) compared to other CO<sub>2</sub> sources and is highly impure; therefore, it will be ignored in this survey. By-product CO<sub>2</sub> from ethylene oxide plants is more substantial ( 100 MM SCFD total) but is low in purity. These plants are included in the overall process vent supply picture, but are not considered as point sources of CO<sub>2</sub> for possible collection schemes due to low individual output and purity.

The potential of SNG by-product CO<sub>2</sub> is enormous. At the present, approximately 80 MMSCFD CO<sub>2</sub> total is being produced by two SNG facilities in Illinois utilizing naphtha and NGL as feedstocks.[10]. Typical 250 MMSCFD SNG coal gasification plants as are being planned will generate over 300 MMSCFD of CO<sub>2</sub> each. This is high quality CO<sub>2</sub> which will require no further purification; the only costs associated with this will be compression and drying, transmission, and injection. Primary sites for the units under current detailed consideration are in the Four Corners area of New Mexico.

The most viable source of CO<sub>2</sub> from process vents today is uncommitted ammonia plant by-product, accounting for 625 MMSCFD or roughly 75 percent of all available process vent CO<sub>2</sub>. A typical 1000 STPD ammonia plant will generate 22-23 MMSCFD of CO<sub>2</sub>. This is a high purity source which, after drying and compression, can be used directly for EOR injection. This makes ammonia vent gas probably the most desirable of all CO<sub>2</sub> sources as of today. Furthermore, 70 percent of all ammonia vent CO<sub>2</sub> (450 MMSCFD) is concentrated in three of the more promising areas for CO<sub>2</sub> EOR: Louisiana, South Texas, and Oklahoma. This source is explored in further detail in Section V.

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<sup>6</sup>Among the more promising of these is a proposed collection system for southern Louisiana described in Section V.

TABLE III-2  
CO<sub>2</sub> SOURCES FROM PROCESS VENTS\*

	<u>CO<sub>2</sub> Sources- Cities</u>	<u>CO<sub>2</sub> Amount MMSCFD</u>	<u>Possible CO<sub>2</sub> Supplies- Geographic Areas</u>	<u>CO<sub>2</sub> Amount MMSCFD</u>
<u>Louisiana</u>	Donaldsonville	103.2	Donaldsonville - Geismar	111.8**
	Luling	46.7	Luling - Taft - Avondale	72.2**
	Sterlington	35.5	Sterlington	35.5
	Lake Charles	14.7	Lake Charles	14.7
	Pollock	26.9		
	Geismar	21.0		
	Avondale	18.9		
	Taft	15.9		
	Michoud	9.2		
	Plaquemine	8.1		
		<u>300.1</u>		
<u>Texas</u>	Beaumont	34.5	Beaumont - Port Neches	44.8
	Borger	18.9	Houston - Pasadena -	
	Seadrift	15.0	Seadrift - Clear Lake	41.1
	Houston	12.9	Borger - Dumas	27.1
	Freeport	11.2		
	Port Neches	10.3		
	Dumas	8.2		
	Pasadena	7.2		
	Odessa	6.8		
	Victoria	6.5		
	Clear Lake	6.0		
	Big Springs	5.5		
	Terrell	5.2		
	Ft. Stockton	4.5		
	Plainview	3.4		
	Deer Park	1.6		
	Orange	1.0		
	Puckett	1.0		
	Longview	0.9		
	Dimmitt	0.7		
Dallas	0.5			
Kerens	0.2			
	<u>162.0</u>			
<u>Oklahoma</u>	Enid	46.6	Enid	46.6
	Verdigris	29.1	Verdigris	29.1
	Woodward	26.4	Woodward	26.4
	Pryor	4.2		
		<u>106.3</u>		

\*Includes Ammonia and Ethylene Oxide Plant Vents  
\*\*Ammonia Plant Vents Only

TABLE III-2 (CONTD.)  
CO<sub>2</sub> SOURCES FROM PROCESS VENTS

	<u>CO<sub>2</sub> Sources- Cities</u>	<u>CO<sub>2</sub> Amount MMSCFD</u>	<u>Possible CO<sub>2</sub> Supplies- Geographic Areas</u>	<u>CO<sub>2</sub> Amount MMSCFD</u>
<u>Mississippi</u>	Pascagoula	46.8	Pascagoula	46.8
	Yazoo City	11.2		
		<u>58.0</u>		
<u>Illinois</u>	Morris	41.8	Morris - Joliet	80.6
	Joliet	38.8		
	East Dubuque	4.9		
		<u>85.5</u>		
<u>California</u>	Wilmington	17.8	Wilmington - Brea - El Segundo	29.2
	Avon	12.1		
	Brea	10.1		
	Helm	8.0		
	El Centro	5.2		
	Ventura	3.6		
	Hanford	3.5		
	Bakersfield	3.4		
	Lathrop	2.8		
	Hercules	2.2		
	El Segundo	1.3		
		<u>70.0</u>		
<u>New Mexico</u>	Carlsbad	13.2		
	Denton	6.5		
		<u>19.7</u>		
<u>Arkansas</u>	Helena	6.4		
	Blytheville	5.2		
		<u>11.6</u>		
<u>Florida</u>	Tampa	5.2		
	Pensacola	2.8		
		<u>8.0</u>		
<u>Wyoming</u>	Cheyenne	6.5		
	Geneva	4.3		
<u>Montana</u>		< 1.0		
<u>Colorado</u>		< 1.0		

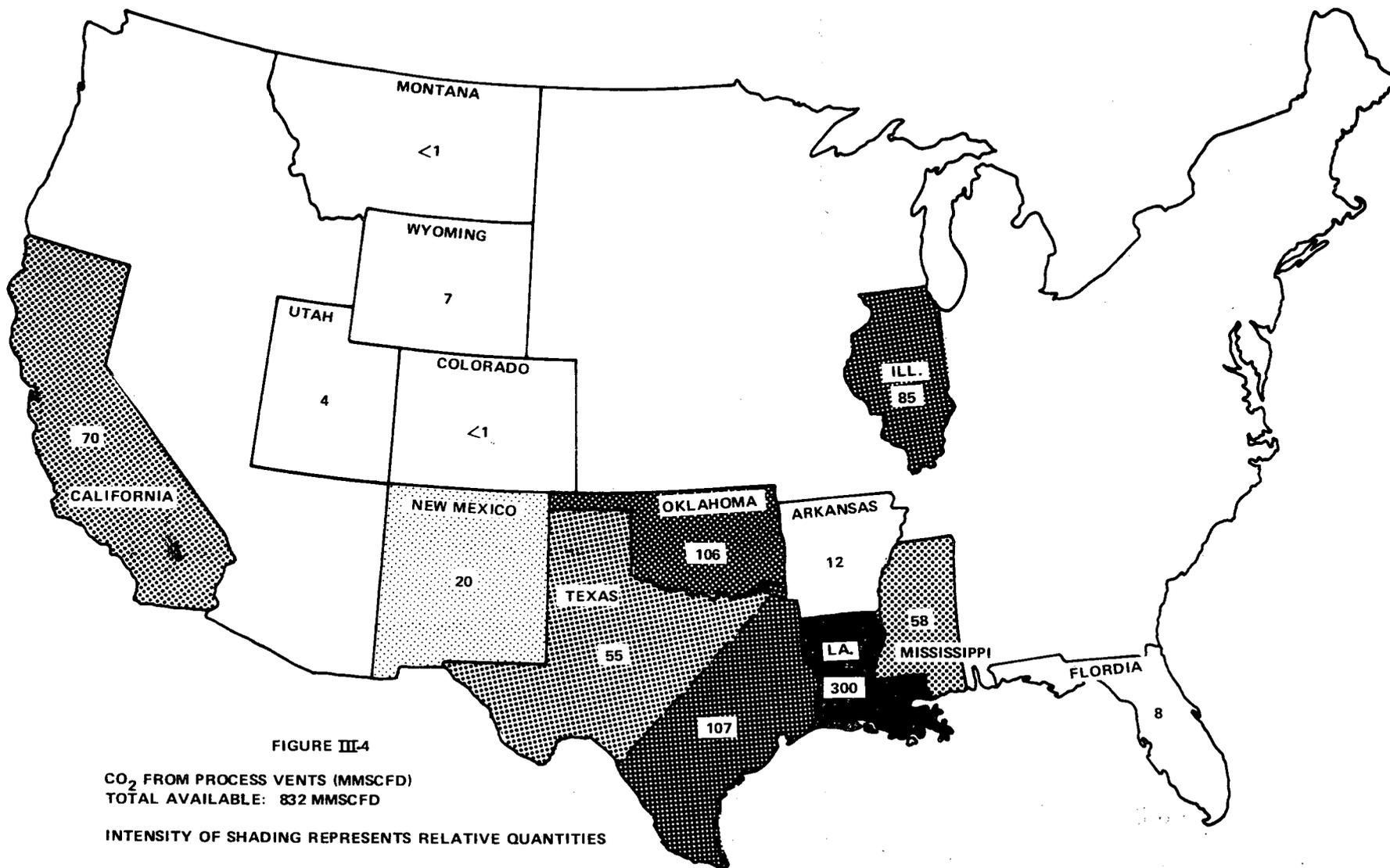


FIGURE III-4

CO<sub>2</sub> FROM PROCESS VENTS (MMSCFD)  
TOTAL AVAILABLE: 832 MMSCFD

INTENSITY OF SHADING REPRESENTS RELATIVE QUANTITIES

### C. NATURALLY OCCURRING CARBON DIOXIDE WELLS

Natural gas wells high in CO<sub>2</sub> also hold promise as a significant source of CO<sub>2</sub>, especially during peak EOR years. The quantity available from a single well can be as high as 87 MM SCFD and purities can run as high as 99.6 percent [7]; however the combination of high output and purity will probably not be very common. No exhaustive survey of CO<sub>2</sub> wells has been completed to date but nevertheless some qualitative assessments can be made.

Areas known to have naturally occurring CO<sub>2</sub> wells within the 13 states are depicted in Figure III-5.[5] The actual quantities available are unknown but it is felt that those areas having the greatest potential of high purity CO<sub>2</sub> are the Four Corners area, Southeast Colorado, Northeast New Mexico, and Central Mississippi. Other areas, notably Southwest Texas, have some potential of producing CO<sub>2</sub> of lower concentrations (30-50 percent).

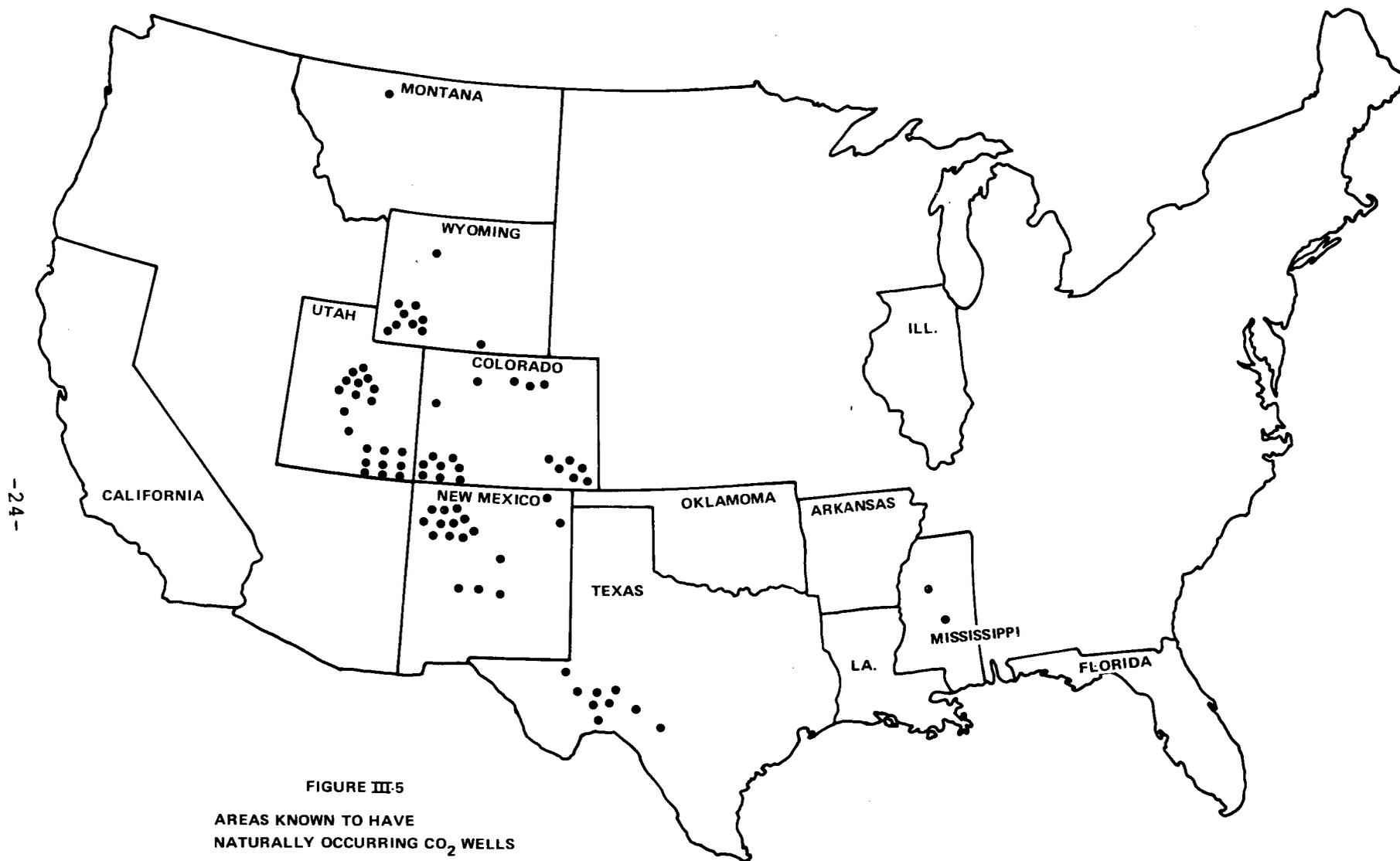
For purposes of establishing the maximum potential CO<sub>2</sub> from natural sources it can be noted that about 731 trillion SCF of natural gas has been discovered in the U.S to date, and current reserves are estimated at 225 trillion SCF. The quantity of CO<sub>2</sub> required to produce all potentially CO<sub>2</sub> recoverable oil is 75 trillion SCF. It seems unlikely that such a quantity of CO<sub>2</sub> could be found from natural sources. The reasonably expected recovery of 4 billion barrels of oil could require 30 trillion SCF, and it is generally conceded that even that quantity of CO<sub>2</sub> is unlikely to be produced from natural sources alone.[7]

In any of these cases there exists the possibility that the CO<sub>2</sub> might be contaminated with hydrogen sulfide. Whereas hydrogen sulfide poses no particular problems for the miscible processes, and might even enhance them[13], there is a concern over the environmental impact regarding the uses of hydrogen sulfide contaminated gases. In particular the Texas Railroad Commission has promulgated Rule 36 restricting permission to use gases contaminated to a certain level.[7] The resulting additional costs of purification of contaminated gases could very well impede development of these sources.<sup>7</sup>

For purposes of this report in the absence of definitive data, several hypothetical natural CO<sub>2</sub> sources, both contaminated and uncontaminated, are considered and costs are developed for each. This is expounded further in Section VII. It is basically assumed that the quantities required for an economical EOR project will be available.

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<sup>7</sup>See Section VII.



NOTES - SECTION III - CO<sub>2</sub> SUPPLY SITUATION

- [1] Doscher, T. M. & F. A. Wise - "Enhanced Crude Oil Recovery Potential - An Estimate" - Journal of Petroleum Technology, May 1976.
- [2] Lewin & Associates, Inc., "Research and Development in Enhanced Oil Recovery" - Final Report, Vol. 2 - IV p. 19. ERDA Pub 77-20/2 under Contract E(49-18) 2294.
- [3] Finney, R. E. & L. J. Heath - "Oilfields & Sources of CO<sub>2</sub> in a nine-state Area of the Southwest United States" - Feb 1977 U.S. ERDA Publication.
- [4] Pappano, W. W., J. T. Sears, W. R. Parr - "Availability and Economics of CO<sub>2</sub> for Enhanced Oil Recovery in Appalachia" - Aug 1976, U.S. ERDA Grant #G0155014.
- [5] Haynes, H. J., et al - "Enhanced Oil Recovery" - Dec. 1976, National Petroleum Council.
- [6] Preliminary GURC Tabulation of Candidate Oil Fields - Private communication, Dec 20, 1976.
- [7] General Consensus at ERDA-MERC Workshop, Houston, Texas, Apr. 1977.
- [8] Chemical Economics Handbook - 1973 Stanford Research Institute.
- [9] Steam-Electric Plant Factors/1975 + June 1976 Suppl. - National Coal Association.
- [10] "Their Time Never Really Came" - Chemical Week, May 19, 1976, p.42.
- [11] Management Plan for Enhanced Oil Recovery, ERDA.
- [12] World Nitrogen - 1976 Stanford Research Institute.
- [13] "Gas Miscible Projects Move at Slow Pace," Oil & Gas Journal, Apr. 5, 1976, p 126.

#### IV. CANDIDATE OIL FIELDS AND RESERVOIRS

Carbon dioxide is effective as an oil recovery agent by miscibly displacing the oil trapped by capillary forces, thereby allowing recovery from the contacted fluid.

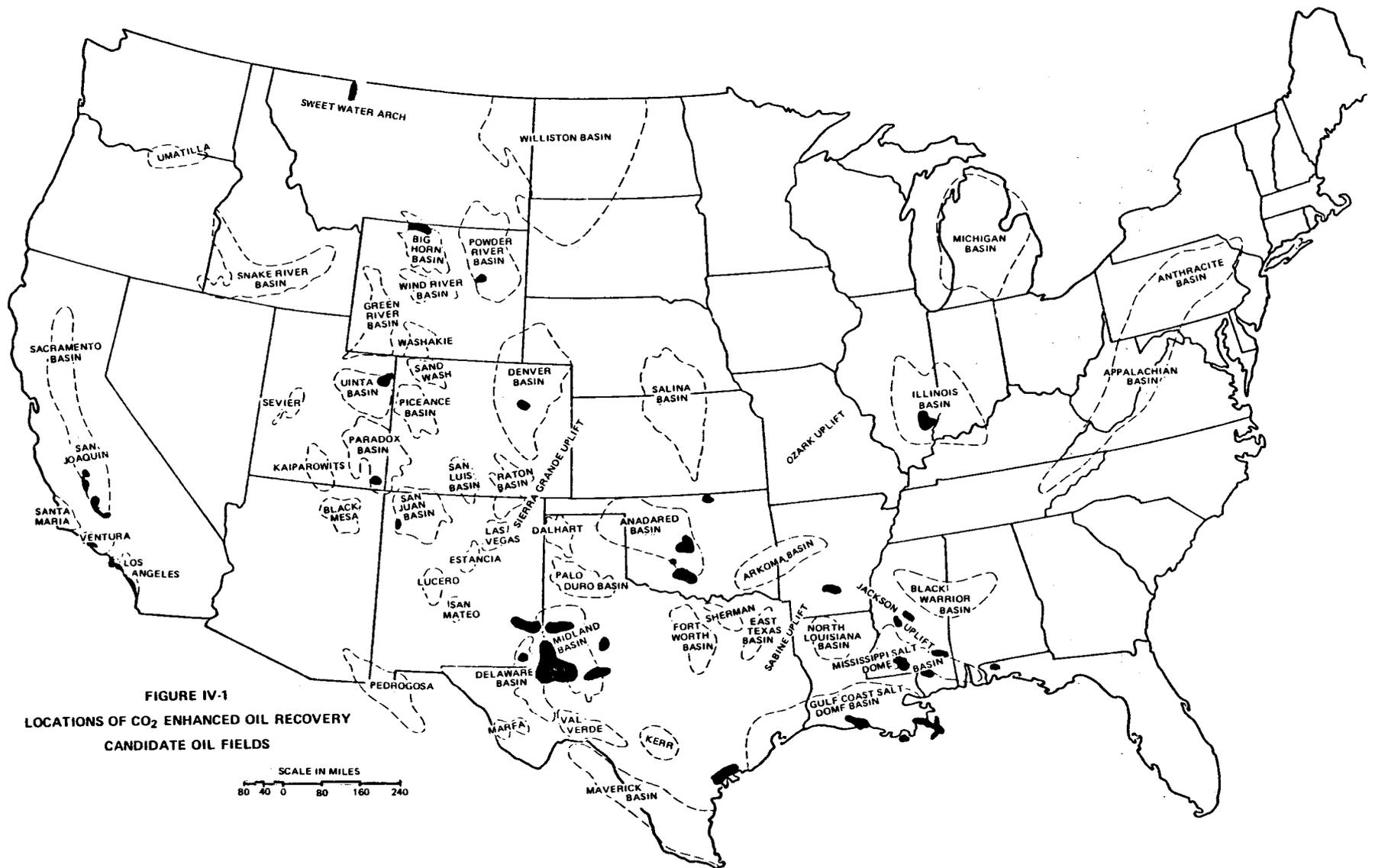
Carbon dioxide is not directly miscible with oil upon initial injection, but as the carbon dioxide contacts the oil, some of the hydrocarbon constituents of the crude are vaporized, and a miscible mixture is formed. Mixing due to flow in the reservoir will tend to alter the miscible composition [1]. Maintaining the operating pressure of the reservoir high enough will keep the carbon dioxide-hydrocarbon mixture miscible with the crude at reservoir temperatures. The presence of methane or nitrogen in the carbon dioxide can drastically increase the pressure required for miscibility, so the source of carbon dioxide used should be of reasonably high purity. At reservoir conditions the carbon dioxide will be in the supercritical state, so its density may be near that of the oil and water thereby reducing segregation between the fluids [2]. Since the viscosity of the carbon dioxide is on the order of one tenth that of most low viscosity crudes, the tendency for the carbon dioxide to channel through the oil is a major problem and tends to reduce the volumetric sweep of the reservoir [3]. In many applications the carbon dioxide is alternated with water injection for the purpose of lowering the overall carbon dioxide requirement.

Based on these and other observed phenomena, a screening procedure taking into account process characteristics, reservoir geological conditions, and fluid properties was developed early in this investigation to locate possible candidate carbon dioxide miscible oil reserves. This was applied to a data bank of over 2500 reservoirs maintained by GURC. The basic screening criteria includes the API gravity of the crude, the depth and thickness of the formation, reservoir temperature, permeability, and oil saturation. Specific parameters selected by GURC are shown below:

API Gravity	> 27
Depth	> 2000 ft.
Thickness	Not a critical parameter
Oil Saturation	> 20 percent PV
Reservoir Temperature	Not a critical parameter
Permeability	Reasonably homogenous

Only 1.5-2 percent of the fields analyzed meet the screening criteria. These candidate fields, located in thirteen states, are mapped in Figure IV-1 and tabulated in Table IX-1 and Table IX-2 in the appendix. Table IX-1 presents qualitative information on the

location of the candidate fields while Table IX-2 lists the estimated potential recovery and carbon dioxide requirements for the states with most promising candidate fields - Texas, Louisiana, Mississippi, and California. These tables, prepared by GURC, are initial estimates only based on reservoir modeling. They should not be taken as proven fact, but should be used only to pass some qualitative judgement on recovery potential.



NOTES - SECTION IV - CANDIDATE OIL FIELDS AND RESERVOIRS

- [1] Doscher, T.M. & F.A. Wise - "Enhanced Crude Oil Recovery Potential - An Estimate" - J. Pet. Tech. May 1976
- [2] Lewin & Associated, Inc., "Research and Development in Enhanced Oil Recovery" - Final Report, Vol. 2 - IV p. 3. ERDA Pub 77-20/2 under Contract E(49-18) 2294.
- [3] Haynes, H. J. et al - "Enhanced Oil Recovery" - Dec. 1976, National Petroleum Council, p. 142.

## V. CARBON DIOXIDE FROM HIGH PURITY PROCESS VENTS

### A. INTRODUCTION

Quite possibly one of the future carbon dioxide EOR projects will utilize high purity process vents as the primary source of carbon dioxide. This is likely because of a fourfold advantage over other sources: (1) there are some reasonable proximities between process vents and oil fields, (2) multiple carbon dioxide vents tend to be clustered within a given industrial area, (3) the quantity of carbon dioxide from each source under consideration will be relatively accurately known (or can be accurately determined), (4) there will not be any need for a purification scheme for carbon dioxide from ammonia plant vents (available at 98 percent purity) - compression and piping is all that will be required.

In order to ascertain the quantity of carbon dioxide available from process vents the Chemical Economics Handbook, 1973 [1] and World Nitrogen, 1976 [2] were consulted for summaries of current fertilizer plants and other plants venting carbon dioxide. The above data are listed by company name and plant whereas the compilation in Table III-2 shows the breakdown by state and city Using Table III-2, it is possible to define which geographical areas have higher concentrations of carbon dioxide output than others.<sup>1</sup> Possible areas are suggested in the second column of Table III-2.

Of these groupings the two that appear the most viable for carbon dioxide EOR efforts, Donaldsonville-Geismar and Luling-Taft-Avondale, are located in southern Louisiana. The total output of these high-purity, ammonia plant carbon dioxide vents (184 MMSCFD) is more than twice any other geographical area and all the vents are contained within a 70-mile stretch along the Mississippi River. Furthermore, there are candidate oil fields/reservoirs located less than 90 miles away in the South Pass Area of coastal Louisiana. This fortunate pairing of a relatively large quantity of high purity carbon dioxide and nearby candidate fields/reservoirs will form the basis for an economic evaluation of costs associated with EOR by use of carbon dioxide from high purity vents.

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<sup>1</sup>See also Figure III-4

## B. PROPOSED SYSTEM FOR SOUTH LOUISIANA

### Background

Preliminary communications with GURC [3] on possible candidate oil fields single out South Louisiana as one area having a number of potential EOR fields. Already several companies have conducted small miscible field tests on several of these, mostly with hydrocarbon gases, [4] and one company has been awarded a contract by ERDA to test carbon dioxide miscible flooding in this area. [5] Definitive results from these tests could be available as early as 1980.

For the twenty-year recovery period 1980-2000, it has been estimated that 875 billion SCF of carbon dioxide might be utilized for EOR efforts in the South Louisiana area, with daily demands ranging from 15 MMSCF during initial efforts (1980-85) to 250 MMSCF during the peak recovery period (1990-2000). Ammonia plant vents from the five cities under consideration will currently provide a total of 184 MMSCFD of carbon dioxide at maximum output.<sup>2</sup> This quantity should be fairly reliable throughout the life of this project due to the reserves of feed gas within the region, and the favorable allocation status accorded to the agricultural industry. For the purposes of this evaluation it will be assumed that 184 MMSCFD is the quantity of carbon dioxide available.

This supply of carbon dioxide is generated from twelve plants owned by eight companies - one plant at Geismar, seven in Donaldsonville, one at Taft, two in Luling and one at Avondale. These sources will form the feeds for a common pipeline transporting the carbon dioxide to the South Pass Area.

### The Pipeline

For ease of cost estimating, the routing of the proposed pipeline will follow existing pipeline and/or railway right of ways wherever possible (as depicted on The Oil and Gas Map of Louisiana [6]). This will avoid the uncertainty of costs for purchasing new right of ways. Also, it is assumed that no railway or river crossings will be required except for the Geismar crossing of the Mississippi River.

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<sup>2</sup>Average output will be slightly over 171 MMSCFD based on 340 stream days/year.

The proposed line begins at Geismar and passes in order Donaldsonville, Taft, Luling, and Avondale, then on to the South Pass Area. Two or three attempts have been made to find a best route based on minimum overall line length; however, no detailed routing study or optimization has been done.<sup>3</sup> A sketch of the route chosen is given in Figure V-1. It has been decided by mutual agreement among Kellogg, ERDA, and GURC that the final carbon dioxide delivery pressure be set at 2,000 psig. Based on experience gained from operation of carbon dioxide pipelines in the supercritical state (SACROC) and subcritical state (Phillips-USOK), it was decided to base this pipeline study on supercritical operation.<sup>4</sup>[7,8] For ease of transportation costs comparison among the three carbon dioxide source cases considered<sup>5</sup> a 200 psi total pressure drop is assumed. Thus, this line will operate in the range 2,000-2,200 psig.

Throughout this report all transmission lines will be sized according to ANSI B31.8 Class 3 type C codes<sup>6</sup> using API 5L-X60 schedule 60 piping. Block valves with bypass (and reheat provision) are assumed every eight miles along the pipeline and the line will be buried under a 30-inch cover. Criteria used in selecting the diameter for a particular section is minimum total pipe weight compatible with allowable pressure drop. There has been no attempt to evaluate pressure drop (and therefore line size) versus compression tradeoff. Line lengths and diameters for the proposed pipeline are shown schematically in Fig. V-2.

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<sup>3</sup>It was originally agreed with ERDA that the trunkline length should be 100 miles, however, this is unrealistic for this study since this length will put the pipeline over 10 miles away from known oilfields.

<sup>4</sup>There have been reports of trouble with the subcritical line occasionally condensing out. West[7] also claims a 20 percent cost reduction for supercritical lines.

<sup>5</sup>That is process vent, stack gas (Sect. VI), and natural sources (Sect. VII).

<sup>6</sup>Areas subdivided for residential or commercial purposes with prevalent height of three stories or less.

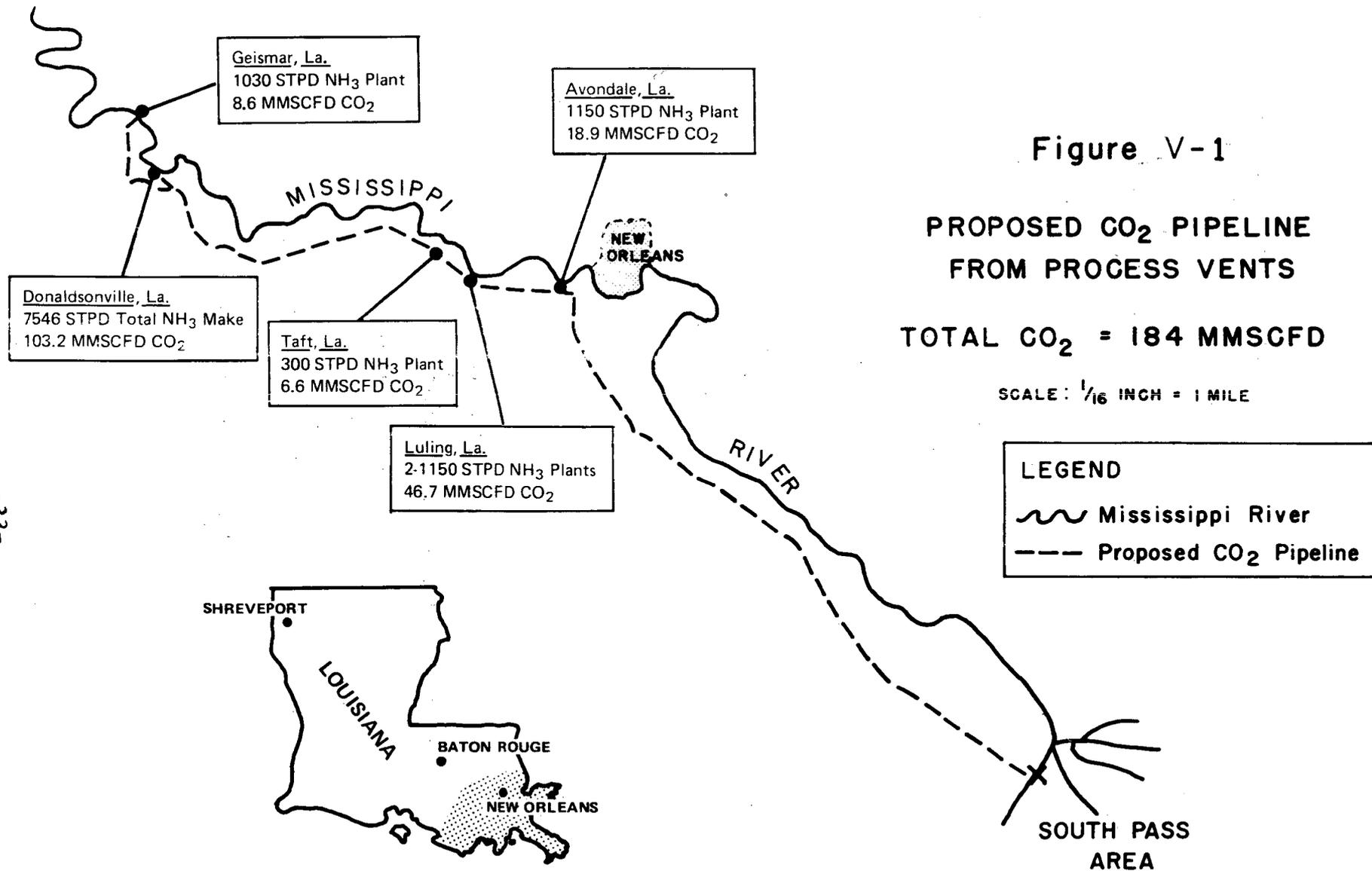
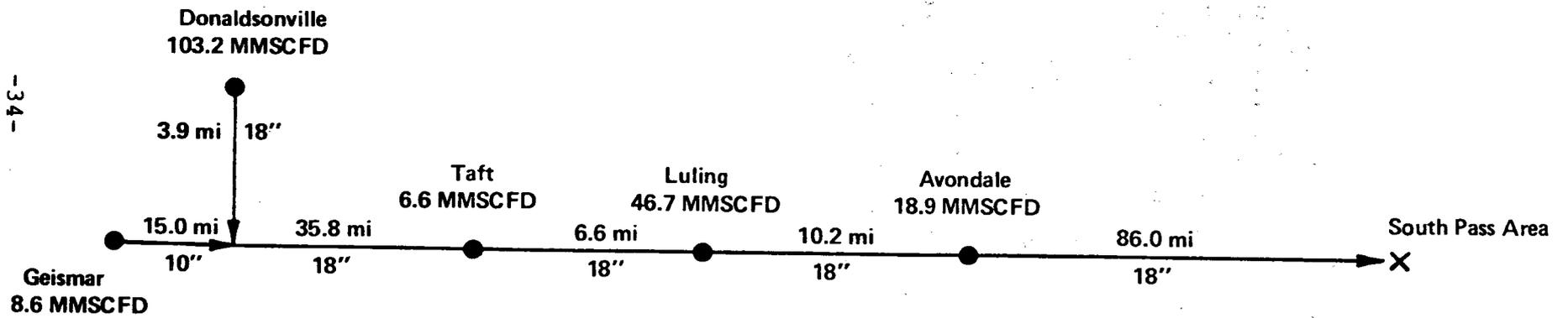


FIGURE V-2  
SCHEMATIC OF CO<sub>2</sub> PIPELINE FROM PROCESS VENTS  
SHOWING LINE SIZES, LENGTHS, AND FEED RATES  
TOTAL CO<sub>2</sub> FLOW TO WELLHEAD: 184 MMSCFD



### Equipment Required

There will be five feed stations to the pipeline each consisting of a compressor, triethylene glycol (TEG) drier, and carbon dioxide collection piping.<sup>7</sup> The carbon dioxide from each plant, at the compressor suction, is assumed to be saturated with water at 140°F and available at 3.5 psig for the Geismar, Taft, and Avondale locations, 2.5 psig at Donaldsonville, and 0.5 psig at Luling. These figures represent plant design conditions with some allowance for piping pressure losses. Before compression to full line pressure, the carbon dioxide will have to be dehydrated in order to remove the water which, in the presence of carbon dioxide, could form corrosive carbonic acid. This is accomplished with the triethylene glycol drier operating between the second and third stages of the carbon dioxide compressor.

The compressors are four-stage centrifugal units driven by steam turbines operating from 900 psig, 900°F superheated steam. It is assumed for this report that such steam will be available in quantity at \$3.80/1,000 lb. Intercoolers reducing the inter-stage temperature to 100°F are provided to improve the overall operating efficiency of the compressors.

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<sup>7</sup>Collection piping not included in cost analysis.

C. ECONOMIC SUMMARY

Table V-1 summarizes the factors used to determine the economics of the pipeline. Because of the large uncertainty in the purchase price of the raw carbon dioxide, its cost will not be included in the economic analysis of this case.<sup>8</sup> Based on Table V-1, it is estimated that carbon dioxide delivered to the well-head will cost \$1.15/MSCF. At 5,000 SCF/bbl oil recovered (net CO<sub>2</sub> - injected minus recycle), this will increase the price of oil by \$5.75/bbl.

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<sup>8</sup>Cost estimates range from 3¢/MSCF[8] to \$2.00/MSCF[9].

TABLE V-1

ECONOMIC SUMMARY  
CARBON DIOXIDE FROM AMMONIA PLANT VENTS  
PIPELINE CAPACITY 184 MMSCFD CO<sub>2</sub>

A. TRANSMISSION COSTS

Compression Investment	\$ 19,840,000
Pipeline Investment	115,000,000
Fixed-Capital Investment	<u>\$134,840,000</u>

<u>DIRECT COSTS</u>	<u>UNITS/ MSCF</u>	<u>UNIT COSTS \$</u>	<u>COST ¢/ MSCF CO<sub>2</sub></u>
Cooling Water (circ) MGAL	0.348	0.02	0.70
Steam - 900 LB & 900°F - MLBS	0.065	3.80	24.70
Chemicals	-	-	<u>0.09</u>
Sub-total direct costs			25.49
 <u>INDIRECT COSTS</u>			
Operating Labor - 2 Men/Shift			0.18
Operating Supplies - 30% Operating Labor			0.05
Supervision and Overhead - 100% Operating Labor			0.18
Maintenance Labor & Supplies - 3.5% Investment/Yr.			7.54
Capital Related Costs - Depreciation, Interest Charges Taxes, Insurance, Return on Investment - @ 38% of Investment/Yr.			<u>81.90</u>
Sub-total Indirect Costs			89.85
 TOTAL TRANSMISSION COSTS ¢/MSCF			 115.34

NOTES: Transmission Costs

- All operating labor \$6.5/manhour.
- Breakdown of capital related costs:
 

Depreciation	10%
Interest Charges	5%
Taxes and Insurance	3%
Return on Investment	<u>20%</u>
	<u>38%</u>
- Onstream Factor           340 days/year
- Investment does not include power generation, cooling tower or boiler feedwater treatment or carbon dioxide collection piping.
- Steam cost based on gas fired steam boiler. Gas cost \$2.00/MSCF delivered.

NOTES - SECTION V - HIGH PURITY PROCESS VENTS

- [1] Chemical Economics Handbook - 1973 Stanford Research Institute
- [2] World Nitrogen - 1976 Stanford Research Institute
- [3] Private Communication with GURC - Oct. 25, 1976
- [4] "Gas Miscible Projects Move at Slow Pace", The Oil and Gas Journal, April 5, 1976, p. 126.
- [5] Perry, G. E. - "Weeks Island-S-Sand Reservoir & Gravity Stable Miscible CO<sub>2</sub> Displacement Iberia Parish, Louisiana", Proceedings of Third ERDA Symposium on Enhanced Oil and Gas Recovery and Improved Drilling Methods, Tulsa, Oklahoma, August 30 - September 1, 1977, Vol. I - Oil, p. C-4/1.
- [6] Oil and Gas Map of Louisiana - Dept. of Conservation (July 1973)
- [7] West, J., "Line Will Move 240 MMSCFD of CO<sub>2</sub>", Oil and Gas Journal, Nov. 8, 1971
- [8] Private Communication U.S. Oil and Refinery Co. to Kellogg - Oct. 29, 1976
- [9] Pappano AW, et al. "Availability and Economics of CO<sub>2</sub> for Enhanced Oil Recovery in Appalachia - Aug. 1976. U.S. ERDA Grant #60155014, p 34.

## VI. CARBON DIOXIDE FROM LOW PURITY STACK GASES

### A. INTRODUCTION

As noted in the discussions concerning the carbon dioxide supply situation, power plant stack gases are by far the largest above-ground source of potential carbon dioxide, representing about 80 percent of the total carbon dioxide available.

The future will undoubtedly see more power plants constructed or modified to burn coal because of its relative abundance compared to other potential fossil fuel sources. This is expected to increase the importance of this source of carbon dioxide relative to power plants based on alternate fuels. This section of this report is therefore directed to development of costs associated with this source. Another reason for investigating carbon dioxide recovery from coal-fired power plants is that recovery costs here are believed to represent a worst case. This will set an upper limit on costs for other sources such as cement plant stack gases or natural gas-fired power plants.

For a power plant the dilution effect of the combustion air limits the concentration of the carbon dioxide in the flue gas. The flue gas will therefore contain in addition to carbon dioxide, quantities of nitrogen and oxygen plus water vapor produced during combustion. In the case of a coal-fired power plant quantities of fly ash, and oxides of sulfur (primarily sulfur dioxide with some sulfur trioxide) are present. The flue gases are normally available at a few inches of water positive pressure.

A number of processes can be considered for recovery of carbon dioxide from flue gases[1]. These include both chemical reactive and physical absorption systems, dry bed absorption systems, and cryogenic systems. The low concentration and available pressure of the carbon dioxide in a flue gas reduces these potential processes to those which can operate effectively at these conditions.

From the available processes, a chemical reactive absorption system employing an alkanolamine-monoethanolamine (MEA) was selected for this study. MEA is preferable to other alkanolamines (diethanolamine, triethanolamine, etc.) which are used in similar processes because of its higher absorption capacity and ease of regeneration.[2] This results in reduced equipment sizes and lower heat requirement for solution regeneration in MEA systems. MEA is considered somewhat more corrosive than other amines; however, this difficulty can be minimized by limiting the concentration of the solution to about 20 percent by weight.

MEA reacts with sulfur oxides and will scrub them along with carbon dioxide from the flue gases at the same time. Recovery of MEA after its reaction with sulfur oxides is not as straightforward as recovery after reaction with carbon dioxide. In the latter case the MEA is recovered (and the carbon dioxide product is obtained) by simply heating the solution and stripping out the carbon dioxide with steam. Chemical treatment is necessary to recover MEA which reacts with sulfur oxides. Sodium carbonate can be used for this (see later discussion).

Equipment and chemical costs to recover MEA could become quite significant if the content of sulfur oxides in the flue gas is high. For purposes of this study, it is assumed that the bulk of any sulfur oxides present in the flue gas has been removed by a pretreatment step. This is a logical assumption in view of the continuing pressures to clean up power plant flue gases as a means of protecting the environment.

A wet scrubbing system for removal of sulfur oxides from flue gases will remove about 90 percent of the amount originally present. The treated flue gas will typically contain about 200 ppm residual sulfur oxides which are essentially all sulfur dioxide.

To develop the economics for supplying carbon dioxide recovered from power plant flue gas, this report assumes the recovery facilities are added on to an existing power plant. No attempt is made to integrate the utility systems with the power plant (for example by use of co-generated steam).

The following section is a description of the MEA process for recovery of carbon dioxide from a coal-fired power plant flue gas.

## B. PROCESS DESCRIPTION

### Introduction

The flue gas composition below is used as a basis for design. It is taken from a job currently under construction by Pullman Kellogg[3] in which the Kellogg/Weir magnesium promoted lime slurry process is used for bulk sulfur oxides removal from the flue gas. It is believed to be representative of a typical flue gas which will be available from a coal fired power generating facility after bulk sulfur oxides removal.

<u>Component</u>	<u>Mole Percent</u>	
Carbon Dioxide	16.5	
Nitrogen	64.6	
Oxygen	5.6	
Water	<u>13.3</u>	
Total	100.0	
Fly Ash, Grains/SCF		0.03
Sulfur Dioxide, PPM (V)		212
Temperature, °F		125
Pressure, PSIA		14.46

To recover 125 MMSCFD of carbon dioxide it is necessary to treat approximately 26 percent of the flue gas exit the sulfur scrubbers. This is slightly more than the output of one of the four parallel units used to treat the flue gas from the 917 megawatt power station (five units are installed including a spare).

The following sections contain a detailed description of the process for recovering carbon dioxide from flue gas using MEA scrubbing. For convenience this description has been divided into the following sections:

- \* Carbon Dioxide Recovery
- \* MEA Recovery (Proposed)
- \* Compression and Drying
- \* Gas Transmission
- \* Utility Systems
- \* Environmental Considerations

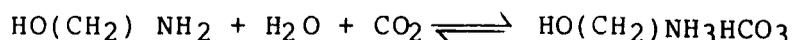
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ambient 14.31 psia

Reference should be made to process flow diagram P-4636-D (figure VI-2) which further depicts the process described in the following sections.

### Carbon Dioxide Recovery

Carbon dioxide is recovered from the flue gas by use of a 20 weight percent aqueous solution of MEA. Flue gas at the inlet of the treatment facilities, after previous bulk sulfur oxides removal, is at 125°F and 14.46 psia. To overcome pressure loss created by the MEA absorption tower, the flue gas is first compressed to about 16.0 psia before it enters the tower. The absorption tower is 46.5 feet in diameter and contains 25 perforated trays including four water wash trays at the top which are included to reduce MEA losses. As the flue gas passes through the absorption tower, the carbon dioxide is removed by reacting with the MEA solution according to the following reversible reaction.



The forward reaction, taking place in the absorber, is favored by moderate operating temperatures in the range of 100-175°F.

Spent MEA solution loaded with carbon dioxide flows from the bottom of the absorber to a transfer pump which transfers the solution to the top of the regenerator tower. A mechanical filter operating on about 25 percent of the spent solution is provided to remove solids such as pipe scale, fly ash, and degradation products from the solution.

Before entering the regenerator the spent solution is heat exchanged against the regenerated MEA solution from the bottom of the regenerator tower.

The regenerator tower is 39.5 feet in diameter contains 22 perforated trays including four wash trays and operates at about 10.5 psig at the bottom of the tower. A steam heated reboiler supplies the necessary heat input to the regenerator. Elevated temperature combined with steam stripping in the regenerator favors the reverse of the reaction which takes place in the absorber, thus affecting regeneration of the MEA solution.

A kettle reboiler with total solution vaporization is provided to achieve a high degree of concentration for the MEA solution, which is sent to MEA recovery (see later discussion).

Carbon dioxide is stripped from the MEA solution and passes through a condenser (at the overhead of the regenerator tower) where the bulk of the water is condensed. Most of the water is returned to the regenerator as reflux. Some flows to the absorber wash trays which include a pump-around system. The excess is pumped to disposal. Excess water results from cooling the water saturated flue gas in the absorber.

MEA solution from the bottom of the regenerator tower is cooled by heat exchange, first against the spent MEA from the absorber tower, and finally against cooling water before flowing to the top of the absorber.

The system includes a sump used for chemical mixing and for collecting drips and spills which occur during operation. Facilities are also provided for MEA storage during initial charging of the system and during shutdowns. Facilities are also required to recover MEA which has reacted with sulfur dioxide present in the flue gas. These are discussed in the next section.

#### MEA Recovery (Proposed)

Solution losses occur in amine systems due to formation of degradation products which are stable at the conditions employed for regeneration of the MEA solution. They also occur due to vaporization of MEA in the absorber and regenerator (wash trays are provided to minimize vaporization losses), and by leaks and spills from the system.

Formation of degradation products may occur for a number of reasons such as overheating the solution and chemical reaction of the amine with a component in the gas being scrubbed. In the present case of a flue gas from a coal fired power plant, MEA will react with the residual sulfur oxides (and may also react with the residual oxygen[4]) to form stable degradation products.

The usual method of controlling degradation products in an MEA system is by the installation of a reclaimer. Degradation products are concentrated in the liquid by boiling and are removed periodically from the reclaimer for disposal. Sodium carbonate or caustic is sometimes added to the reclaimer to enhance MEA recovery and/or prevent corrosion[5].

For the present system operating on flue gas, the quantity of potential degradation products formed by the reaction of MEA with sulfur oxides is of such a magnitude that a somewhat different approach is needed to recover the MEA solution. Addition of a compound to the solution which is a stronger base than MEA will liberate MEA from its thermally stable reaction product with sulfur oxides. Either caustic or sodium carbonate will serve this purpose. Because the quantity of sulfur oxides remaining in a flue gas, even after bulk removal, will tie up significant quantities of the MEA, a continuous reclaiming process is proposed.

In this process of reclamation, sodium carbonate is preferred because sodium hydroxide will displace MEA from its reaction product with carbon dioxide equally as well as from its undesirable degradation products. This would lead to high and unnecessary caustic consumption.

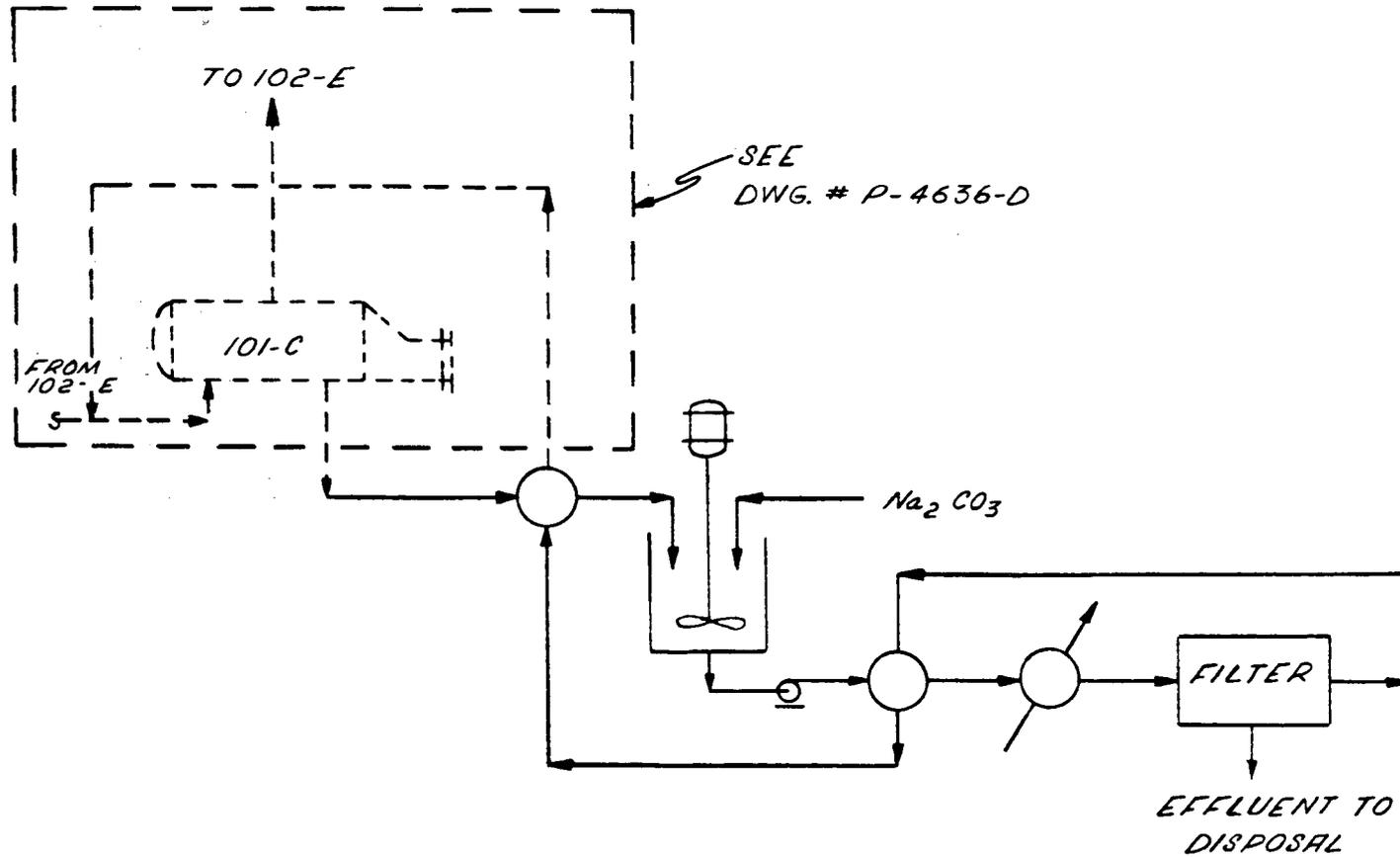
Figure VI-1 shows the type of recovery process proposed. A slipstream of MEA solution is withdrawn from the regenerator reboiler and cooled by heat exchange against the reclaimed solution returning to the reboiler. Sodium carbonate is added to the solution (see chemical summary) in a mixtank which also serves as a holdtank for the mixture. Thus, residence time is provided for the dissociation reactions to liberate the MEA. Solution from the mixtank is cooled to effect precipitation of sodium sulfate and sodium sulfite which are removed in a filter along with other degradation products. Purified MEA solution is returned to the system.

The proposed MEA recovery system is not well enough defined at this time for an estimate of its cost to be included in this study. Additional work, including laboratory study, is believed necessary to prepare a final design for such a system.

#### Compression and Drying

Carbon dioxide is delivered to the compression step at about 5 psig and 110°F saturated with water vapor. It is compressed in a three case centrifugal compressor powered by a steam turbine to a final discharge pressure of 2,200 psig for delivery to the gas pipeline. As the gas is compressed and cooled between stages, water condenses and is removed in knockout vessels. Between the second and third case the gas is dried to final pipeline quality by use of a triethylene glycol dryer.

FIG. VI-1  
CONTINUOUS MEA RECOVERY  
WITH  
SODIUM CARBONATE



### Gas Transmission

Transport of the recovered carbon dioxide to the candidate oil-field is by pipeline operating in the supercritical state. A twenty-five mile pipeline is assumed because it is felt that this potential source of carbon dioxide will be attractive only if the high costs associated with recovery are offset by low transportation costs. For a 200 psig pressure loss, a twelve (12) inch nominal pipe diameter is required for this case. Additional features of the pipeline which are common to all pipelines included in this study are discussed in Section V of this report (Page 30).

### Utility System

Utilities (presented later in this section) are based on use of steam driven turbines for the carbon dioxide compressor and flue gas blowers, and electric drives for all remaining rotating equipment. Small additional steam requirements are also included for regeneration of the glycol solution in the triethylene glycol dryer.

Two steam pressure levels were selected. Steam imported from offsite is assumed available at 900 psig - 900°F (identical import steam conditions were selected for all cases in this study). A second level at 175 psig supplies heat to the amine reboiler through a letdown station to 150 psig.

The turbine drivers for the carbon dioxide compressor and flue gas blowers are both driven by the 900 psig steam and exhaust to the 175 psig header. The exhaust steam from the turbines provides most of the amine reboiler heat; however, some additional 900 psig letdown to the 175 psig level is required. A desuperheat station is provided at the inlet of the amine reboiler. The 150 psig steam condensate returns to battery limits from the amine reboiler.

Cooling water is assumed available at battery limits at 90°F.

### Environmental Considerations

Effluent streams will be produced during normal operation of the recovery and gas transmission facilities. The following is a brief discussion of the expected effluent streams, and possible methods of handling them. Costs for treatment facilities are not included in plant investment.

Excess water will be produced in the recovery plant by condensation of water vapor from the flue gas as it passes through the MEA absorber. This effluent stream will be relatively clean. It will contain dissolved carbon dioxide plus traces of other gaseous components absorbed from the raw flue gas and also a small amount of dissolved MEA. This water can be reused in a process plant, usually after stream stripping, for boiler feedwater makeup or as makeup water to a cooling tower. Stripper overhead rich in MEA can be recycled to the process.

Because the process for MEA recovery using sodium carbonate is not fully defined, it is impossible to define in detail the effluent expected from the process. The major component should be sodium sulfite with perhaps some sodium sulfate. If a crystallization process is used, the product could be reasonably pure. The degree of purification could be improved (as necessary) by further processing such as recrystallization or washing.

Water will be produced from the product gas as it is compressed and cooled between stages. This water can be combined with the excess water from the MEA system for disposal.

Regeneration of the triethylene glycol solution in the TEG dryer will produce a gaseous effluent consisting mostly of water vapor plus traces of TEG. This effluent stream can be vented to the atmosphere.

C. PROCESS FLOW DIAGRAM

Process flow diagram P-4636-D (figure VI-2) for recovery of carbon dioxide from a coal-fired power plant flue gas is presented on the following page.



D. MATERIAL BALANCE

On the following page a material balance for recovery of 125 MMSCFD of carbon dioxide from a coal-fired power plant flue gas is presented.

MATERIAL BALANCE

CARBON DIOXIDE

FROM POWER PLANT

FLUE GASES

<u>STREAM NO. AND SOURCE</u>	<u>COMPONENT</u>	<u>LB MOL/HR</u>	<u>LBS/HR</u>
(1) Gas to Absorber	CO <sub>2</sub>	15,318.2	674,154
	NO <sub>2</sub>	60,089.6	1,683,290
	O <sub>2</sub>	5,239.4	167,656
	SO <sub>2</sub>	19.8	1,268
	Dry Gas	80,667.0	2,526,368
	H <sub>2</sub> O	12,391.5	223,223
	Total	93,058.5	2,749,601
(2) Gas from Absorber	CO <sub>2</sub>	1,591.8	70,055
	N <sub>2</sub>	60,089.6	1,683,290
	O <sub>2</sub>	5,239.4	167,656
	Dry Gas	66,920.8	1,921,001
	H <sub>2</sub> O	6,470.2	116,561
	Total	73,391.0	2,037,562
(3) Lean Soln	MEA	37,404.1	2,284,642
	H <sub>2</sub> O	507,275.5	9,138,568
	CO <sub>2</sub>	3,740.4	164,615
	Total	548,420.0	11,587,825
(4) Rich Soln	MEA	37,404.1	2,284,642
	H <sub>2</sub> O	516,136.9	9,298,206
	CO <sub>2</sub>	17,467.9	768,762
	SO <sub>2</sub>	19.8	1,268
	Total	571,028.7	12,352,878
(5) Stripper Vent (Compressor Feed)	CO <sub>2</sub>	13,724.6	604,020
	H <sub>2</sub> O	1,046.8	19,372
	Total	14,771.4	623,392
(6) Excess Water	CO <sub>2</sub>	1.8	79
	H <sub>2</sub> O	4,894.3	88,171
	Total	4,896.1	88,250
(7) CO <sub>2</sub> Product Gas (125 MMSCFD)	CO <sub>2</sub>	13,724.6	604,020
	H <sub>2</sub> O	0.7	13
	Total	13,725.3	604,033

E. CHEMICAL, UTILITY, ECONOMIC SUMMARIES

This section includes the following tables:

Table VI-1    Chemical Summary

Table VI-2    Utility Summary

Table VI-3    Economic Summary

TABLE VI-1

CHEMICALS SUMMARY FOR RECOVERY OF  
CARBON DIOXIDE FROM POWER PLANT FLUE GASES

	<u>Initial Charge-lbs</u>	<u>Est. Annual Consumption-lbs**</u>	<u>Unit Cost ¢/lb</u>	<u>Annual Cost \$</u>	<u>Cost ¢/MSCF CO<sub>2</sub></u>
<u>I. Recovery Plant</u>					
MEA	480,000	460,000	38.00	174,800	0.41
Na <sub>2</sub> CO <sub>3</sub>	-	17,128,000	4.50	770,760	1.81
Misc.*	-	-	-	<u>10,000</u>	<u>0.02</u>
Sub-Total				955,560	2.24
<u>II. Transmission System</u>					
TEG	24,000	80,000	35.00	28,000	0.07
Misc.*	-	-	-	<u>10,000</u>	<u>0.02</u>
Sub-Total				38,000	0.09
TOTAL COST				993,560	2.33

\*Includes antifoam for MEA and other miscellaneous consumables, such as lubricants, for either system.

\*\*Basis is 340 days/year at 125 MMSCFD CO<sub>2</sub> recovery.

TABLE VI-2

UTILITY SUMMARY FOR RECOVERY OF  
CARBON DIOXIDE FROM POWER PLANT FLUE GASES

The following are expected utility consumptions for the recovery plant and gas transmission systems when 125 MMSCFD of CO<sub>2</sub> is being transmitted.

	Consumption per MSCF OF CO <sub>2</sub>	
	<u>Recovery*</u> <u>Plant</u>	<u>Transmission</u> <u>System</u>
Electric Power, KWH	0.384	-
Cooling Water Circulation - M Gallons 90°F - 120°F	1.037	0.104
Steam - 900 PSIG & 900°F, MLBS	0.075	0.161
175 PSIG & 600°F, MLBS	0.161	(0.161)

\* Excludes utilities for unit to recover MEA

( ) Export Quantity

TABLE VI-3

ECONOMIC SUMMARY  
CARBON DIOXIDE FROM POWER PLANT FLUE GAS  
PLANT CAPACITY: 125 MMSCFD CO<sub>2</sub>

A. RECOVERY COSTS

Fixed-Capital Investment      \$34,040,000

<u>DIRECT COSTS</u>	<u>Units/ MSCF</u>	<u>Unit Cost \$</u>	<u>Cost ¢/ MSCF CO<sub>2</sub></u>
Electric Power - KWH	0.384	0.035	1.34
Cooling Water (circ) - MGAL	1.037	0.020	2.05
Steam-900 PSIG & 900°F - MLBS	0.075	2.80	21.00
-175 PSIG & 600°F - MLBS	0.161	2.74	44.11
Chemicals	-	-	<u>2.24</u>
Sub-Total Direct Costs			70.74
 <u>INDIRECT COSTS</u>			
Operating Labor - 1 man/shift			0.13
Operating Supplies - 30% Operating Labor			0.04
Supervision and Overhead - 100% Operating Labor			0.13
Maintenance Labor & Supplies - 3.5% Investment/Year			2.80
Capital Related Costs - Depreciation, Interest Charges, Taxes, Insurance, Return on Investment - @ 38% of Investment/Yr.			<u>30.44</u>
Sub-Total Indirect Costs			33.54
Total Recovery Cost ¢/MSCF			104.28

NOTES Recovery and Transmission Costs

- All operating labor \$6.5/manhour.
- Breakdown of capital related costs:
 

Depreciation	10%
Interest Charges	5%
Taxes and Insurance	3%
Return on Investment	<u>20%</u>
	38%
- Onstream Factor                      340 days/year
- Plant Investment does not include power generation, cooling tower or boiler feedwater treatment, or costs of equipment to recover MEA. It does include initial charge of chemicals.
- Steam cost based on coal fired steam boiler, and coal price of 50 ¢/MM BTU LHV.

TABLE VI-3 (CONTD.)

ECONOMIC SUMMARY  
CARBON DIOXIDE FROM POWER PLANT FLUE GAS  
PLANT CAPACITY: 125 MMSCFD CO<sub>2</sub>

B. TRANSMISSION COSTS

Compression Investment	\$ 9,660,000		
Pipeline Investment (25 miles)	9,490,000		
Fixed-Capital Investment	<u>\$19,150,000</u>		
	<u>Units/</u>	<u>Unit</u>	<u>Cost ¢/</u>
<u>DIRECT COSTS</u>	<u>MSCF</u>	<u>Cost \$</u>	<u>MSCF CO<sub>2</sub></u>
Cooling Water (circ) - MGAL	0.104	0.02	0.21
Steam-900 PSIG & 900°F - MLBS	0.161	2.80	45.08
-175 PSIG & 600°F - MLBS	(0.161)	2.74	(44.11)
Chemicals			<u>0.09</u>
Sub-Total Direct Costs			1.27
( ) Denotes Export			
<u>INDIRECT COSTS</u>			
Operating Labor - 2 men/shift			0.27
Operating Supplies - 30% Operating Labor			0.08
Supervision and Overhead - 100% Operating Labor			0.27
Maintenance Labor & Supplies - 3.5% Investment/Year			1.58
Capital Related Costs - Depreciation, Interest Charges, Taxes, Insurance, Return on Investment - @ 38% of Investment/Yr.			<u>17.12</u>
Sub-Total Indirect Costs			19.32
Total Transmission Cost ¢/MSCF (25 miles)			20.59
C. <u>TOTAL RECOVERY AND TRANSMISSION COST</u>			
1. Recovery Costs			104.28
2. Transmission Costs (25 miles)			<u>20.59</u>
Total Recovery and Transmission Costs			124.87

NOTES - SECTION VI - CARBON DIOXIDE FROM LOW PURITY STACK GASES

- [1] Pappano, A. W., et al, "Availability and Economics of CO<sub>2</sub> For Enhanced Oil Recovery in Appalachia", Final Report to the United States ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION", Grant #G0155014, August 1976.
- [2] "Gas Conditioning Fact Book", The Dow Chemical Company, 1962, pg. 145.
- [3] Pullman Kellogg Job 5202-02, Location furnished with client permission.
- [4] Kohl, A. L., Riesenfeld, F. C., Gas Purification, Second Edition, 1974, pg. 101-112.
- [5] Ibid.

## VII. CARBON DIOXIDE FROM NATURALLY OCCURRING SOURCES

### A. INTRODUCTION

A prime example of the use of carbon dioxide from natural sources is the ongoing SACROC (Scurry Area Canyon Reef Operation Committee) project in West Texas.[1] Natural gas wells in the Val Verde basin with carbon dioxide contents of 18-53 percent were selected to supply the carbon dioxide for the project, as they were considered the only reliable and economical supply for the carbon dioxide volumes required.

The natural gas is supplied through four major treatment plants which include sulfur removal and carbon dioxide recovery processes. From these four plants up to 240 MMSCFD of carbon dioxide has been made available to the project since early 1972. A 16-inch pipeline conducts the high pressure carbon dioxide some 200 miles to the Kelly-Snyder field in Scurry County.

As discussed in Section III of this report, no exhaustive survey of naturally occurring carbon dioxide wells has been made to date. Some information concerning location of naturally occurring carbon dioxide wells in the thirteen states surveyed is available, and was presented in Figure III-5.

Bureau of Mines data sheds additional light on the location of known sources and purity[2]. It is anticipated that exploration currently under way by a number of oil companies in the Rocky Mountain areas will add to the known reserves picture in this area. (See Section VIII which contains recommendations for future study of natural sources of carbon dioxide.)

In spite of the current lack of published information concerning the supply situation, carbon dioxide from natural sources will almost certainly be a significant source of supply in future EOR efforts. In an effort to develop costs related to this important source of supply, this report has considered the following four hypothetical cases for potential sources of naturally occurring carbon dioxide.

- Case I - 98% CO<sub>2</sub>, 2% Hydrocarbons
- Case II - 96% CO<sub>2</sub>, 2% Hydrocarbons, 2% H<sub>2</sub>S
- Case III - 50% CO<sub>2</sub>, 50% Hydrocarbons
- Case IV - 48% CO<sub>2</sub>, 50% Hydrocarbons, 2% H<sub>2</sub>S

Compositions for Cases I and III are intended to approximate the quality of carbon dioxide sources which are known to exist in states surveyed by this study. Possible contamination of such sources is allowed for by assuming two percent hydrogen sulfide levels for each case.

In the course of this study a number of processes were considered for recovery and purification of carbon dioxide from natural sources as represented by the hypothetical cases II through IV (Case I is acceptable as is and requires only compression and drying).

For Case II a simple one step treatment process based on the British Gas Council's Stretford process was selected for study. Vendors offering the Stretford process advise that carbon dioxide interferes with hydrogen sulfide removal by the process and that current design experience is limited to carbon dioxide partial pressures in the gas of about one atmosphere. Unfortunately this feedback of information was not received until late in the study. It is felt that because of the hypothetical nature of the gas composition, further expense to investigate this case is not warranted at this time. Thus, Case II will not be given further consideration in this report.

The Selexol process, a physical absorbent process, was selected as being an attractive process for treatment and recovery of carbon dioxide in Cases III and IV. In Case IV, the Stretford process was selected to remove hydrogen sulfide (and recover the sulfur) from a gas stream containing approximately 75 percent carbon dioxide which leaves the Selexol process. This is possible in this particular case since the gas stream is at low pressure, and the partial pressure of carbon dioxide is within the acceptable design range.

For all cases studied in this section, 125 MMSCFD of carbon dioxide is produced at a purity of 98 percent minimum. Allowable hydrogen sulfide level in the carbon dioxide is set at 1/4 grain per 100 SCF. The raw gas is assumed available at the battery limits of the treatment plant at 250 psig and ambient temperature (75°F). After recovery the carbon dioxide is compressed, dried, and delivered to a candidate oilfield 100 miles away at a wellhead pressure of 2,000 psig.

## B. CASE I

### 1. Process Description

#### Introduction

In the first hypothetical case of naturally occurring carbon dioxide, the gas is assumed to contain 98 percent carbon dioxide and 2 percent hydrocarbon (methane). In this case the gas from the source wells meets the established purity requirements for the carbon dioxide and no gas treatment section is required. The processing steps reduce simply to drying and compression of the carbon dioxide and its delivery to a candidate oilfield.

The process description for Case I which follows may be divided into the following sections:

- \* Drying and Compression
- \* Gas Transmission
- \* Utility Systems
- \* Environmental Considerations

Reference should be made to process flow diagram P-825-A (Figure VII-1) which further depicts the process described in the following sections.

#### Drying and Compression

A single case centrifugal compressor powered by a steam turbine compresses the carbon dioxide from 250 psig and 75°F to a final discharge pressure of 2200 psig for injection into the gas pipeline. Before the gas is compressed it is dried in a triethylene glycol dryer.

#### Gas Transmission

After drying and compression, the carbon dioxide is transported to the candidate oilfield in the gaseous state at supercritical pressure.

A sixteen-inch nominal pipe diameter pipeline is required for this case, and for all the hypothetical cases assumed for naturally occurring carbon dioxide based on a pipeline length of 100 miles and 200 psig pressure loss through the pipeline. Further features of the pipeline which are common to all pipelines in this study are discussed in Section V of this report.

### Utility Systems

Utilities for Case I are based on use of a steam turbine driver for the carbon dioxide compressor. Steam imported from offsite is assumed available at 900 psig - 900°F. A condensing turbine exhausting to four inches mercury vacuum is utilized. Small additional steam requirements are included for regenerating the triethylene glycol dryer.

Power requirements for this case will be small and are essentially associated with the glycol circulation pumps.

Cooling water is assumed available at 90°F.

### Environmental Considerations

The only effluent stream expected for this case is the overhead vapors from the triethylene glycol dryer.<sup>1</sup> This can be vented to the atmosphere since it is essentially water vapor plus trace amounts of TEG.

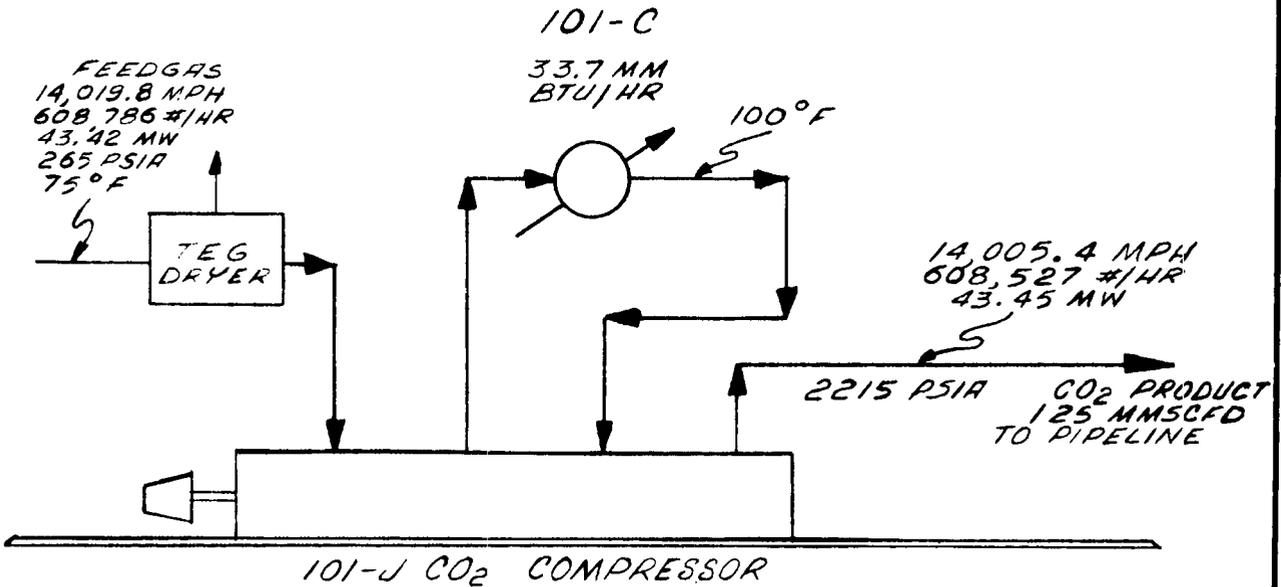
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<sup>1</sup>In this report it is assumed that transmission of the carbon dioxide product is environmentally acceptable. It is thus not considered to be an effluent stream in this discussion.

2. Process Flow Diagram

Process flow diagram P-825-A (figure VII-1) for Case I, Carbon Dioxide Recovery From A Naturally Occurring Source is presented on the following page.

# FIGURE VII-1



					ENGINEERED:	<b>THE M. W. KELLOGG COMPANY</b> a division of PULLMAN INCORPORATED			
					RELEASED FOR DESIGN:	U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION			
					DATED:	125 MMSCFD CO <sub>2</sub> FROM NATURAL SOURCES CONTAINING 98% CO <sub>2</sub> - 2% METHANE - CASE I			
					SCALE:	<b>PROCESS FLOW DIAGRAM</b>			
					DRAWN:				
					CHECKED:				
					APPROVED:				
					DATED:				
					ISSUED FOR FABRICATION	J-5236-01		P-825-A	
NO	DESCRIPTION	DATE	BY	CHECKED	APPROVED	CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER

3. Material Balance

A material balance for Case I, Carbon Dioxide Recovery From A Naturally Occurring Source is presented on the following page.

MATERIAL BALANCE  
CARBON DIOXIDE  
FROM NATURAL SOURCES  
CONTAINING  
98% CARBON DIOXIDE - 2% HYDROCARBON

<u>STREAM NO. AND SOURCE</u>	<u>COMPONENT</u>	<u>LB MOL/HR</u>	<u>LBS/HR</u>
(1) Gas to Compressor	CO <sub>2</sub>	13,724.6	604,020
	CH <sub>4</sub>	280.1	4,494
	Dry Gas	<u>14,004.7</u>	<u>608,514</u>
	H <sub>2</sub> O	15.1	272
	Total	<u>14,019.8</u>	<u>608,786</u>
(2) CO <sub>2</sub> Product Gas (125 MMSCFD)	CO <sub>2</sub>	13,724.6	604,020
	CH <sub>4</sub>	280.1	4,494
	Dry Gas	<u>14,004.7</u>	<u>608,514</u>
	H <sub>2</sub> O	0.7	13
	Total	<u>14,005.4</u>	<u>608,527</u>

4. Chemical, Utility, Economic Summaries

This section includes the following tables:

Table VII-1 Chemical Summary

Table VII-2 Utility Summary

Table VII-3 Economic Summary

TABLE VII-1

CHEMICALS SUMMARY FOR RECOVERY OF  
 CARBON DIOXIDE FROM NATURAL RESOURCES  
 CONTAINING 98% CARBON DIOXIDE - 2% HYDROCARBON

	<u>Initial Charge-lbs</u>	<u>Est. Annual Consumption-lbs**</u>	<u>Unit Cost ¢/lb</u>	<u>Annual Cost \$</u>	<u>Cost ¢/MSCF CO<sub>2</sub></u>
I. <u>Transmission System</u>					
TEG	24,000	80,000	35.00	28,000	0.07
Misc.*	-	-	-	<u>10,000</u>	<u>0.02</u>
TOTAL COST				38,000	0.09

\*Includes other consumables such as lubricants.

\*\*Basis is 340 days/year at 125 MMSCFD CO<sub>2</sub> recovery.

TABLE VII-2

UTILITY SUMMARY FOR RECOVERY OF  
CARBON DIOXIDE FROM NATURAL SOURCES  
CONTAINING 98% CARBON DIOXIDE - 2% HYDROCARBON

The following are expected utility consumptions for the recovery plant and gas transmission systems when 125 MMSCFD of CO<sub>2</sub> is being transmitted.

	Consumption per MSCF OF CO <sub>2</sub>
	Transmission System
Electric Power, KWH	0.01
Cooling Water Circulation - M Gallons 90°F - 120°F	0.116
Steam - 900 PSIG & 900°F, MLBS	0.025

TABLE VII-3

ECONOMIC SUMMARY  
 CARBON DIOXIDE FROM NATURAL SOURCES  
 CONTAINING 98% CARBON DIOXIDE - 2% HYDROCARBON  
 PLANT CAPACITY 125 MMSCFD CO<sub>2</sub>

A. TRANSMISSION COSTS

Compression Investment	\$ 4,370,000
Pipeline Investment (100 miles)	\$58,540,000
Fixed-Capital Investment	<u>\$62,910,000</u>

<u>DIRECT COSTS</u>	<u>Units/ MSCF</u>	<u>Unit Cost \$</u>	<u>Cost ¢/ MSCF CO<sub>2</sub></u>
Electric Power - KWH	0.010	0.035	0.04
Cooling Water (circ) - MGAL	0.116	0.020	0.23
Steam-900 PSIG & 900°F - MLBS	0.025	3.800	9.50
Chemicals	-	-	<u>0.09</u>
Sub-Total Direct Costs			9.86
 <u>INDIRECT COSTS</u>			
Operating Labor - 2 men/shift			0.27
Operating Supplies - 30% Operating Labor			0.08
Supervision and Overhead - 100% Operating Labor			0.27
Maintenance Labor & Supplies - 3.5% Investment/Year			5.18
Capital Related Costs - Depreciation, Interest Charges, Taxes, Insurance, Return on Investment - @ 38% of Investment/Yr.			56.25
Sub-Total Indirect Costs			62.05
Total Transmission Cost ¢/MSCF (100 miles)			71.91

NOTES Transmission Costs

- All operating labor \$6.5/manhour.
- Breakdown of capital related costs:
 

Depreciation	10%
Interest Charges	5%
Taxes and Insurance	3%
Return on Investment	<u>20%</u>
	38%
- Onstream Factor 340 days/year
- Plant Investment does not include power generation, cooling tower or boiler feedwater treatment.
- Steam cost based on gas fired steam boiler. Gas cost \$2.00/MSCF delivered.

## C. CASE III

### 1. Process Description

#### Introduction

The third hypothetical gas stream considered as a naturally occurring carbon dioxide source is assumed to be composed of 50 percent carbon dioxide and 50 percent hydrocarbon (methane). A number of different processes, including both chemical reactive and physical absorption systems, have been considered for recovery and purification of the carbon dioxide.

Chemical reactive absorbent systems utilize basic compounds which, in aqueous solutions, react reversibly with acidic constituents in a sour gas stream such as hydrogen sulfide or carbon dioxide. Soluble sulfide and carbonate salts are formed by these reactions in the absorber and these salts are thermally decomposed and the acid gases released in the stripper column. Compounds which are normally employed as absorbents in such systems include ethanolamines, and promoted carbonates (primarily potassium carbonate). Of the chemical reactive processes, monoethanolamine is particularly well suited for acid gas removal when the gas is available at low pressure. An MEA process was selected for carbon dioxide recovery from power plant flue gas as discussed in Section VI of this report.

Physical absorbents are primarily neutral organic compounds containing minimal quantities of water and other ingredients. Absorption of the acid gases depends on their solubilities in these compounds. As such, physical absorption systems are particularly well suited to feed gas streams where the acid gases are present at high partial pressures and where moderate carbon dioxide leakages (one percent) can be tolerated in the treated gas. Because there is no chemical reaction between the acid gas and the solvent in physical absorption systems, the solvent can be regenerated by simply flashing the absorbed acid gas from the solvent at reduced pressure. Thus, no reboiler heat input is required to regenerate the solvent.

Since no regeneration heat is required to regenerate the solvent, a physical absorbent system operates at lower temperatures as compared to a chemical system. For a noncorrosive solvent this allows the system to be constructed of non-alloy steel throughout. Thus, physical absorbent systems may be considered to offer capital savings as well as energy savings for treatment of gas streams such as proposed in this case. These were the main criteria used for selection of a physical solvent process for this hypothetical case of naturally occurring carbon dioxide.

One physical solvent process with extensive development and commercial experience is the Selexol process offered by Allied Chemical. Selexol is Allied's trademark for the dimethyl ether of polyethylene glycol. The investment costs and operating utilities presented later for this case as well as the process description which follows are based on a system designed in accordance with Allied's Selexol process.

The process description for Case III may be divided into the following sections:

- \* Carbon Dioxide Recovery
- \* Compression and Drying
- \* Gas Transmission
- \* Utility Systems
- \* Environmental Considerations

Reference should be made to process flow diagram P-4693-D (figure VII-2) which further depicts the process described in the following sections.

#### Carbon Dioxide Recovery

Naturally occurring carbon dioxide containing 50 percent carbon dioxide and 50 percent hydrocarbon (methane) and saturated with water vapor is available at the battery limits of the recovery plant at 265 psia and 75°F. The gas is first cooled by cross exchange against the absorber overhead gas. This serves to recover some of the refrigeration required in the process and tends to lower the absorber operating temperature which aids absorption. Removal of the carbon dioxide in the feed gas takes place in a conventional, counter-current, packed absorption column. The carbon dioxide and a minimal amount of methane dissolve in the solvent. The methane product gas exiting this absorber contains only 2.3 percent carbon dioxide and is essentially dry. Over 97.7 percent of the total methane is recovered in the overhead product stream.

Solvent regeneration and the corresponding carbon dioxide recovery takes place in a series of pressure reduction flashes. The loaded rich solution existing the absorber bottom is first flashed from 265 psia to about 150 psia through a hydraulic turbine. This turbine is connected to the lean solution circulation pumps and serves to recover pumping energy. This keeps the net process energy requirements to a minimum.

Some methane is picked up by the solvent in the absorber along with the carbon dioxide. As the methane is the less soluble component, it will preferentially desorb in this first flash. The methane rich vapor from this drum is recompressed (the heat of compression is removed by interchange with another downstream flashed vapor stream) and recycled back to the absorber. This recycle assists in reducing the methane losses from the absorber overhead and increases the final product purity. The pressure level in this recycle drum is selected to ensure that product purity would meet the 98 percent specification.

The liquid stream exiting the recycle drum is further regenerated by two successive adiabatic flashes, one at 85 psia, followed by another at 20 psia. The pressure letdown to each drum is accomplished through hydraulic turbines for energy recovery. The vapor streams from these two flash drums constitute the bulk of the total product stream. The vapor from the 85 psia flash is fed directly to the carbon dioxide product compressor. The vapor from the 20 psia flash is first used to cool the compressed gas stream being recycled to the absorber, and then it too is directed to the compressor. The two flash drum pressures were selected to interface efficiently with the product compressor design to yield minimum compression costs.

Over 84 percent of the total carbon dioxide product is recovered from the solvent in the first two flash drums. However, to achieve the carbon dioxide leakage specified in the absorber overhead, a lean solution is required which cannot be obtained simply by atmospheric flashing. Consequently, the solution regeneration is completed (and the remaining carbon dioxide is recovered) in a flash operation at 5 psia. The lean solvent exiting this flash drum is pumped back to the top of the absorber to complete the cycle. A refrigeration unit on this stream maintains the overall process heat balance and provides a cold lean solution to enhance the absorption operation. The carbon dioxide vapor stream exiting the final flash drum goes to the product compressor where it is compressed and combined with the previous flash vapor streams.

#### Compression and Drying

Carbon dioxide is delivered to the product compressor at three different pressure levels from the process. A three-case, six-stage centrifugal compressor powered by a steam turbine is used to compress the flashed product gases to the final discharge

pressure of 2,200 psig. Intercoolers are provided to remove the heat of compression and a triethylene glycol dryer is located between stages on the third case. It will dry the gas to pipeline specifications. A total of 125 MMSCFD of carbon dioxide is delivered to the pipeline at 98 percent purity.

#### Gas Transmission

After compression, the gas is transmitted to the candidate oil-field through a sixteen-inch nominal diameter pipeline. Additional features of the gas transmission pipeline are discussed in Section V of this report.

#### Utility Systems

Utilities for Case III are based on use of a steam turbine driver for the carbon dioxide compressor and electric drives for all remaining equipment. Steam imported from offsite is assumed available at 900 psig - 900°F. A condensing turbine exhausting to four inches mercury vacuum is utilized. Small additional steam requirements are included for regenerating the triethylene glycol dryer.

Cooling water is assumed available at 90°F.

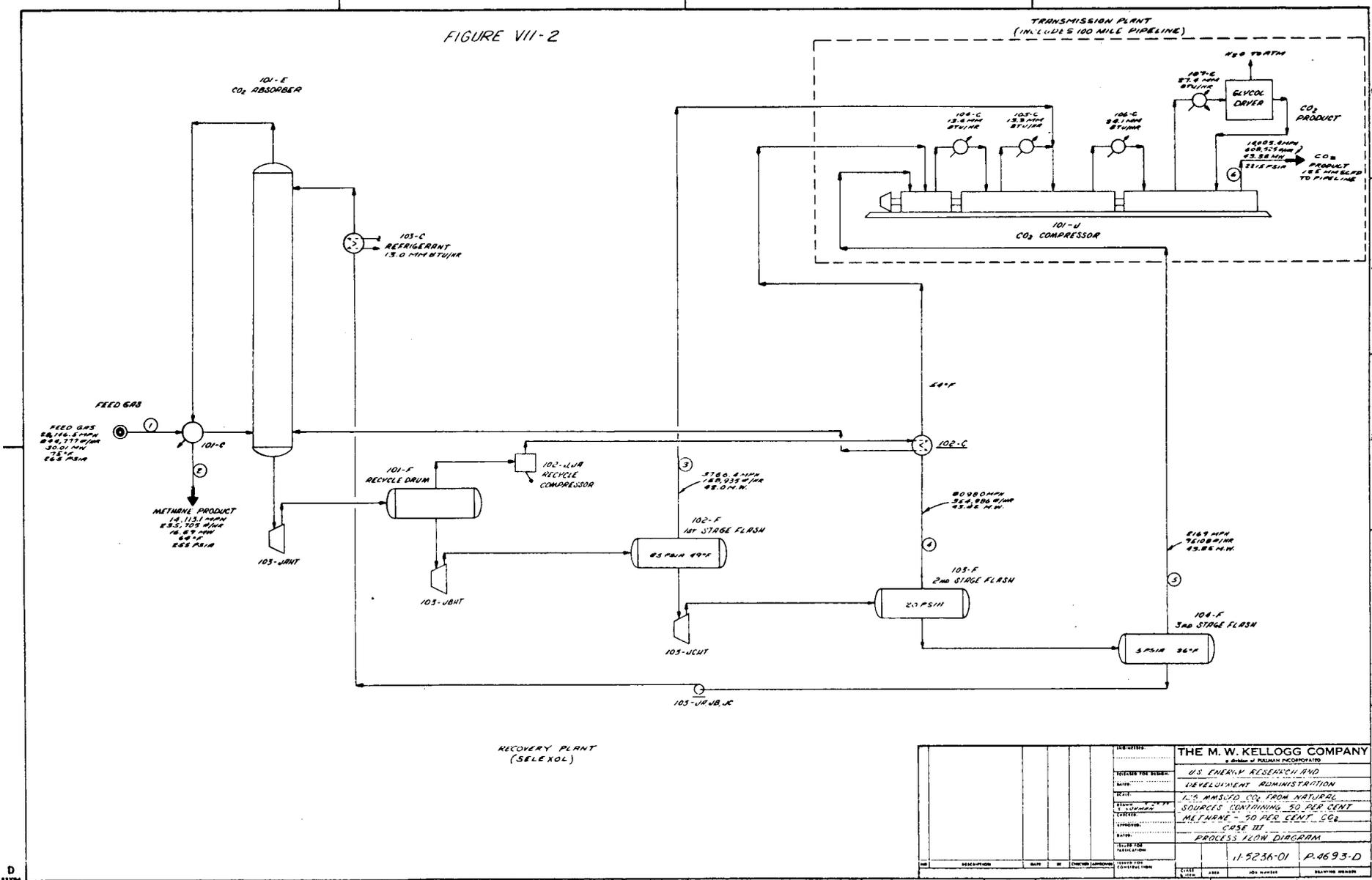
#### Environmental Considerations

The only effluent streams expected for this case are vapors from the triethylene glycol dryer and the product methane gas. Vapors are produced during regeneration of the glycol solution and can be vented to the atmosphere since they are essentially water vapor plus trace amounts of TEG. The methane product gas would be expected to be highly marketable especially in the quantity available from the treatment facility (128 MMSCFD). It is assumed here that this gas can be transmitted in the usual manner for natural gas and would not be a problem. (See also discussion of environmental considerations for Case I).

2. Process Flow Diagram

Process flowsheet P-4693-D (figure VII-2) for Case III, Carbon Dioxide Recovery From A Naturally Occurring Source is presented on the following page.

FIGURE VII-2



RECOVERY PLANT  
(SELEXOL)

TRANSMISSION PLANT  
(INCLUDES 100 MILE PIPELINE)

THE M. W. KELLOGG COMPANY a Division of FULFLEX INCORPORATED							
PROJECT FOR REVIEW:	US ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION						
DATE:							
TITLE:	U.S. AMENDED CO <sub>2</sub> FROM NATURAL SOURCES CONTAINING 50 PER CENT METHANE - 50 PER CENT CO <sub>2</sub>						
DATE:							
TITLE FOR PUBLICATION:	CASE III PROCESS FLOW DIAGRAM						
NO.	11-5236-01 P. 0693-D						
DESCRIPTION	DATE	BY	PROJECT NUMBER	DATE FOR COMPLETION	SCALE	APP. NUMBER	SCALE NUMBER

D H G F E D C B A

3. Material Balance

A material balance for Case III, Carbon Dioxide Recovery from a Naturally Occurring Source is presented on the following page.

MATERIAL BALANCE  
CARBON DIOXIDE  
FROM NATURAL SOURCES  
CONTAINING  
50% CARBON DIOXIDE  
50% METHANE

<u>STREAM NO. AND SOURCE</u>	<u>COMPONENT</u>	<u>LB MOL/HR</u>	<u>LBS/HR</u>
(1) Feed Gas to Absorber	CO <sub>2</sub>	14,058.1	618,697
	CH <sub>4</sub>	14,058.1	225,534
	Dry Gas	28,116.2	844,231
	H <sub>2</sub> O	30.3	546
	Total	28,146.5	844,777
(2) Gas From CO <sub>2</sub> Absorber (Methane Product Gas)	CO <sub>2</sub>	333.5	14,677
	CH <sub>4</sub>	13,778.0	220,999
	Dry Gas	14,111.5	235,676
	H <sub>2</sub> O	1.6	29
	Total	14,113.1	235,705
(3) 85 Psia Flash Vapors	CO <sub>2</sub>	3,522.3	155,016
	CH <sub>4</sub>	241.8	3,878
	Dry Gas	3,764.1	158,894
	H <sub>2</sub> O	2.3	41
	Total	3,766.4	158,935
(4) 20 Psia Flash Vapors	CO <sub>2</sub>	8,046.7	354,135
	CH <sub>4</sub>	37.0	593
	Dry Gas	8,083.7	354,728
	H <sub>2</sub> O	14.3	258
	Total	8,098.0	354,986
(5) 5 Psia Flash Vapors	CO <sub>2</sub>	2,155.6	94,869
	CH <sub>4</sub>	1.3	21
	Dry Gas	2,156.9	94,890
	H <sub>2</sub> O	12.1	218
	Total	2,169.0	95,108
(6) CO <sub>2</sub> Product Gas (125 MM SCFD)	CO <sub>2</sub>	13,724.6	604,020
	CH <sub>4</sub>	280.1	4,492
	Dry Gas	14,004.7	608,512
	H <sub>2</sub> O	0.7	13
	Total	14,005.4	608,525

4. Chemical, Utility, Economic Summaries Case III

This section includes the following tables:

Table VII - 4	Chemical Summary
Table VII - 5	Utility Summary
Table VII - 6	Economic Summary

TABLE VII-4

CHEMICALS SUMMARY FOR RECOVERY OF CARBON DIOXIDE  
FROM NATURAL SOURCES CONTAINING  
50% HYDROCARBON-50% CARBON DIOXIDE

---

	<u>Initial Charge-lbs</u>	<u>Est. Annual Consumption-lbs**</u>	<u>Unit Cost ¢/lb</u>	<u>Annual Cost \$</u>	<u>Cost ¢/MSCF CO<sub>2</sub></u>
<u>I. Recovery Plant</u>					
Selexol	2,000,000	42,500	100.00	42,500	0.10
Miscellaneous*				<u>10,000</u>	<u>0.02</u>
Subtotal				52,500	0.12
<u>II. Transmission System</u>					
TEG	24,000	80,000	35.0	28,000	0.07
Miscellaneous*				<u>10,000</u>	<u>0.02</u>
Subtotal				38,000	0.09
TOTAL COST				90,500	0.21

\* Includes other consumables, such as lubricants, for either system.

\*\* Basis is 340 days/year at 125 MM scfd CO<sub>2</sub> recovery.

TABLE VII-5

UTILITY SUMMARY FOR RECOVERY OF  
CARBON DIOXIDE FROM NATURAL SOURCES  
CONTAINING 50% HYDROCARBON - 50% CARBON DIOXIDE

The following are expected utility consumptions for the recovery plant and gas transmission systems when 125 MMSCFD of carbon dioxide is being transmitted.

	<u>Consumption per</u> <u>MSCF of CO<sub>2</sub></u>	
	<u>Recovery</u> <u>Plant</u>	<u>Transmission</u> <u>System</u>
Electric Power, KWH	0.74	-
Cooling Water Circulation - M Gallons 90°F - 120°F	0.020	0.275
Steam - 900 PSIG & 900°F, MLBS	-	0.051



TABLE VII-6 (CONTD.)

B. TRANSMISSION COSTS

Compression Investment	\$ 9,320,000
Pipeline Investment (100 miles)	<u>\$58,540,000</u>
Fixed-Capital Investment	\$67,860,000

<u>DIRECT COSTS</u>	<u>Units/ MSCF</u>	<u>Unit Cost \$</u>	<u>Cost ¢/ MSCF CO<sub>2</sub></u>
Cooling Water (circ) - MGAL	0.275	0.02	0.55
Steam-900 PSIG & 900°F - MLBS	0.051	3.80	19.38
Chemicals	-	-	<u>0.09</u>
Sub Total Direct Costs			20.02

INDIRECT COSTS

Operating Labor - 2 men/shift	0.27
Operating Supplies - 30% Operating Labor	0.08
Supervision and Overhead - 100% Operating Labor	0.27
Maintenance Labor & Supplies - 3.5% Investment/Yr.	5.59
Capital Related Cost - Depreciation, Interest Charges, Taxes, Insurance, Return on Investment - @ 38% of Investment/Yr.	<u>60.67</u>
Sub Total Indirect Costs	66.88
Total Transmission Cost ¢/MSCF (100 miles)	86.90

C. TOTAL RECOVERY AND TRANSMISSION COST

1. Recovery Costs	-161.52
2. Transmission Costs (100 miles)	<u>86.90</u>
Total Recovery and Transmission Costs	-74.62

## D. CASE IV

### 1. Process Description

#### Introduction

A fourth feedgas composition was considered as representative of a possible naturally occurring carbon dioxide source contaminated with hydrogen sulfide. This hypothetical case was composed of 50 percent hydrocarbon (methane), 48 percent carbon dioxide and 2 percent hydrogen sulfide. Though similar to the feedgas in Case III, the presence of the hydrogen sulfide in the gas poses significant additional processing difficulties.

The hydrogen sulfide in the feedgas must be removed from both the carbon dioxide and methane product streams in this case. The quantity in the feedgas is too small to use a direct sulfur removal process such as a Claus process. In addition, the partial pressure of the carbon dioxide is above the current design experience for a process such as Stretford.

It was concluded that the process for this case must have two distinct functions. First it must upgrade the hydrogen sulfide content to a level permitting recovery, and second it must recover the carbon dioxide economically.

One of the properties of a physical solvent such as Selexol is its natural selectivity between the various acid gas constituents. For Selexol, absorption of hydrogen sulfide is preferred over carbon dioxide by a ratio of about seven to one.

After review of alternate process schemes, the dual nature of a physical solvent process such as Selexol seemed ideally suited to this case. In addition, it was believed that such a process would offer low utilities and investment costs. These were the main criteria again for selecting Selexol for the treatment of this hypothetical natural carbon dioxide source.

As is discussed later in this section, the hydrogen sulfide is available from the Selexol process as approximately a 75 percent gaseous mixture with carbon dioxide. It is possible to separate the hydrogen sulfide from the carbon dioxide in this gas, and recover the sulfur using a Stretford process. The reason this is possible is that the gas stream is at low pressure (18 psia). Although the carbon dioxide still interferes with the process, the partial pressure of carbon dioxide is within demonstrated design limits for the Stretford process.

Based on the above criteria a two stage absorption system using Selexol was designed in which the hydrogen sulfide is recovered as elemental sulfur by use of a Stretford process, and in which 125 MMSCFD of carbon dioxide at 98 percent purity is recovered.

The process description for Case IV which follows may be divided according to the following sections:

- \* Hydrogen Sulfide Removal
- \* Carbon Dioxide Recovery
- \* Compression and Drying
- \* Sulfur Recovery (Stretford Process)
- \* Gas Transmission
- \* Utility Systems
- \* Environmental Considerations

Reference should be made to process flow diagram P-4691-D (figure VII-4) which further depicts the process discussed in the following sections. Figure VII-3 also presents a simplified flow scheme for the Stretford process.

#### Hydrogen Sulfide Removal

The first stage of the absorption process is devoted to the selective separation and recovery of the hydrogen sulfide from the feedgas. The feedgas, available at 265 psia and 75°F, is interchanged with the methane product gas to recover process refrigeration. This cooled gas then enters the first of two absorbers connected in series. A Selexol solution, lean with respect to hydrogen sulfide but presaturated with carbon dioxide, enters the top of this absorber. Essentially all of the hydrogen sulfide in the feedgas is removed by conventional counter current absorption in the packed tower. The overhead gas from this absorber contains less than 1/4 grain of hydrogen sulfide per 100 SCF of gas.

Carbon dioxide and, to a certain extent, methane are also soluble in Selexol and will tend to be absorbed in this first tower. However, the hydrogen sulfide is by far the more soluble component in the feedgas-about seven times more so than carbon dioxide. The hydrogen sulfide absorber is designed so the hydrogen sulfide acts as the controlling component in the absorption. The Selexol solvent circulation rate is limited to the absolute minimum required to remove

the hydrogen sulfide down to the desired level. Restricting the circulation rate in this manner will serve to minimize the quantities of other gases absorbed. The loaded Selexol solution exiting the absorber bottom will be disproportionately rich in hydrogen sulfide.

The hydrogen sulfide content in the feedgas is only two percent. After absorption, the hydrogen sulfide comprises about 16 percent of the dissolved gases in the loaded solution. To increase this level the loaded solution exiting the hydrogen sulfide absorber bottom at 265 psia is flashed to 75 psia. Because of their lower solubilities the carbon dioxide and methane will preferentially desorb from the solution. These flashed vapors are recompressed, cooled against a downstream flashed vapor stream, and then recycled back to the hydrogen sulfide absorber. This recycle drum serves to further enrich the final hydrogen sulfide stream. The pressure level in the recycle drum is set so that the dissolved gases remaining in the flashed liquid stream will contain over 25 percent hydrogen sulfide. At this point the hydrogen sulfide can be stripped from the solution and the sulfur recovered in a sulfur plant.

With the low leakages specified in the absorber overhead, a solvent very lean in hydrogen sulfide is required at the absorber top. The high solubility of hydrogen sulfide in the solvent prevents obtaining this degree of leanness by simple flashing, so stripping is required to completely regenerate the solvent.

The liquid stream from the recycle drum is heated by cross-exchange with the stripper bottoms and then flashed to the top of the stripper. The hydrogen sulfide and carbon dioxide remaining in solution are stripped out by steam as the liquid descends through the tower. The reboiler heat to generate this stripping steam is furnished by 50 psig steam. The lean solution exiting the stripper bottom is cooled against the incoming stripper liquid and then pumped to the carbon dioxide removal section of the process. Here, it forms a portion of the total lean solution going to the top of the carbon dioxide absorber.

The stripper overhead gas is cooled with cooling water in an overhead condenser. The condensed steam is separated from the

gas in a knockout drum and, together with makeup water, returned to the stripper top. It is necessary to maintain a 95 wt. percent Selexol - 5 wt. percent water solvent solution in the process to enable steam generation in the stripper bottom. At water contents lower than 5 percent, temperature limitations would prohibit the use of 50 psig steam in the reboiler or provide insufficient stripping. Higher water contents would add significantly to the energy requirements and equipment sizes with no corresponding increase in absorption capacity or selectivity.

The stripper overhead gas exiting the knockout drum is fed to the sulfur plant for processing. The carbon dioxide stream from the sulfur plant is essentially pure carbon dioxide (1/4 gr H S/100 SCF gas). This effluent gas is combined with the product streams from the bulk carbon dioxide removal section and sent to the product gas compressor.

#### Carbon Dioxide Recovery

Once the hydrogen sulfide has been removed, carbon dioxide can be easily separated from the gas stream. This bulk removal section of the process is very similar to that used in Case III. The overhead gas from the hydrogen sulfide absorber contains a 50-50 mixture of carbon dioxide and methane. This gas is fed directly to the bottom of the carbon dioxide absorber where it is contacted with a lean solvent solution. Carbon dioxide is removed from the gas stream by convention counter-current absorption. The final overhead gas contains only 2.0 percent carbon dioxide. A minimal quantity of methane is also absorbed in this column; however, over 98 percent of the total methane in the feedgas stream is recovered in the carbon dioxide absorber overhead. Solution from the bottom of the absorber is split into two separate streams. The smaller of these streams forms the presaturated lean solution to the hydrogen sulfide absorber. The remainder is flashed in successive stages to recover the dissolved carbon dioxide.

The first solvent regeneration step for the bulk carbon dioxide is to flash the rich solution from 263 psia to 150 psia pressure. As the quantity of liquid flashed here is substantial, the potential for power recovery justifies employing hydraulic turbines in this pressure letdown step. Methane

dissolved in the solvent from the absorber will preferentially desorb in this flash. The methane rich flash vapor stream is recompressed, cooled by interchange with a downstream flashed vapor stream, and recycled to the carbon dioxide absorber. This recycle reduces the overall methane losses from the absorber overhead and increases the purity of the carbon dioxide product.

The liquid stream from the recycle drum is flashed at two intermediate pressure levels, 85 psia and 20 psia. Both of these pressure reductions are accomplished using hydraulic turbines for power recovery. The vapor streams from these two flashes constitute the bulk of the carbon dioxide product gas. The vapor from the 85 psia flash goes directly to the second case of the product compressor. The 20 psia vapor stream is first used to cool the vapor streams recycled to both the hydrogen sulfide and carbon dioxide absorbers. After interchange with these streams, it is combined with the effluent stream from the sulfur plant and directed to the first case of the product compressor.

The solution exiting the 20 psia flash drum undergoes one further regeneration step. As in the Case III design, the low leakage desired from the carbon dioxide absorber cannot be achieved using a lean solution regenerated by atmospheric flashing alone. The solution can be completely regenerated and the remaining carbon dioxide recovered by flashing at 5.8 psia. The liquid stream exiting this flash drum is combined with the lean, stripping solvent stream from the hydrogen sulfide removal section, and then pumped to the top of the carbon dioxide absorber. A refrigeration unit located on this combined lean stream maintains the overall process heat balance. The flash vapor stream representing a portion of the total carbon dioxide product, flows to the first stage of the product compressor.

#### Compression and Drying

Carbon dioxide is delivered to the product compressor at three different pressure levels from the Selexol process. These levels were selected according to process requirements and also to minimize compression costs. A three case, six stage centrifugal compressor, driven by a steam turbine, is used to compress the product gas to the final delivery pressure. Compressor interstage cooling is provided by cooling

water, and condensate is removed by interstage knockout drum. A triethylene glycol drier, located just prior to the last compression step, reduces the water content of the product gas to pipeline specifications. A total of 125 MMSCFD of carbon dioxide of 98 percent purity is delivered at 2,200 psig from the compressor.

#### Sulfur Recovery (Stretford Process)

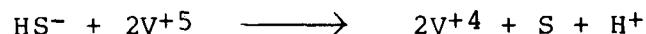
In the Stretford process hydrogen sulfide is converted to elemental sulfur according to the following overall equation:



The reaction is initiated in an absorber. Here an alkaline solution of sodium carbonate containing a vanadium salt along with anthraquinone - disulfonic acid (ADA), absorbs the hydrogen sulfide gas and converts it to hydrosulfide ion.



The solution then flows to a reaction vessel where elemental sulfur is formed.



In the third stage of the process, an oxidation step employing air is used to regenerate the solution, and the sulfur is removed as a floating froth.



The regenerated solution is then returned to the absorber tower completing the absorption step.

It is usually more economical when treating large gas quantities, as in the present case, to remove the bulk of the sulfur in a pretreatment step using liquid eductors. Here the inlet gas is brought into intimate contact with the gas stream and contacted with about 80 percent of the solution flow. Liquid from the eductors flows to the reaction vessel where the reaction to elemental sulfur takes place. The gas is further contacted in an absorber to remove the hydrogen sulfide to a level of less than 1/4 gr sulfur per 100 SCF.

The sulfur froth typically contains about 7-10 percent sulfur. A variety of methods are available to recover the sulfur from the froth. These include filtrating, centrifuging and more recently, the use of a sulfur melter.

In the sulfur melter method the sulfur froth is heated and the molten sulfur separates by gravity from the Stretford solution which is returned to the process. It is possible to recover 99.5 percent pure elemental sulfur by this technique. The utilities and costs for the Stretford process in this study assume that a sulfur melter technique is to be used. Assuming two percent hydrogen sulfide in the inlet natural carbon dioxide gas source, 220 short tons per day of elemental sulfur are recovered.

Figure VII-3 presents a block flow diagram for the Stretford process described above.

#### Utility Systems

Utilities presented later in this section, are based on use of a steam driven turbine for the carbon dioxide compressor, and electric drives for all remaining rotating equipment. Small additional steam requirements are also included for regeneration of the glycol solution in the triethylene glycol dryer.

Two steam pressure levels were selected. Steam imported from offsite is assumed available at 900 psig - 900°F (identical import steam conditions were selected for all cases in this study). A second level at 75 psig supplies reboiler heat to the hydrogen sulfide stripper reboiler and the Stretford plant through a letdown station to 50 psig.

The 75 psig steam header is supplied by extraction steam from the carbon dioxide compressor turbine. This turbine also exhausts to a vacuum condenser at four inches mercury vacuum.

Cooling water is assumed to be available at 90°F.

## Environmental Considerations

Effluent streams will be produced during normal operation of the recovery and gas transmission facilities. The following is a brief discussion of the expected effluents, and possible methods of handling these. Costs for any treatment facilities which may be required are not included in plant investment.

Water will be produced from the product gas as it is compressed and cooled between stages. Also water will condense from the inlet raw gas feed. The water balance of the system is such that a slight excess of water above that obtained from these sources will be required as makeup to the hydrogen sulfide stripper. Therefore, it should be possible to recycle these streams back to the process to eliminate the effluents and also to reduce the makeup water requirements.

Regeneration of the triethylene glycol solution in the TEG dryer will produce a gaseous effluent consisting mostly of water vapor plus traces of TEG. This effluent stream can be vented to the atmosphere.

The formation of byproduct salts such as sodium thiosulfate and sodium sulfate require a purge stream of Stretford solution from the sulfur recovery plant. Usually this can be avoided during the first six months to one year of operation, but then must be done on a routine basis. In this manner these salts are prevented from building up in the process and plugging equipment such as the absorber.

Treatment of this purge stream will almost certainly be required from an environmental and economic standpoint, and a number of different processes are available to do this, each in various stages of development. Among these are processes offered by Peabody Engineering (Holmes Stretford), and Sun Oil (J. F. Pritchard Co. Licensee).

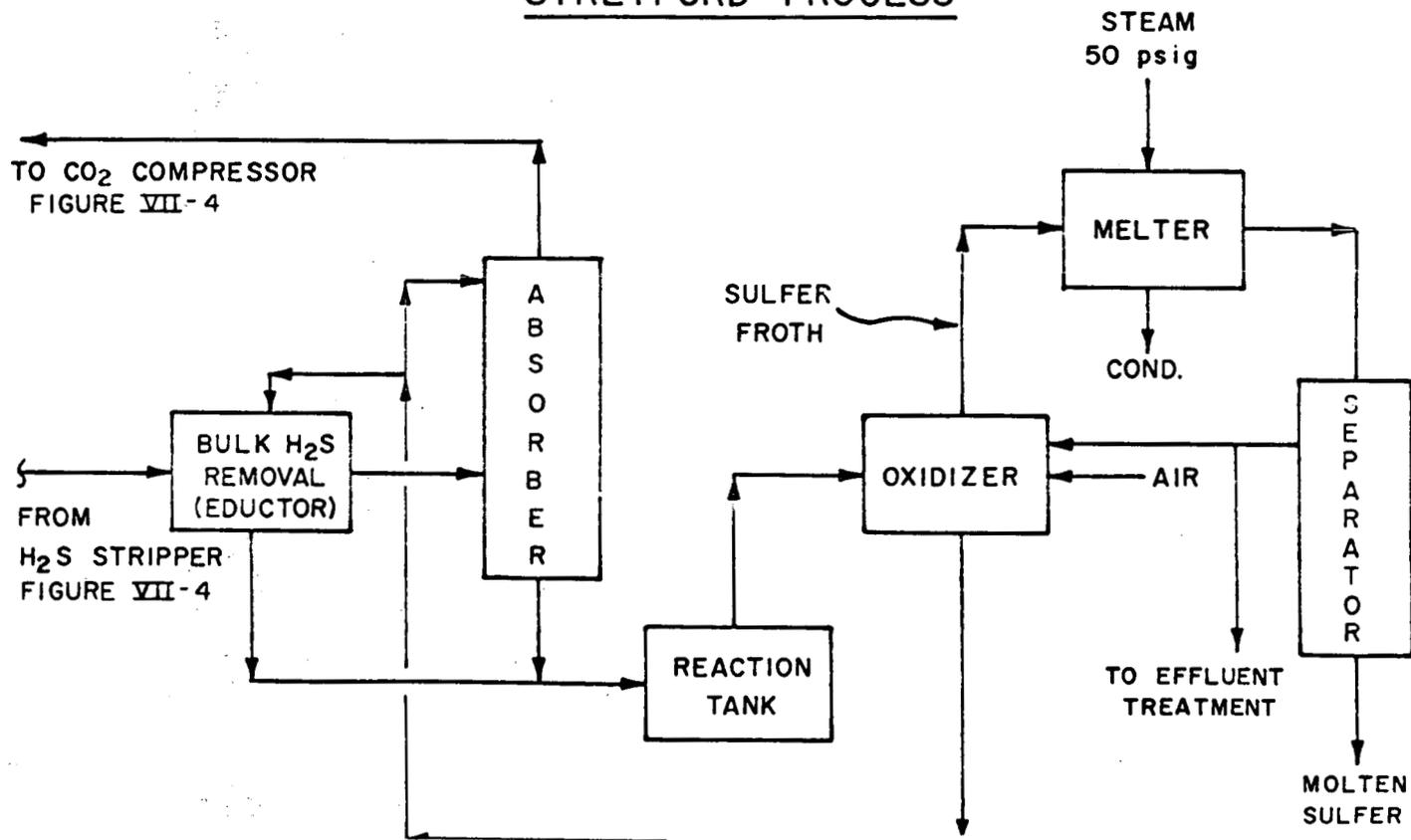
Methane gas is a byproduct in this case. This will be highly marketable and it is assumed here that this gas can be transmitted in the usual manner for natural gases and will not pose a problem.

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<sup>2</sup>See also discussion for Case I.

FIG. VII-3

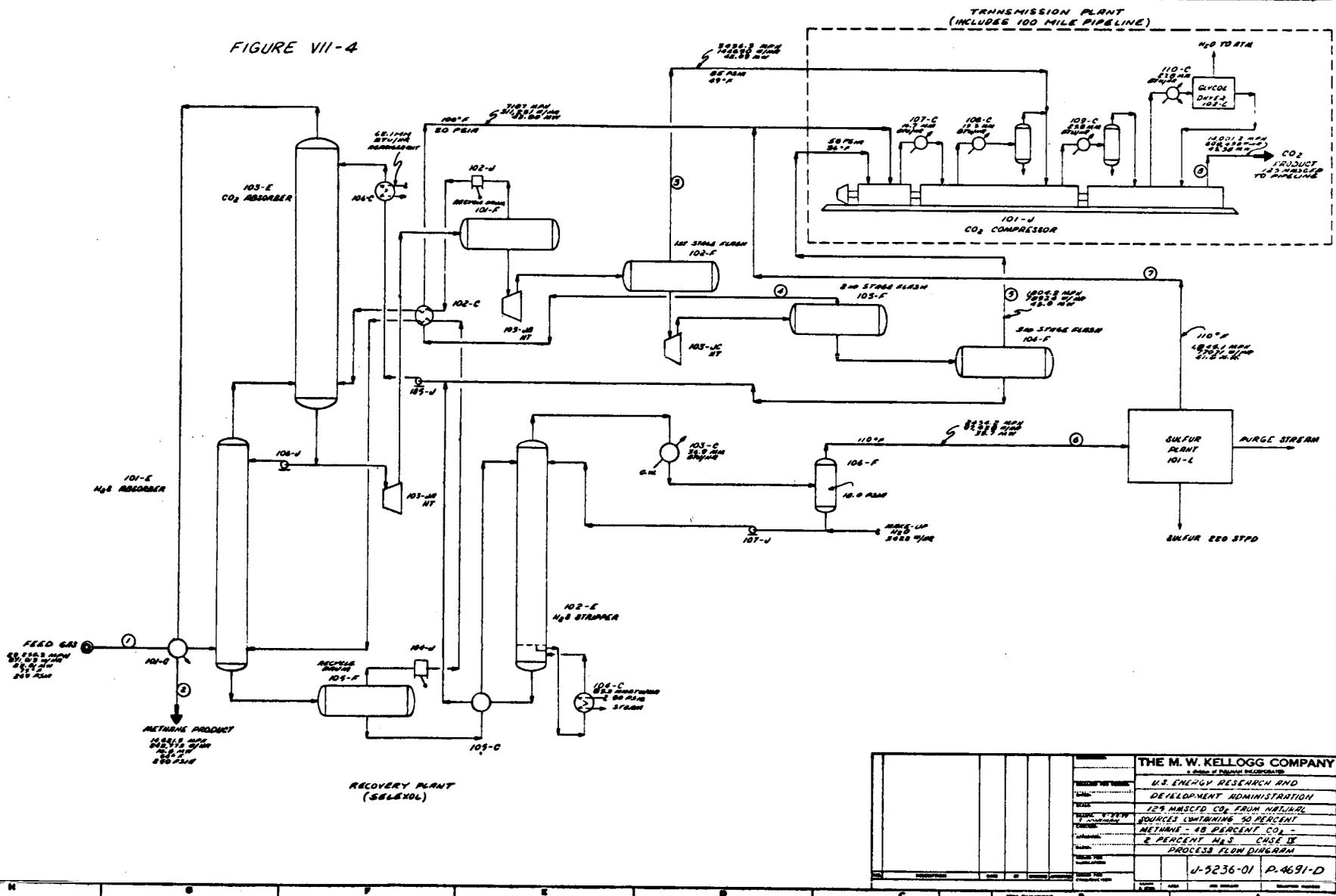
BLOCK FLOW DIAGRAM  
STRETFORD PROCESS



2. Process Flow Diagram

Process flow diagram P-4691-D (figure VII-4) for Case IV, Carbon Dioxide Recovery From A Naturally Occurring Source, is presented on the following page.

FIGURE VII-4



-93-

THE M. W. KELLOGG COMPANY	
U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION	
12% MASCED CO <sub>2</sub> FROM NATURAL SOURCES CONTAINING 50 PERCENT METHANE - 48 PERCENT CO <sub>2</sub> - 2 PERCENT H <sub>2</sub> S CASE IX PROCESS FLOW DIAGRAM	
J-5236-01	P. 4691-D

3. Material Balance

A material balance for Case IV, Carbon Dioxide Recovery From A Naturally Occuring Source, is presented on the following page.

MATERIAL BALANCE  
CARBON DIOXIDE  
FROM NATURAL SOURCES  
CONTAINING  
50% METHANE  
48% CARBON DIOXIDE  
2% HYDROGEN SULFIDE

<u>STREAM NO. AND SOURCE</u>	<u>COMPONENT</u>	<u>LB MOL/HR</u>	<u>LBS/HR</u>
(1) Feed to Plant	CO <sub>2</sub>	14,017.3	616,903
	H <sub>2</sub> S	584.0	19,903
	CH <sub>4</sub>	14,601.5	234,251
	Dry Gas	29,202.8	871,057
	H <sub>2</sub> O	47.5	856
	Total	29,250.3	871,913
(2) Gas From CO <sub>2</sub> Absorber (Methane Product Gas)	CO <sub>2</sub>	292.7	12,884
	CH <sub>4</sub>	14,325.6	229,831
	Dry Gas	14,618.3	242,715
	H <sub>2</sub> O	3.2	58
	Total	14,621.5	242,773
(3) 1st Stage Flash Gases	CO <sub>2</sub>	3,200.7	140,862
	CH <sub>4</sub>	231.9	3,721
	Dry Gas	3,432.6	144,538
	H <sub>2</sub> O	3.7	67
	Total	3,436.3	144,650
(4) 2nd Stage Flash Gases	CO <sub>2</sub>	7,050.8	310,306
	CH <sub>4</sub>	34.1	548
	Dry Gas	7,084.9	310,854
	H <sub>2</sub> O	22.1	397
	Total	7,107.0	311,251
(5) 3rd Stage Flash Gases	CO <sub>2</sub>	1,786.1	78,607
	CH <sub>4</sub>	0.5	1
	Dry Gas	1,786.6	78,608
	H <sub>2</sub> O	17.6	316
	Total	1,804.2	78,924
(6) Feed to Sulfur Plant	CO <sub>2</sub>	1,687.0	74,243
	H <sub>2</sub> S	584.0	19,903
	CH <sub>4</sub>	9.4	151
	Dry Gas	2,280.4	94,297
	H <sub>2</sub> O	173.8	3,131
	Total	2,454.2	97,428
(7) Effluent Gas *	CO <sub>2</sub>	1,687.0	74,243
	CH <sub>4</sub>	9.4	151
	Dry Gas	1,696.4	74,394
	H <sub>2</sub> O	148.7	2,677
	Total	1,845.1	77,071
(8) CO <sub>2</sub> Product Gas (125 MM SCFD)	CO <sub>2</sub>	13,724.6	604,020
	CH <sub>4</sub>	275.9	4,425
	Dry Gas	14,000.5	608,445
	H <sub>2</sub> O	0.7	13
	Total	14,001.2	608,458

\*Some absorption of Carbon dioxide may take place in Stretford plant.

4. Chemical, Utility, Economic Summaries

This section includes the following tables:

Table VII-7	Chemical Summary
Table VII-8	Utility Summary
Table VII-9	Economic Summary

TABLE VII-7

CHEMICALS SUMMARY FOR RECOVERY OF CARBON DIOXIDE  
FROM NATURAL SOURCES CONTAINING  
50% HYDROCARBON-48% CARBON DIOXIDE-2% HYDROGEN SULFIDE

	<u>Initial Charge-lbs</u>	<u>Est. Annual Consumption-lbs**</u>	<u>Unit Cost ¢/lb</u>	<u>Annual Cost \$</u>	<u>Cost ¢/MSCF CO<sub>2</sub></u>
<u>I. Recovery Plant</u>					
Selexol	2,500,000	42,500	100.00	42,500	0.10
Stretford Chemicals	950,000	990,000	110.00	1,089,000	2.56
Miscellaneous*				<u>10,000</u>	<u>0.02</u>
Subtotal				1,141,500	2.68
<u>II. Transmission System</u>					
TEG	24,000	80,000	35.0	28,000	0.07
Miscellaneous*				<u>10,000</u>	<u>0.02</u>
Subtotal				38,000	0.09
TOTAL COST				1,179,500	2.77

\* Includes other consumables for either system such as lubricants.

\*\* Basis is 340 days/year at 125 MMSCFD CO<sub>2</sub> recovery.

TABLE VII - 8

UTILITY SUMMARY FOR RECOVERY OF CARBON DIOXIDE  
 FROM NATURAL SOURCES CONTAINING  
50% HYDROCARBON-48% CARBON DIOXIDE-2% HYDROGEN SULFIDE

The following are expected utility consumptions for the recovery plant and gas transmission systems when 125 MMSCFD of carbon dioxide is being transmitted.

	<u>Consumption per MSCF of CO</u>	
	<u>Recovery Plant</u>	<u>Transmission System</u>
Electric Power, KWH	4.04	-
Cooling Water Circulation - M Gallons 90°F-120°F	0.115	0.276
Steam - 900 PSIG & 900°F, MLBS	-	0.077
75 PSIG & 500°F, MLBS	0.025	(0.025)

( ) Export quantity

Table VII - 9

ECONOMIC SUMMARY FOR RECOVERY OF CARBON DIOXIDE  
 FROM NATURAL SOURCES CONTAINING 50% HYDROCARBON-  
 48% CARBON DIOXIDE-2% HYDROGEN SULFIDE  
PLANT CAPACITY: 125 MMSCFD

A. RECOVERY COSTS

Fixed-Capital Investment \$48,000,000

<u>DIRECT COSTS</u>	<u>Units/ MSCF</u>	<u>Unit Cost \$</u>	<u>Cost ¢/ MSCF CO<sub>2</sub></u>
Electric Power - KWH	4.040	0.035	14.14
Cooling Water (circ) - MGAL	0.115	0.020	0.23
Steam -75 PSIG & 500°F - MLBS	0.025	3.380	8.45
Chemicals			<u>2.68</u>
Subtotal Direct Costs			25.50
 <u>INDIRECT COSTS</u>			
Operating Labor - 1 man/shift			0.13
Operating Supplies - 30% Operating Labor			0.04
Supervision and Overhead - 100% Operating Labor			0.13
Maintenance Labor & Supplies - 3.5% Investment/Yr.			3.95
Capital Related Costs - Depreciation, Interest Charges, Taxes, Insurance, Return on Investment - @ 38% of Investment/Yr.			<u>42.92</u>
Subtotal Indirect Costs			47.17
 <u>BYPRODUCT CREDIT</u>			
Sulfur from Stretford Plant 220 Short Tons/Day @ \$50 ST			-8.80
Methane gas 133.2 MM SCFD @\$1.75/MSCF (100% CH <sub>4</sub> )			<u>-182.70</u>
Total Recovery Cost ¢/MSCF			-118.83

Notes Recovery and Transmission Costs\*

- All operating labor \$6.5/manhour
- Breakdown of capital related costs:

Depreciation	10%
Interest Charges	5%
Taxes and Insurance	3%
Return on Investment	<u>20%</u>
	<u>38%</u>

\*Continued on Page 99

Table VII - 9 (Contd.)

ECONOMIC SUMMARY FOR RECOVERY OF CARBON DIOXIDE  
 FROM NATURAL SOURCES CONTAINING 50% HYDROCARBON-  
 48% CARBON DIOXIDE-2% HYDROGEN SULFIDE  
PLANT CAPACITY: 125 MMSCFD

B. TRANSMISSION COSTS

Compression Investment	\$ 9,720,000
Pipeline Investment (100 miles)	\$58,540,000
Fixed-Capital Investment	\$68,260,000

<u>DIRECT COSTS</u>	<u>Units/ MSCF</u>	<u>Unit Cost \$</u>	<u>Cost ¢/ MSCF CO<sub>2</sub></u>
Cooling Water (circ) - MGAL	0.276	0.02	0.55
Steam - 900 LB & 900°F - MLBS	0.077	3.80	29.26
75 LB & 500°F - MLBS	(0.025)	3.38	(8.45)
Chemicals			<u>0.09</u>
Subtotal Direct Costs			21.45
( ) Denotes Export			

INDIRECT COSTS

Operating Labor - 2 Men/Shift			0.27
Operating Supplies - 30% Operating Labor			0.08
Supervision and Overhead - 100% Operating Labor			0.27
Maintenance Labor & Supplies - 3.5% Investment/Yr.			
Capital Related Costs - Depreciation, Interest Charges, Taxes, Insurance, Return on Investment - @ 38% of Investment/Yr.			5.62
			<u>61.03</u>
Subtotal Indirect Costs			67.27
Total Transmission Costs ¢/MSCF (100 miles)			88.72

C. TOTAL RECOVERY AND TRANSMISSION COST

1. Recovery Costs	-118.83
2. Transmission Costs (100 miles)	<u>88.72</u>
Total Recovery and Transmission Costs	-30.11

Table VII - 9 (Contd.)

ECONOMIC SUMMARY FOR RECOVERY OF CARBON DIOXIDE  
FROM NATURAL SOURCES CONTAINING 50% HYDROCARBON-  
48% CARBON DIOXIDE-2% HYDROGEN SULFIDE  
PLANT CAPACITY: 125 MMSCFD

Notes (Contd.)

- Onstream Factor                    340 days/year
- Plant Investment does not include power generation, cooling tower, boiler feedwater treatment, or treatment of Stretford plant purge stream. Includes initial chemical charge and process royalties.
- Steam cost based on gas fired steam boiler. Gas cost \$2.00/MSCF delivered.

NOTES - SECTION VII - CARBON DIOXIDE FROM  
NATURALLY OCCURRING SOURCES

- [1] OIL & Gas Journal, "Line Will Move 240 MMSCFD of CO<sub>2</sub>", Nov. 8, 1971.
- [2] See appendix

## VIII. CONCLUSIONS AND RECOMMENDATIONS

### A. CONCLUSIONS

The focal point of this study is the thirteen state region, identified by GURC as having candidate oil fields believed suitable for EOR with carbon dioxide miscible flooding. It is within this region that future EOR with carbon dioxide miscible flooding will more than likely take place on a commercial scale.

Review of the carbon dioxide supply situation in the thirteen state region (see Section III) shows that more than sufficient carbon dioxide is available from aboveground sources to satisfy the projected future demand for EOR applications even without substantial new discoveries of high carbon dioxide-content natural gases. Additionally based on preliminary compilations of candidate oil fields and estimated carbon dioxide requirements, it appears that each state could be self supporting in carbon dioxide. This appears to be true even though areas having the greatest abundance of aboveground sources are not located in regions expected to have the greatest potential for EOR.

Of the sources considered in this study, stack gas sources, including power plant and cement plant sources, are the most widespread and abundant sources accounting for 80 percent of the above-ground sources. However, the quality of these sources is low - typically less than 20 percent carbon dioxide.

Considering only power plant sources, a single plant can easily support a commercial EOR project requiring 100 MSCFD or more of carbon dioxide. Surveys of current power plant installations indicate that presently high output coal-fired power plants are generally located at an unfavorable distance from candidate reservoirs; however, this situation could change in the future as more power plants are converted to coal firing.

The highest quality sources of carbon dioxide expected to be available (with the possible exception of some naturally occurring gas deposits) are process vents from fertilizer and chemical plants. Future sources of carbon dioxide from process vents could include significant quantities as by-product from SNG manufacture. The most significant future source could be as a by-product from SNG plants based on gasification of coal.

Presently, the most likely source of carbon dioxide from process vents appears to be uncommitted by-product carbon dioxide from ammonia manufacture. This high purity source (typically 98 percent) accounts for roughly 75 percent of the by-product carbon dioxide currently available from process vents.

Prospects for an EOR project based at least in part on use of ammonia plant by-product carbon dioxide appear good, given the necessary economic incentive. This optimism is based on the fact that 70 percent of the available ammonia plant by-product carbon dioxide is located in three of the more promising areas for EOR by carbon dioxide miscible flooding - namely, Louisiana, South Texas, and Oklahoma. Hindrances to development of this source of carbon dioxide include multiple ownership of supplies (the amount available from a single plant would probably not support an EOR project), and competition from other potential uses such as urea.

Natural gas wells rich in carbon dioxide have great potential as a source of carbon dioxide for future EOR efforts. Information currently available shows that the areas with greatest potential for naturally occurring carbon dioxide wells are the Four Corners area (Utah, Colorado, Arizona, New Mexico), southeast Colorado, northeast New Mexico and central Mississippi. Other areas including southwest Texas have potential for producing carbon dioxide of lower purity (30-50 percent).

The quantities of carbon dioxide available from natural sources are not known since no exhaustive survey of this source exists at present. However, based on historical data for natural gas discoveries it is generally concluded that natural sources alone cannot supply all the carbon dioxide for future EOR efforts.

Costs developed during this study (summarized in Table VIII-1) allow additional assessment of the carbon dioxide supply situation for EOR.

For example, the best source of low cost carbon dioxide for EOR will be a natural source containing by-product natural gas to offset the cost of producing the carbon dioxide. (The presence of contaminant hydrogen sulfide makes the economic picture less favorable if it must be removed.) This assessment assumes that the by-product credit for natural gas can be applied toward the cost associated with development of the carbon dioxide source.

If the carbon dioxide is available as a by-product from development of natural gas supplies which seems likely for the cases studied in this report the methane by-product credit will no longer apply. In this case, the cost of carbon dioxide would depend on a number of considerations including to what extent the costs of recovering the natural gas and developing the wells are charged against the cost of carbon dioxide.

Carbon dioxide from above-ground sources will be expensive. The most expensive source appears to be power plant flue gases, even though these are the most abundant. This is due to the high cost of recovery from the flue gas.

It is conceivable that an EOR project could utilize a combination of specific sources of carbon dioxide supply. For example, a low cost natural source could be combined with a more expensive power plant source. In this way sources which at first may seem uneconomical could very well be developed for a specific location.

In the last analysis, it is impossible to predict whether any of the sources considered here will be developed for use in EOR by carbon dioxide miscible flooding. This will depend on a great many factors including the future cost of petroleum, the effectiveness of the process itself, and government policy insofar as it influences development of EOR programs.

TABLE VIII-1

Investment and Cost Summary

<u>Carbon Dioxide Source</u>	<u>Carbon Dioxide Capacity</u> <u>MMSCFD</u>	<u>Investment</u> <u>MM\$ U.S.</u>		
<u>Aboveground</u>				
Ammonia Plant Vents	184	Transmission System	134.8	1.15
Power Plant Fluegas	125	Recovery Plant	34.1	1.04
		Transmission System	<u>19.2</u>	<u>0.21</u>
		Total	53.3	1.25
<u>Natural Sources</u>				
Case I (98% CO <sub>2</sub> -2% CH <sub>4</sub> )	125	Transmission System	62.9	0.72
Case III (50% CO <sub>2</sub> -50% CH <sub>4</sub> )	125	Recovery Plant	11.4	-1.62
		Transmission System	<u>67.9</u>	<u>0.87</u>
		Total	79.3	-0.75
Case IV (48% CO <sub>2</sub> -50% CH <sub>4</sub> -2% H <sub>2</sub> S)	125	Recovery Plant	48.0	-1.19
		Transmission System	<u>68.3</u>	<u>0.89</u>
		Total	116.3	-0.30

Notes -

- U.S. Gulf Coast Location is assumed
- Investment Costs 2nd Quarter 1977
- All investment + 25%
- Transmission systems pipelines
  - Ammonia Plant Vents - 145 mile trunkline
  - Power Plant - 25 mile
  - Natural Sources - 100 mile

## B. RECOMMENDATIONS

As stated during the introduction to this study, it was necessary to make certain assumptions and to limit the overall scope of this study. This is evident in regard to development of the systems selected to study costs of delivering carbon dioxide to candidate oil fields. For example, lacking a clear definition of sources of naturally occurring carbon dioxide, these were simply hypothesized. Gas compositions and boundary limit conditions were assumed for the gases at the treatment plant, and delivery systems were selected on the basis of best guesses as to probable optimum length.

Although the purpose of the study is to determine the cost of carbon dioxide delivered at the boundary limits of the reservoir, a portion of this cost namely that of purchasing the carbon dioxide can not be developed within the scope of this study. Because of this, there are some sizable costs not accounted for particularly in the case of naturally occurring deposits where sizable costs could be associated with purchasing the carbon dioxide from the owner and drilling the wells.

A more comprehensive picture of the carbon dioxide supply situation is needed (including more fully developed economics). This requires a more extensive survey of the available sources of carbon dioxide (as compared to this report). The survey should, for example, attempt to define more clearly the sources and quantities of carbon dioxide available from natural sources. It will require contacting gas producers/processors to determine the amount of carbon dioxide which is currently being vented from natural gas processing units. Attempts will have to be made to determine the amounts, if any, available from non-producing gas wells. The survey should also focus greater attention on carbon dioxide from process vents including SNG plants. Specific attention should be given to SNG plants based on coal.

Regional maps for the various sources should be prepared based on this survey. These would clearly define the location, total quantities and approximate flow rates of the various sources.

Development of the economic picture requires definition of the costs of purchasing carbon dioxide or the cost of producing it from natural sources - costs which were beyond the scope of this report. Development of these costs will require a survey of reliable suppliers to ascertain the cost of purchasing carbon dioxide on the existing market, and for some naturally occurring sources it will require determination of cost data for source development and transmission to the processing plant.

The remaining areas of the picture, gas processing and transportation, require further development, and the costs should be presented in a more generalized manner. For example, in the area of gas processing, effort should be directed at reducing the recovery cost for flue gas sources possibly through revised processing techniques. For each source, especially natural sources, enough cases should be studied so that the effects of pressure, carbon dioxide content, impurities and the quantity of gas treated can be determined and taken into account.

In the area of gas transportation, further consideration should be given to the optimum means for transporting the gas. For example, a sub-critical pipeline might result in the lowest cost of transportation for smaller quantities over short distances, whereas, a supercritical pipeline would be optimum for a different set of conditions.

Based on this comprehensive supply and economic picture, a person with a known candidate oil reservoir and a ceiling price for carbon dioxide could determine the location, and availability of carbon dioxide at the ceiling price. Conversely, a person with a known source and destination would be able to determine the delivered cost of carbon dioxide at the candidate field. Thus, it is apparent that such information would be of great utility in the area of enhanced oil recovery by carbon dioxide miscible flooding.

## IX. APPENDIX

### A. PHYSICAL AND EQUILIBRIUM PROPERTIES OF CARBON DIOXIDE

Sources for the physical and equilibrium properties of carbon dioxide are numerous, and the consistency among these sources is very good. The recommended primary source is the tabulation given by Vargaftik (1975). Besides the basic physical and thermodynamic functions, this source includes:

- viscosity and thermal conductivity data for both the liquid and gas phases.
- data on the velocity of sound and the adiabatic exponent.
- detailed tabulation of all properties in the critical region.

An alternate source for the basic thermodynamic properties is Din (1962). This latter source also includes data on the solid-vapor saturation properties which are not contained in the primary reference.

For the melting line of carbon dioxide use the equation (Michels et al. 1942):

$$\log_{10} (P + 3515) = 2.86702 \log_{10} T - 3.1498832$$

where P is in atmospheres and T is in Kelvin.

Not explicitly given in either of the two references, but alluded to elsewhere in the literature (See Vukalovich and Altunin, 1968) is the abnormal behavior of carbon dioxide in the supercritical region.

The discussion below is based on a limited amount of information, almost exclusively from the Russian technical literature.

#### Phase Behavior of Carbon Dioxide at Supercritical Temperatures

The phase separation boundary below the critical temperature is easily determined experimentally and no abnormal behavior is noted. It has been suggested, however, that a liquid/vapor (gas) phase transition occurs in the supercritical region also. This transition results from a structural change, and as opposed to the subcritical region, the transition is a continuous one. No direct visual observation of such a phase change has been reported. Nevertheless, accurate optical and acoustic measurements strongly suggest such a change.

A rigorous theoretical analysis (Kalafati, 1961) shows that a supercritical phase transition, if it is present at all, must occur in a region bounded by the line of maxima of  $C_p$  along the isobars, and the line of maxima of the derivative  $(\partial v/\partial T)_p$ . A detailed analysis of the data in Vargaftik (1975) shows that for all practical purposes these two lines of maxima coincide. The dotted line in Figure IX-1 has been drawn on this assumption, and represents the boundary along which a phase transition based on structural change is believed to occur. Also included in Figure IX-1 is the conventional portion of the vapor pressure curve of carbon dioxide.

Notes - Section IX-A

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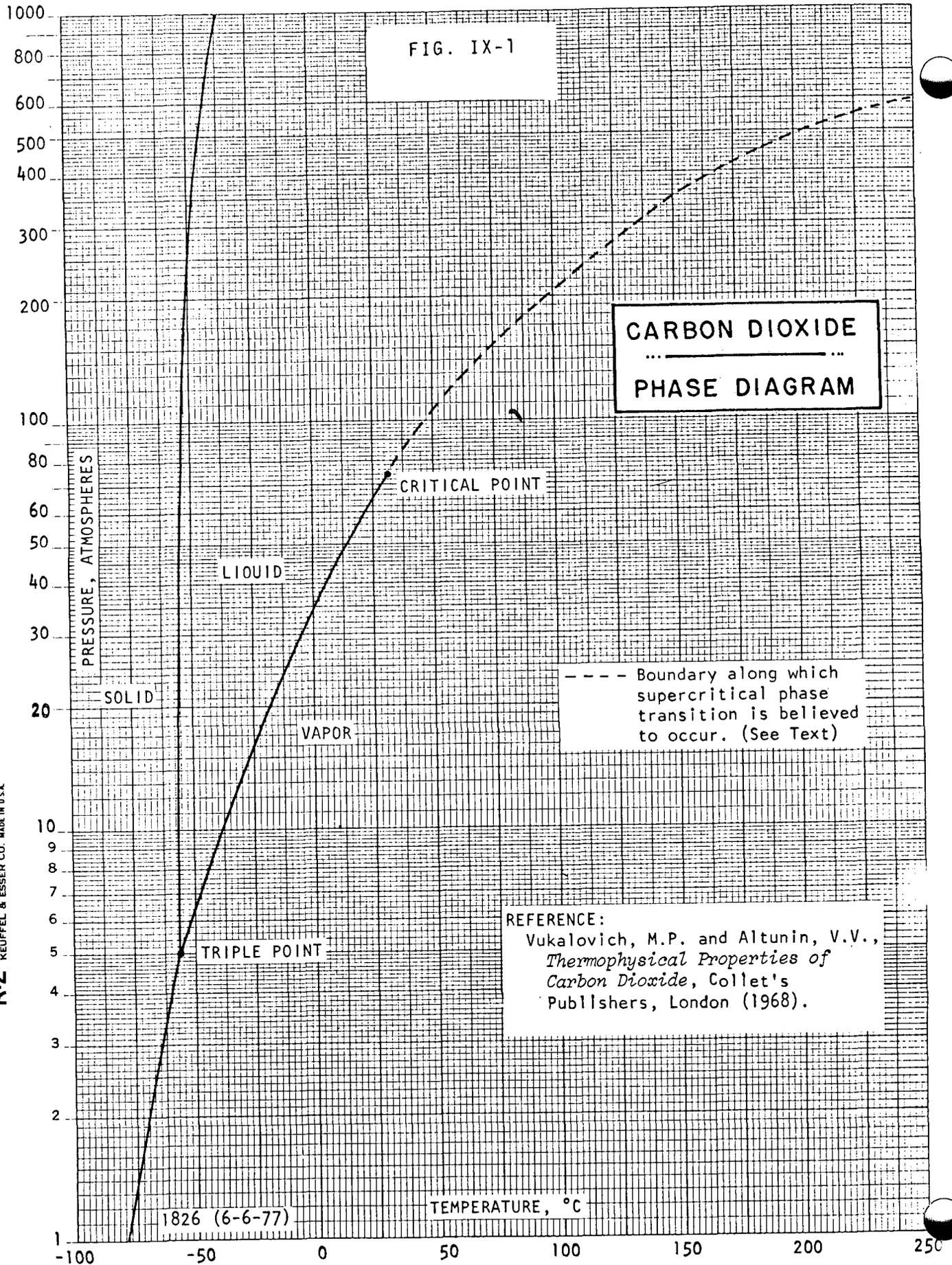
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B. U.S. BUREAU OF MINES DATA FOR NATURALLY OCCURRING CARBON DIOXIDE

Since the early 1950's, the U.S. Bureau of Mines has periodically published analyses of natural gas samples sent in voluntarily from all over the United States. Purpose of this project was primarily to locate helium; however, these tabulations are believed to indicate fairly well where high-carbon dioxide natural gas reservoirs may be located. Some data on pressure and flow rate appears in the tabulations, but these data are spotty at best. The following indicates the relatively low incidence of high-carbon dioxide wells found by the Bureau of Mines.

Year	Number of Wells Sampled	Number of Source States	Number with CO <sub>2</sub> > 5%	Number with CO <sub>2</sub> > 30%
1951	1,940	30	108	38
1957	1,456	27	48	22
1963	1,213	23	74	24
1972	<u>236</u>	<u>22</u>	<u>11</u>	<u>3</u>
Total	4,845	--	241	87
% of Total	100	--	4.97	1.80

Of the 87 wells testing higher than 30 percent carbon dioxide, the Bureau of Mines received pressure and "open flow" rate data on only 26 wells (0.5 percent of total wells). Location of these was in the following states:

Colorado ... 8	Montana ... 1
New Mexico... 2	(West) Texas ... 8
Utah ... 2	West Virginia... 3
Wyoming ... 1	Mississippi ... 1

It appears that the largest reservoirs of high-carbon dioxide, natural gasses are in the Rocky Mountain states (on the left above). Substantial amounts are in nearby West Texas (e.g., those being used for SACROC). Flow of the West Virginia wells was relatively small, as was the one reported for Mississippi.

C. CANDIDATE CARBON DIOXIDE ENHANCED OIL RECOVERY FIELDS

This section includes the following tables:

Table IX-1 - Candidate Fields With Reservoir That Meet GURC  
Critical Parameters for Miscible CO<sub>2</sub>.

Table IX-2 - Carbon Dioxide Miscible Flooding - Candidate  
Field/Reservoirs Located in Producing Trends or  
Areas.

TABLE IX-1

CANDIDATE FIELDS WITH RESERVOIRS THAT  
MEET GURC CRITICAL PARAMETERS FOR MISCIBLE CO<sub>2</sub>\*

ARKANSAS	LOUISIANA (Contd.)
Smackover	Garden Island Bay
CALIFORNIA	Grand Bay
Coastal Area	Lafitte
Ventura	Lake Washington
Los Angeles Basin Area	Timbalier Bay
Cheviot Hills	Venice
Coyote West	Weeks Island (Shell/ERDA pilot)
Dominquez	West Bay
Inglewood	West Cote Blanche
Los Cienegas	MISSISSIPPI
Long Beach	Baxterville
Los Angeles Downtown	Brookhaven
Montebello	Eucutta East
Rosecrans	Eucutta West
Santa Fe Springs	La Grange
Seal Beach	Little Creek (Shell pilot)
Whittier	Mallalieu East
Wilmington	Mallalieu West
San Joaquin Valley	Pickens
Elk Hills	Tinsley
McKittrick	West Yellow Creek
Midway Sunset	MONTANA
COLORADO	Cut Bank
Adena	Cut Bank West
FLORIDA	NEW MEXICO
Jay	Arrowhead
ILLINOIS	Bisti
Clay Consolidated	Caprock
Dale consolidated	Empire
Iola Consolidated	Eumont
LOUISIANA	Eunice South
North Onshore	E-K
Delhi South	Grayburg
Delhi West	Hobbs
Delhi-West Delhi	Langlie-Mattix
Offshore	Loco Hills
South Pass Block 24	Lovington
South Pass Block 27	Lovington West
West Delta Block 30	Lynch
South Onshore	Maljamar
Avery Island	Pearl
Bay de Chene	Penrose-Skelly
Bay St. Elaine	Rhodes
Black Bay West	Shugart
Caillou Island	Skaggs
Cote Blanche Island	Square Lake
	Vacuum
	Wilson

\*List supplied by Alan Lohse, GURC - October 15, 1976

TABLE IX-1  
CANDIDATE FIELDS WITH RESERVOIRS THAT  
MEET GURC CRITICAL PARAMETERS FOR MISCIBLE CO<sub>2</sub>  
(CONTD.)

OKLAHOMA

Apache  
 Burbank  
 Cement  
 Golden Trend  
 Healdton  
 Jennings  
 Maysville East  
 Oklahoma City  
 Postle East  
 Sho-Vel-Tum  
 Sooner Trend  
 Velma

TEXAS

District 1  
 Big Foot  
 Big Wells  
 Hilbig  
 San Miguel Creek  
 District 2  
 Clayton  
 Greta  
 Greta Deep  
 Greta North  
 Helen Gohlke  
 Heyser  
 Lake Pasture  
 Maurbro  
 Tom O Conner  
 West Ranch  
 District 3  
 Anahuac  
 Clear Lake  
 Conroe  
 Dickinson  
 Gillovk  
 Hastings  
 Magnet Withers  
 Magnet Withers South  
 Old Ocean  
 Oyster Bayou  
 Pierce Junction  
 Saratoga  
 Thompson  
 Thompson North  
 Thompson South  
 Tomball  
 Trinity Bay  
 Trinity Bay

TEXAS (CONTD.)

District 3 (Contd.)  
 Village Mills East  
 Webster  
 District 4  
 Alazan North  
 Borregos  
 Kelsey  
 Kelsey East  
 Kelsey South  
 Plymouth  
 Ricon  
 Seeligson  
 Stratton  
 Sun  
 Tijerina-Canales-Blucher  
 Willamar West  
 District 5  
 Van  
 District 6  
 East Texas  
 Fairway  
 Hawkins  
 Neches  
 District 7B  
 Nena Lucia  
 Round Top  
 District 7C  
 McCamey  
 Todd Deep  
 District 8  
 Andector  
 Block 31  
 Cowden North  
 Cowden South  
 Cowden South-Foster  
 Cowden South-Johnson  
 Crossett (Shell-SACROG  
 Branch Line)  
 Dollarhide  
 Dune  
 Fullerton  
 Fullerton East  
 Fullerton North  
 Fullerton South  
 Fullerton Southeast  
 Goldsmith  
 Goldsmith East  
 Goldsmith North  
 Goldsmith Northwest

TABLE IX-1

CANDIDATE FIELDS WITH RESERVOIRS THAT  
MEET GURC CRITICAL PARAMETERS FOR MISCIBLE CO<sub>2</sub>  
(CONTD.)

TEXAS (CONTD.)

District 8 (Contd.)  
 Goldsmith West  
 Howard-Glasscock  
 Keystone  
 Mabee  
 McElroy  
 Means  
 Means East  
 Means North  
 Means South  
 Midland Farms East  
 Midland Farms Northeast  
 Midland Farms Southeast  
 Midland Farms West  
 Pecos Valley  
 Sand Hills  
 Ward-Estes North  
 District 8A  
 Cogdell Area  
 Diamond M  
 Kelly-Snyder (SACROC)  
 Levelland  
 Prentice  
 Salt Creek  
 Seminole  
 Seminole East  
 Seminole North  
 Seminole Northwest  
 Seminole Southwest  
 Seminole West  
 Slaughter  
 Spraberry  
 Spraberry West  
 Wasson  
 Wasson East  
 Wasson Northeast  
 Wasson North  
 Wasson Southeast  
 Wasson 66  
 Wasson 72  
 Welch  
 District 10  
 Farnsworth  
 Panhandle field

UTAH

Altamont  
 Greater Aneth  
 Red Wash

WYOMING

Byron  
 Elk basin  
 Fourbear  
 Garland  
 Salt Creek  
 Teapot east  
 Teapot Naval Petroleum  
 Reserve 3  
 Teapot Outside Reserve

Shell Oil Planning  
 pilot tests with  
 trucked CO<sub>2</sub>  
 Shell testing

TABLE IX-2  
Carbon Dioxide Miscible Flooding - Candidate  
Fields/Reservoirs Located in Producing Trends or Areas

<u>State</u> No. of fields/reservoirs	<u>Estimated Potential Oil Recoverable by Carbon Dioxide Miscible Flooding</u> (MMBLS)	<u>SCF/BBL</u>	<u>Estimated Quantity of Carbon Dioxide Required For Miscible Flooding</u> (BSCF)
<u>Texas</u> - west *,**			
40	2,308	2,660	6,139
<u>Texas</u> - Gulf Coast			
11	225	2,542	572
<u>Louisiana</u> - south **			
18	269	3,461	931
<u>Mississippi</u> - southwest **			
4	129	2,527	326
<u>California</u>			
10	<u>322</u>	<u>3,963</u>	<u>1,197</u>
Totals - 83	3,253	3,031 (avg.)	9,165

\*"Full scale" project currently underway  
\*\*Field Text planned or in progress

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