FOSSIL ENERGY

DOE/MC/08333-3(Vol.1)
(DE82004814)

FEASIBILITY AND ECONOMICS OF BY-PRODUCT CO_2 SUPPLY FOR ENHANCED OIL RECOVERY

Final Report
Vol. 1: Technical Report

January 1982
Date Published

Work Performed Under Contract No. AM21-78MC08333

Science Applications, Inc.
Morgantown, West Virginia

Bartlesville Project Office
U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma

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Microfiche A01

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DOE/MC/08333-3(Vol.1)
(DE82004814)
Distribution Category UC-92a

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Vol. 1: Technical Report

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Work Performed for the Department of Energy
Under Contract No. DE-AT21-78MC08333, Task 36

Date Published—January 1982

UNITED STATES DEPARTMENT OF ENERGY

ACKNOWLEDGEMENT

The authors would like to acknowledge the excellent support provided by the following individuals:

Carol Molisee, Paula Ringer, Sharon Hillberry, and Betty Wiley for typing;

Richard Deaner for drafting; and Katherine Lessing for editing. The support provided by Mr. Tahir Zarti, a graduate student, in the collection of data is also appreciated.

The authors also acknowledge the following persons for their useful comments in improving the final report:

Mr. Royal Watts of DOE/METC,

Dr. Harley Jennings of Chevron, and

Dr. James Wasson of West Virginia University.

The authors thank the many institutions and organizations who provided data and permission to reprint tables/figures. The sources of the data are provided in the text and list of references and proper credits are given.

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EXECUTIVE SUMMARY

This report provides an analysis of the technical and economic feasibility of using by-product sources of CO_2 for enhanced oil recovery. The report includes a comprehensive survey of existing and future by-product sources in the conterminous United States. The potential demand for CO_2 was determined for the four regions where reasonably good data were available: Permian Basin, Williston Basin, Appalachian Basin, and Los Angeles Basin. Data were insufficient to assess the CO_2 demand for EOR from oil reservoirs in Louisiana and Mississippi.

The total CO_2 demand for each field was based on available data on the residual oil in place (ROIP) in candidate reservoirs for CO_2 flooding. The CO_2 demand was calculated using the following guidelines:

Oil Type	% ROIP Recoverable	Purchased CO_2 Required (MSCF/Barrel)
Secondary Recovery		
Light oil	25.6	6.8
Heavy oil	15.9	13.9
Tertiary Recovery		
Light oil	16.2	7.8

This demand was then spread over 15 years to get an average daily demand figure. The percent of light oil that is recoverable using secondary recovery seems high; however, it includes both secondary and tertiary oil recoverable due to CO_2 flooding.

The analysis of CO_2 sources included a survey of natural CO_2, as this source is generally economically preferable to by-product CO_2, and a study of on-site generation of CO_2. By-product CO_2 sources considered were flue gases from power plants and cement plants, and off-gases from ammonia plants, refinery fluid-catalytic cracking units, and hydrogen plants.

The composition of each of the by-product CO_2 source streams considered is shown in Table 1 on the next page.

Daily supply and demand data (based on 300 operating days per year) is also summarized on the next page in Table 2.

Table 1: Composition of By-Product CO_2 Source Streams

Source	Average Gas Composition						
	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$	CO_2 Emitted (MSCF/Unit)
1. Coal-Fired Power Plant (Depends on coal source)							
New Mexico coal	14.0	3.0	74.1	0.34	0.078	8.5	33.6/ton coal
North Dakota coal	12.9	1.7	68.3	0.44	0.078	17.0	23.4/ton coal
Texas coal	13.5	1.9	71.4	0.42	0.26	12.5	26.1/ton coal
2. Oil-Fired Power Plant	12.3	2.6	75.0	0.086	0.086	9.9	8.9/barrel oil
3. Gas-Fired Power Plant	9.1	1.7	72.1	--	--	17.0	1.1/MSCF gas
4. Pre-1963 Coal-Fired Wet Cement Plant	21.0	1.7	39.6	0.17	0.09	37.5	18.8/ton cement
5. Post-1963 Coal-Fired Wet Cement Plant	25.8	1.6	37.2	0.16	0.09	35.2	16.9/ton cement
6. Pre-1963 Gas-Fired Wet Cement Plant	22.5	0.85	36.0	--	--	40.3	16.9/ton cement
7. Post-1963 Gas-Fired Wet Cement Plant	23.6	0.89	37.9	--	--	37.3	15.3/ton cement
8. Pre-1963 Coal-Fired Dry Cement Plant	27.9	2.4	63.1	0.16	0.09	6.4	18.8/ton cement
9. Post-1963 Coal-Fired Dry Cement Plant	29.3	2.3	61.9	0.14	0.08	6.3	16.9/ton cement
10. Pre-1963 Gas-Fired Dry Cement Plant	25.4	1.6	61.6	--	--	11.2	16.9/ton cement
11. Post-1963 Gas-Fired Dry Cement Plant	28.6	1.6	59.5	--	--	10.1	15.3/ton cement
12. Ammonia Plant	97.5	--	0.02	--	--	2.4	16.0-21.9/ton NH_3
13. Refinery FCCU	14.6	1.7	75.8	--	--	7.9	.2/barrel feedstock
14. Hydrogen Plant	97.5	--	0.02	--	--	2.4	.25/MSCF hydrogen

Table 2: Daily Supply and Demand Data

BASINS	PERMIAN and Surrounding Area	WILLISTON	APPALACHIAN	LOS ANGELES
DEMAND (MMSCFD)	10,011	236	83	376
SUPPLY (MMSCFD)				
Natural CO_2	1,350*	--	17	--
Nat. Gas Proc. Plants	235	--	20	--
Ammonia Plants	196	4	12	17
Hydrogen Plants	52	4	5	21
Ethanol Plants	17	--	--	--
Ethylene Oxide Plants	43	--	--	--
Power Plants	10,066	887	7,732	2,405
Cement Plants	524	33	172	216
Refinery FCCU	331	18	47	48
TOTAL BY-PRODUCT SUPPLY	11,464	946	7,988	2,707

* Includes Natural CO_2 from Jackson Dome Area.

The calculations were based on prediction of the amount of oil recoverable by CO_2 flooding for each reservoir, knowledge of mode of reservoir, and ultimate CO_2 requirements for each reservoir. Daily demand was calculated based on 15-year life of CO_2 flooding operations in areas under consideration.

Within each of the four regions considered in this study, the total potential CO_2 supply exceeds the potential CO_2 demand. Natural CO_2 and high purity sources can satisfy less than 20% of the demand. If the cost of by-product supply is considered, then the supply (excluding on-site production) from existing sources is insufficient to meet all the demand at delivered CO_2 prices of under $2.50 in the Permian Basin.

The processes for recovering CO_2 from low purity by-product sources were evaluated. Because of the low partial pressure of CO_2 in these sources, monoethanolamine (MEA) and potassium carbonate (K_2CO_3) were considered. Both of these processes use chemical solvents for CO_2 absorption. The MEA process requires lower capital investment and higher operating costs, whereas the K_2CO_3 process requires higher capital investment and lower operation costs. The CO_2 recovery systems using these processes for power and cement plants, and refinery fluid catalytic cracker unit (FCCU) regenerator flue gases were designed and costed. These designs are preliminary; costs are believed to be accurate within 30 percent.

The economic analysis showed that the recovery of CO_2 from cement plants and refinery FCCU regenerator units may not be economically feasible due to their smaller sizes.

The recovery costs for CO_2 from power plants are summarized in Table 3, based on 90% recovery, a 15-year plant life, 15% return on equity, a 75% debt/equity ratio, and the same fuel is used for steam generation for CO_2 recovery as is used for power generation.

Table 3: CO_2 Recovery Costs for 90% Recovery ($/MSCF)

SOURCE	CO_2 VOLUME (MMSCFD)	RECOVERY COST	
		MEA	K_2CO_3
Gas-Fired Power Plant	75	2.10	1.86
	30	2.27	2.09
	15	2.63	2.39
Coal-Fired Power Plant (High Sulfur)	75	1.41	1.28
	30	1.65	1.53
	15	2.05	1.87
Coal-Fired Power Plant (Low Sulfur)	86.5	1.06	1.19
	75	1.07	1.21
	30	1.32	1.43
	15	1.72	1.77
Optimistic Design Coal-Fired Power Plant . . . (Low Sulfur)	86.5	1.04	.67

The variation in cost between MEA and K_2CO_3 was small (5 to 8%) when compared to the accuracy of this preliminary study (within 30%). Also, the impact of recovery percentage on cost was small (10%) with a recovery rate of from 90% to 60%. However, the cost does increase substantially as the recovery rate is lowered to 30%.

Compression and drying costs were determined for two cases: (1) using steam for the compressors; and (2) using electrically driven compressors. The cost in the former case varied from $0.18 at 60 MMSCFD to $0.35 at 10 MMSCFD. In the latter case, the cost varied from $0.42 at 50 MMSCFD to $0.57 at 10 MMSCFD. Costs in both cases increased very rapidly for CO_2 volumes below 10 MMSCFD.

Pipeline, rail, road, and barge were studied as possible means of transportation for CO_2. Barge transport was ruled out due to the absence of navigable waterways in the Permian Basin, while rail and road were generally more expensive than pipelines. The pipeline costs are summarized in Table 4:

Table 4: CO_2 Transportation Cost (Pipeline, $/MSCF).

CO_2 VOLUME (MMSCFD)	50 Miles	200 Miles	500 Miles
300	.055	.22	.55
75	.11	.44	1.10
30	.19	.76	1.90
15	.31	1.24	3.10
10	.39	1.56	3.90
5	.54	2.16	5.40

On-site generation of CO_2 was also investigated, although no such plants are currently available for commercial application. Two systems were studied in detail as being the most promising: wet air oxidation, and the combustion of lignite in a fluidized bed boiler, with subsequent recovery of CO_2 from the flue gas by an activated K_2CO_3 recovery system. Wet air oxidation is the more economical of the two methods, and is competitive with by-product sources.

The CO_2 cost varies from $1.67/MSCF to $3.05/MSCF for a 22 MMSCFD plant (depending on the size of the energy credit taken for the steam produced). This is the total delivered cost, since the CO_2 is produced on-site at the required pressure and purity.

On the basis of the recovery, compression and drying, and transportation costs, together with estimates of purchase costs of the by-product stream ($0.10 for power plants, cement plants, and refinery FCCU, and $1.00 or $1.50 for ammonia plants, hydrogen plants, etc.), the total delivered CO_2 cost was calculated. This is summarized in Table 5 for various sources and volumes at 50, 200, and 500 miles.

Table 5: Delivered CO_2 Cost ($/MSCF)

Type of Plant	Calendar Day CO_2 Output (MMSCFD)	MEA			K_2CO_3		
		50 Miles	200 Miles	500 Miles	50 Miles	200 Miles	500 Miles
Gas-Fired Power Plant	75	2.42	2.75	3.41	2.25	2.58	3.24
	30	2.78	3.35	4.49	2.60	3.17	4.31
	15	3.33	4.26	6.12	3.09	4.02	5.88
Coal-Fired Power Plant (High Sulfur)	75	1.80	2.13	2.79	1.67	2.00	2.64
	30	2.16	2.73	3.87	2.04	2.61	3.75
	15	2.75	3.68	5.54	2.57	3.50	5.36
Coal-Fired Power Plant (Low Sulfur)	75	1.46	1.79	2.45	1.60	1.93	2.59
	30	1.83	2.40	3.54	1.94	2.51	3.65
	15	2.42	3.35	5.21	2.47	3.40	5.26
Refinery FCCU	30	3.08	3.65	4.79	2.85	3.42	4.56
	15	3.57	4.50	6.36	3.34	4.27	6.13
	5	5.46	7.08	10.32	5.31	6.93	10.17
Gas-Fired Cement Plant	10	3.73	4.90	7.24	2.93	4.10	6.44
	5	5.06	6.78	9.92	4.86	6.58	9.72
	3	6.68	8.78	12.98	6.68	8.78	12.98
Coal-Fired Wet Cement Plant	13	2.50	3.52	5.56	2.65	3.67	5.71
	10	2.83	4.00	6.34	2.93	4.10	6.44
	5	4.09	5.71	8.95	4.20	5.82	9.06
		Purchased at $1/MCF			Purchased at $1.50/MCF		
Ammonia Plant and other High-Purity Sources	30	1.63	2.20	3.34	2.13	2.70	3.84
	15	1.81	2.75	4.64	2.31	3.25	5.14
	5	2.21	3.83	7.07	2.71	4.33	7.57

Based on: 90% recovery, 15-year life, 75% debt

Based on these results, the maximum economic transportation distance for each source was considered for total delivered costs in the range of $2.50 to $4.00. The results for $2.50/MSCF and $3.00/MSCF are shown in Figures 1 and 2.

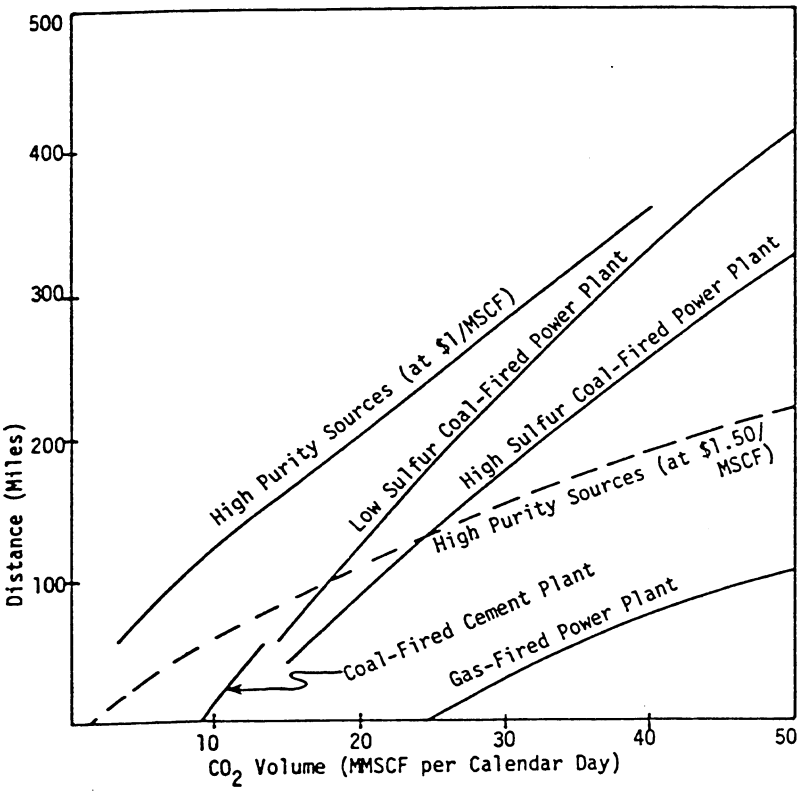

Figure 1: Maximum Transportation Distance for By-Product CO_2 Delivered at $2.50/MSCF

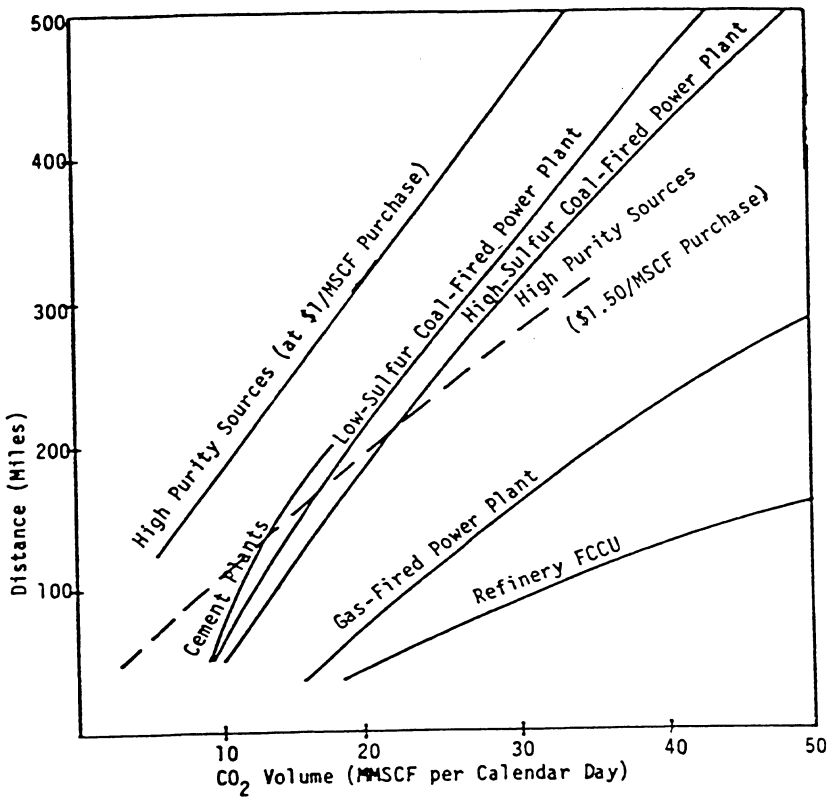

Figure 2: Maximum Transportation Distance for By-Product CO_2 Delivered at $3.00/MSCF

The potential demand for CO_2 requires an inexpensive CO_2 source in order to allow a sufficient margin with respect to the price of the oil so that the operation will be profitable. At an oil price of \$32/bbl it can be estimated that approximately \$18/bbl are spent on investment costs, operating costs, and royalty and taxes. This leaves a maximum of \$14/bbl for CO_2 costs. It is estimated that approximately 6.8 MSCF/bbl of CO_2 are required for secondary recovery applications with light oil (see Section 2). This suggests that to make a CO_2 flooding EOR operation profitable, CO_2 should be delivered to the field at about \$2/MSCF.

The only by-product sources that can provide CO_2 for under \$2/MSCF delivered are coal-fired power plants, ammonia plants, and other high purity sources, provided the transportation distance is small (50 to 100 miles).

Only a few by-product CO_2 sources can be used with present technology. Improvements in this technology may be needed prior to the wide-spread use of by-product CO_2 from low purity sources in EOR.

Several alternatives have been presented in this report for extending the technology. Higher active-species concentrations of absorption media are recommended, as well as the adoption of the vacuum carbonate type process. Using these and/or other improvements (e.g., packed or spray tower design) suggested in this report, the cost of CO_2 recovery from large CO_2 by-product sources was lowered from \$1.30 to \$0.72/MSCF using the K_2CO_3 process for CO_2 recovery from a low-sulfur coal-fired power plant (see Exhibit 5-10). With such an optimistic design, the potential cost for CO_2 recovery from low-purity by-product sources could be competitive with the smaller high-purity sources and even with natural CO_2 sources, depending on the transportation requirements.

This report presents a CO_2 supply/demand analysis for EOR use and provides a preliminary design for and an economic analysis of CO_2 recovery from low-purity by-product sources and on-site CO_2 generation. These costs are compared with high-purity CO_2 sources. The Appendices provide detailed data on by-product CO_2 sources, supporting information for design calculations, and computer programs used in the economic analysis.

1. INTRODUCTION

The main objective of this study is to determine the technical and economic feasibility of supplying carbon dioxide for use in enhanced oil recovery, from other than naturally occurring sources, to all suitable oil fields.

Carbon dioxide miscible displacement is one of the most promising technologies for use in EOR. It has been estimated that over 50 trillion SCF of CO_2 will be required to recover oil by CO_2 miscible displacement in the Permian Basin alone. Pullman Kellogg[41*] has estimated that at most, only 18 trillion SCF of natural CO_2 reserves exist in and around west Texas. Except for the west Texas area and the Appalachian Basin, no known CO_2 reserves exist within the other basins discussed in this study. Thus, it is apparent that natural sources alone can not supply the CO_2 demand for all potential EOR projects. To exploit the maximum number of reservoirs targeted for additional oil recovery with CO_2 miscible displacement, sources other than naturally occurring CO_2 must be considered.

Several studies have been conducted on CO_2 supply for use in EOR including:

- Pullman Kellogg - Sources and Delivery of CO_2 for EOR: Ref. 41
- West Virginia University - Carbon Dioxide Sources: Ref. 55
- Pullman Kellogg - The Supply of Carbon Dioxide for Enhanced Oil Recovery: Ref. 40
- Lawrence-Allison and Associates Corporation - A Study of CO_2 Recovery and Tertiary Oil Production Enhancement in the Los Angeles Basin: Ref. 47
- Gulf Universities Research Consortium - Naturally Occurring CO_2 Sources in the United States: Ref. 21
- Science Applications, Inc. - Alternate Concepts of Supply CO_2 for EOR Projects: Ref. 45
- West Virginia University - Determination of the Effects of Sulfur Dioxide on Recovery Systems for CO_2: Ref. 46
- MITRE Corporation - Feasibility of Utilizing CO_2 Produced During the High Btu Coal Gasification Process for EOR: Ref. 29

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*References are listed in Alphabetical Order in Section 10.

For the most part, prior studies have not adequately addressed availability, processing, and economics of CO_2 supply from by-product sources. Where appropriate, results of previous studies have been utilized; care has been taken to minimize any duplication. This study provides exhaustive data on CO_2 supply from by-product sources and the preliminary costs associated with these sources.

Section 2 provides information on target reservoirs for CO_2 flooding, and the ultimate CO_2 requirements for CO_2 flooding in these reservoirs. CO_2 requirements are identified in terms of MSCF/bbl of oil recovered according to the type of oil (heavy or light) in the reservoir, and the envisaged recovery mode (secondary or tertiary) of the reservoir. Estimates of potential CO_2 demand on a county-by-county basis for four major basins, (i.e., Permian, Appalachian, Williston, and Los Angeles) are provided.

Section 3 provides detailed information on by-product CO_2 supply sources. The CO_2 availability from power, cement, ammonia, ethanol, and ethylene oxide plants, and refineries; the quality of gas from such plants; and their locations are identified. The methodology and assumptions in the determination of the quality of by-product gases are discussed. Future by-product CO_2 supply sources including proposed power, alcohol, and SNG plants and refineries, their CO_2 generation capacities, locations (where available), and quality of gas emitted from these plants are identified.

Section 4 provides an analysis of the regional supply/demand balance. The total CO_2 demand in each of the four basins is identified. The total CO_2 supply from each source, regional supply from each source, and the locations of these sources are identified. This Section shows that currently known, naturally occurring, high purity CO_2 sources can provide less than 15% of the total CO_2 demand; however, the total supply from by-product CO_2 sources is shown to be more than sufficient to meet this demand.

Section 5 provides a detailed discussion on the techno-economic analysis of CO_2 recovery systems. A discussion on acid-gas removal processes that can be used for recovering CO_2 from various sources is included. Detailed discussions of MEA and Potassium Carbonate Processes and the design of CO_2 recovery systems for CO_2 from low purity sources are provided. Descriptions of the compression and drying systems and their economics are included.

Results of the technical and economic analysis of MEA and K_2CO_3 systems are discussed.

Section 6 provides information on CO_2 transportation, storage, and injection costs. Transportation costs using pipeline, truck, rail, and barges for various volumes versus transportation distances are provided. CO_2 injection and associated costs are identified.

Section 7 provides information on the the feasibility and economics of CO_2 generation at EOR sites. The processes and economics of on-site CO_2 generation using wet air oxidation and fluidized bed combustion of coal are discussed. The feasibility and economics of locating SNG plants at EOR fields are also discussed.

Section 8 provides the methodology to determine total CO_2 costs. Reported costs on CO_2 and flue gas purchases are identified. The methodology for determining total CO_2 costs, including gas purchase, purification, compression and drying, and transportation costs using low and high purity sources, is shown with examples. The maximum economic transportation distances for providing CO_2 from low- and high-purity CO_2 sources are indicated for various size plants at maximum CO_2 costs of \$2.00, \$2.50, \$3.00 and \$4.00. A transportation model is provided which can be used to identify the best economic source(s) for various demand points. The results of applying the model to the Permian Basin are provided using data generated in the study.

Section 9 provides conclusions and recommendations.

Appendices A through R are provided in a separate volume. They include detailed data on target reservoirs; CO_2 requirements by reservoirs; a list of all known present and proposed CO_2 sources; their locations; the volume of CO_2 available; and its quality. The methodology of MEA, K_2CO_3, and compression- and drying systems' designs with examples are provided. The methodology and assumptions for the economic analysis and the transportation model program are included.

2. TARGET RESERVOIRS FOR CO_2 FLOODING

2.1 INTRODUCTION

The identification of reservoirs amenable to CO_2 miscible flooding is a large enough project to warrant a separate study. This work is being performed for the Department of Energy by Gruy Federal, Inc.; the results presented in this chapter draw heavily on Gruy Federal's preliminary work.[19]

A number of guidelines for the applicability of the CO_2 flooding process have been published.[15,20,27,32] Various guidelines for selecting reservoirs for CO_2 flooding are presented in Exhibit 2-1. In addition, no extremely high permeability thief zones should exist. Gruy Federal used the following guidelines for the selection of candidate carbonate reservoirs for CO_2 flooding:

Average Formation Permeability	$\geq$2 md
Average Current Oil Saturation	$\geq$38%
Oil Gravity	$\geq 30^{o}$ API
Oil Viscosity	$\leq$10 cp

Gruy Federal[19] reviewed 19 CO_2 injection projects in 16 oil fields located in five states. The field test data suggested that CO_2 injection is technically capable of displacing oil from reservoir rocks over a wide range of geological and physical conditions. The data review and analysis showed that projects have been conducted at depths ranging from 2,100 feet to 12,700 feet over a reservoir temperature range from $74^{o}F$ to $248^{o}F$ in rocks where lithologies included unconsolidated Gulf Coast sands, cemented sandstones, limestones, and cherty dolomites. These projects included reservoirs whose stock tank oil gravity ranged from 15° to 45° API. It should be noted that all field tests were not successful. This spectrum of parameters is much less restrictive than the guidelines presented in Exhibit 2-1.

By extensively applying the guidelines presented above, and by reviewing existing literature, Gruy Federal[19] identified over 280 carbonate fields in the Permian Basin and Rocky Mountain States which could be deemed amenable to CO_2 miscible flooding recovery methods. Indeed, a number of fields were identified in the literature as potentially amenable to CO_2 even though they

Exhibit 2-1: Screening Criteria for CO_2 Miscible Displacement

SCREENING PARAMETERS	DOE MANAGEMENT PLAN[1]	GURC REPORT[2]	PETROLEUM ENGINEER INTERNATIONAL[3]	NATIONAL PETROLEUM COUNCIL[4]
Viscosity, centipoise at reservoir conditions	< 12		< 5	≤ 10
Gravity, °API				
Other than California crudes	> 30	> 27	> 35	> 27
California crudes	> 26			
Oil Concentration, B/AF	NC[5]			
Oil Saturation, percent(%)	> 25	> 20	> 25	
Depth, feet	> 3000	> 2000	> 2000	≥ 2300
Temperature, °F	NC	NC	NC	≤ 250°F
Orignial Bottomhole Pressure, psi	> 1500			
Net Pay Thickness	NC	NC	NC	
Gas Cap	NC		NC	
Permeability, millidarcy (mD)	NC	Prefer reasonably homogeneous permeability	> 5	
Transmissibility, permeability x thickness/visc.	NC			
Natural Water Drive[6]	none to weak			
Gas Cap[6]	none to minor			
Fractures	none to minor			
Lithology	NC			
Salinity, parts per million (ppm) TDA	NC			
Hardness, parts per million (ppm) Calcium and magnesium	NC			

1. ERDA (DOE), Management Plan for Enhanced Oil Recovery, Volume 1, Program Strategy, Petroleum and Natural Gas Program: Report No. ERDA 77-15/1, Section III, p.3, February 1977.
2. Gulf Universities Research Consortium, Candidate Reservoirs for Enhanced Oil Recovery, Guidelines for Their Selection, and Appraisal for Significant Tests to Date: for DOE Report No. FE-2025-T1, p.3, March 1977.
3. McRee, B. C., Petroleum Engineer International, CO_2 -- How It Works, Where It Works: p.52, November 1977.
4. National Petroleum Council, Enhanced Oil Recovery - An Analysis of Potential for Enhanced Oil Recovery from Known Fields in the U.S. -- 1976 to 2000: Washington, D.C., December 1976.
5. NC = not a critical factor.
6. These criteria apply to reservoirs with substantial remaining capacity.

did not necessarily meet all the criteria outlined. As a result of this analysis, the following geographical basins were determined as containing at least some of the fields of interest (see Exhibit 2-2 for location).

- Appalachian Basin
- Arkla Basin
- Illinois Basin
- Los Angeles Basin
- Louisiana Salt Dome Basin
- Mississippi Salt Dome Basin
- Paradox Masin
- Permian Basin
- Texas Gulf Coast Basin
- Williston Basin

The quantity of oil that was potentially recoverable by CO_2 miscible flooding and the ultimate amount of CO_2 required to recover this oil were then estimated on a field-by-field basis. The majority of the recoverable oil - over fifty percent - was found to be in the vicinity of the Permian Basin in west Texas.

It was decided to also study three other very different basins in detail in order to broaden the applicability of the results. The study therefore, concentrated on the Appalachian, Los Angeles, Permian, and Williston Basins and the regions surrounding these Basins. The locations of each of the four regions are illustrated in Exhibit 2-2 by heavy black lines. Exhibit 2-3 illustrates the counties and fields with potential for CO_2 EOR.

In addition to Gruy Federal's[19] target reservoir study, other studies[12,18,47] were used in identifying locations of fields amenable to CO_2 flooding for enhanced oil recovery.

2.2 LOCATION OF FIELDS AMENABLE TO CO_2 MISCIBLE FLOODING

The names of the ten geographical basins containing fields amenable to CO_2 flooding identified in Exhibit 2-2 and county and state locations within each basin are given in Appendix A. Where possible, information is also included on important reservoir characteristics, the original oil in place (OOIP), the residual oil in place (ROIP), and whether the field is currently operating in a primary recovery mode or has undergone water flooding (secondary recovery mode). Few of the large fields listed are producing by means of CO_2 enhanced oil recovery methods with the notable exception of Chevron's Sacroc Unit at the Kelly Snyder Field located in Scurry County, west

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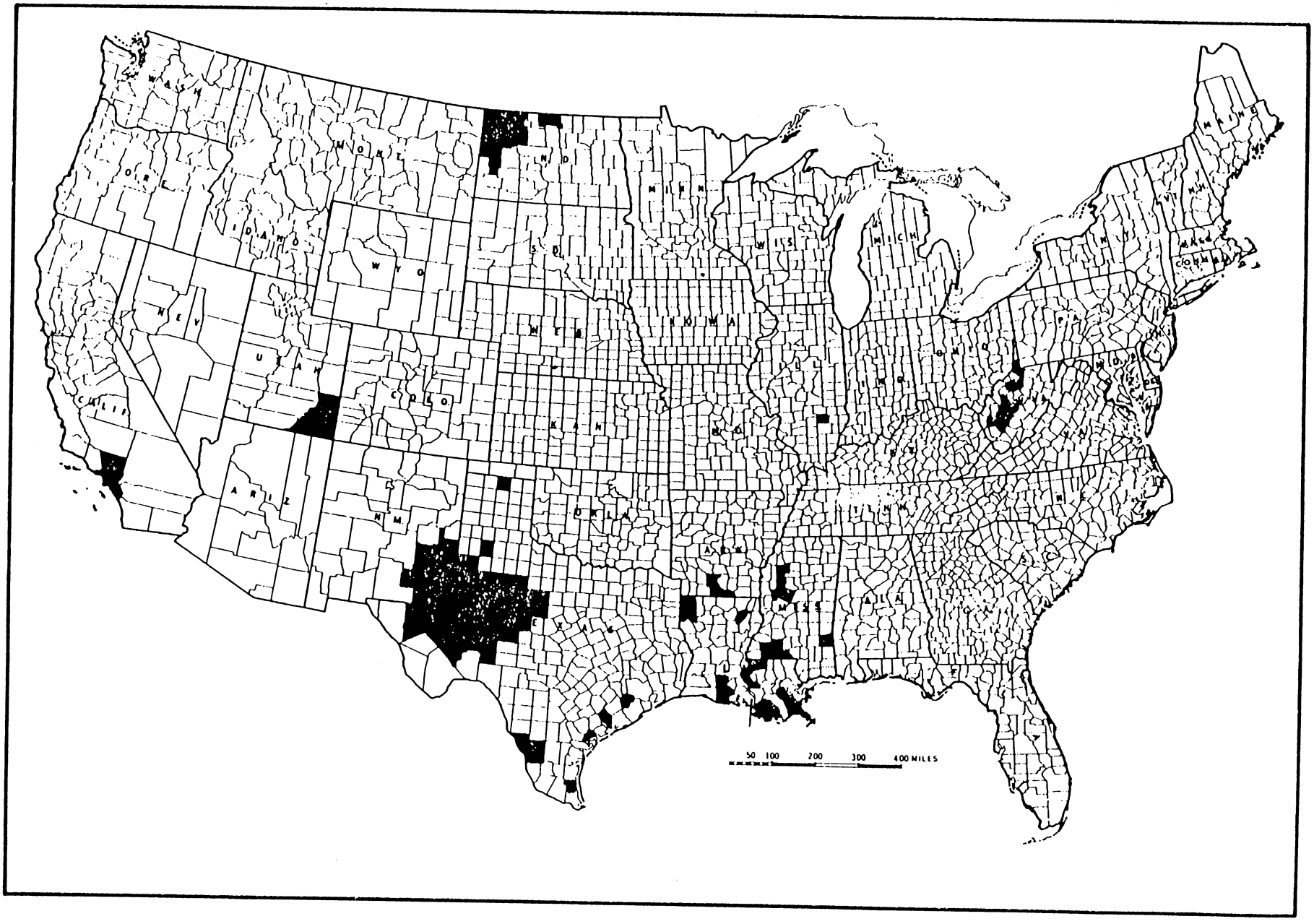

Exhibit 2-3: Counties with Potential for EOR Using Carbon Dioxide Included in this Study

Texas. A successful large scale water driven CO_2 flood has been on going there since the early seventies when waterflood operations were essentially terminated.

Appalachian Basin: Gruy Federal in 1979[18] evaluated the petroleum reservoirs of West Virginia amenable to enhanced oil recovery technology, particularly CO_2 injection. Their work identified seventeen candidate fields for CO_2 recovery processes and four fields for other EOR techniques. Of the seventeen fields targeted for enhanced recovery using CO_2, data permitting volumetric calculations were available for only ten fields. No data were available for reserves in other states in this Basin.

Arkla Basin: The Gulf Universities Research Consortium report on candidate reservoirs for enhanced oil recovery was used to isolate the one field in the Arkla Basin that is believed to have the potential for tertiary recovery using CO_2.[20] The paucity of accurate reservoir data did not permit accurate determinations of the OOIP and the ROIP. However, approximate estimates of these values were made by assuming that the production-to-date was ten percent of the OOIP. Production volumes were obtained from the International Oil and Gas Development Yearbook.[23]

Illinois Basin: The target fields for CO_2 enhanced recovery operations were again identified from the Gulf Universities Research Consortium report.[20] Data on important reservoir characteristics were obtained from the Illinois Geological Survey.

Los Angeles Basin: Information isolating the prime candidate fields for CO_2 miscible flooding was obtained from the study by Lawrence-Allison and Associates Corporation on CO_2 recovery and tertiary oil production in the Los Angeles Basin.[47] Sufficient data on reservoir characteristics were provided in the report to calculate the OOIP and ROIP values for several fields.

Louisiana Salt Dome Basin: The Gulf Universities Research Consortium report identified the two fields in the Louisiana Gulf Coast Basin that were amenable to CO_2 miscible flooding.[20] In the absence of accurate reservoir data, very approximate estimates of the OOIP and ROIP were made from the International Oil and Gas Development Yearbook by assuming that the quoted production-to-date was ten percent of the OOIP.[23]

Mississippi Salt Dome Basin: The likely fields for CO_2 floods were again identified from the Gulf Universities Research Consortium report;[20] and approximate estimates of the OOIP and ROIP for each field were made by assuming that the production-to-date quoted in the International Oil and Gas Development Yearbook was ten percent of the OOIP.[23]

Paradox Basin: The two prime fields for CO_2 flooding were isolated from two different sources; the Ismay field from the Gruy Federal report,[19] and the Greater Aneth field from the Gulf Universities Research Consortium report.[20] Reservoir data were available to permit the calculation of the ROIP and OOIP for the Ismay field but these quantities had to be approximately estimated for the Greater Aneth field from production data in the International Oil and Gas Development Yearbook.[23]

Permian Basin: The work reported by Gruy Federal contains detailed information on fields in carbonate reservoirs within the Permian Basin that are amenable to CO_2 flooding.[19] These data have been used in the tabulation of the reservoir characteristics and ROIP and OOIP values found in Appendix A. A small number of candidate fields in sandstone reservoirs were also identified from the Gulf Universities Research Consortium report,[20] but unfortunately in most cases little detailed information about these fields was available.

Texas Gulf Coast Basin: The names of fields that appear to be most susceptible to a CO_2 miscible flood were obtained from an Energy Information Administration study.[12] The report contained detailed information on reservoir characteristics, OOIP, and the ultimate amount of recoverable oil. These values were used in Appendix A.

Williston Basin: The Gruy Federal report contained information on CO_2 candidate fields within the Williston Basin.[19] This has been used in the compilation of reservoir data, OOIP, and ROIP in Appendix A.

2.3 CO_2 REQUIREMENTS BASED ON RESERVOIR CHARACTERISTICS AND RECOVERY MODE

Before discussing the quantity of CO_2 required to recover a barrel of oil, it is well worth mentioning the quality of CO_2 which is acceptable for the recovery process. The acceptable level of impurities in CO_2 is dependent on: (1) the physical processes by which the CO_2 displaces the in situ oil; and (2) the allowable concentration of certain impurities with respect to corrosion considerations. From a review of the literature, the following conservative limits have been set for CO_2-bearing gas streams:

Gas Stream Constituent	Allowable Level	
CO_2	90-95% by volume	
H_2O (vapor)	< 2 lb. per MMSCF CO_2	
H_2S	< 100 ppm	
SO_x	< 300 ppm	
NO_x	< 20 ppm	
N_2	< 5% by volume	will depend on depth and allowable miscibility pressure of the reservoir
CH_4 (and other light hydrocarbons)	< 5% by volume	

The presence of nitrogen and methane are undesirable since they impede the miscibility of the CO_2 with the oil. In fact, the greater the concentration of these gases in the CO_2 bearing stream, the greater the injection pressure of the CO_2 must be in order to render it miscible with the oil and initiate the enhanced recovery process.

Water vapor is undesirable in large quantitites since it forms an acidic mixture with CO_2 which, over a period of time, would corrode pipeline and injection equipment. The presence of the other gases - H_2S, SO_x, NO_x - is also undesirable since they too exhibit a corrosion threat when present in association with water. The corrosion problems caused by the use of carbon dioxide for enhanced oil recovery have been fully discussed by the SumX Corporation.[52]

In terms of the quantity of carbon dioxide required, at present no one can accurately predict the volume (MSCF) of CO_2 required to recover one barrel of oil. However, a number of oil companies are at present contemplating CO_2

floods of one type or another, and according to data published in the Enhanced Recovery Weekly,[13] over twenty proposed commercial operations have been analyzed. As a result of this analysis, the volume of CO_2 to be injected has been determined to be strongly dependent on: (1) the gravity of the oil to be recovered; and (2) whether the use of CO_2 will directly follow primary recovery operations (CO_2 as secondary recovery) or water-flooding (CO_2 as tertiary recovery). Another complicating factor is that with increasing time, increasing amounts of CO_2 (dissolved in oil) will be produced at the production site. This CO_2 must be separated from the crude and for economic reasons it will be reinjected. The percentage of injected CO_2 coming from such a recycling process will strongly depend on the nature of the reservoir and the age of the CO_2 flood itself. Commercial data indicate that over the normal life of a project, an average of 35 to 50 percent of all injected CO_2 will come from recycling. The ultimate amount of CO_2 that a project needs to purchase in order to recover one additional barrel of oil is therefore, considerably less than the volume of CO_2 injected to recover one additional barrel of oil.

The analysis conducted as part of this study has determined the following CO_2 requirements.

Type of Recovery with CO_2	Oil Type	CO_2 Injected per Additional Barrel of Oil Recovered (MSCF/Bbl)	Ultimate Amount of CO_2 Required per Additional Barrel of Oil Recovered (MSCF/Bbl)
Secondary	Light	13.5	6.8
Tertiary	Light	16.4	7.8
Secondary	Heavy	28.4	13.9

The analysis also revealed the percentages of the OOIP and ROIP that can be expected to be recovered by employing CO_2. The recovery is again dependent on the oil gravity and whether CO_2 is to be used as either a secondary or a tertiary recovery medium as shown below.

Type of Recovery with CO_2	Oil Type	% OOIP Recoverable	% ROIP Recoverable
Secondary	Light	22.5	25.6
Tertiary	Light	10.7	16.2
Secondary	Heavy	12.8	15.9

The 22.5 percent OOIP figure for CO_2 secondary recovery of light oils seems particularly high; however, it is believed that in the cases quoted CO_2 will be used for secondary recovery and subsequent tertiary recovery, thereby accounting for the large value.

The results of the preceding survey have been applied to the CO_2 target fields listed in Appendix A in order to determine both the amount of oil recoverable by CO_2 injection and the ultimate amount of CO_2 required per day for each field over a 15-year CO_2 injection project life. Although the injection period for an individual reservoir is five to ten years, at decreasing injection rates of new CO_2, 15 years was chosen to allow for the phasing-in of various reservoirs within a field at different times. Estimates of the recoverable oil have been based both on the ROIP and the OOIP for comparative purposes where values of the ROIP and OOIP are deemed sufficiently accurate. All values are listed for each field alongside the reservoir characteristics in Appendix A.

Exhibits 2-4, 2-5, 2-6, and 2-7 show the potential demand for CO_2 on a county-by-county basis in the Appalachian, Los Angeles, Permian, and Williston Basins, respectively. It is evident that there is a vast demand for CO_2 concentrated in west Texas. The total demand in each of the four basins studied in detail is shown below.

	Total CO_2 Demand
Permian (Basin and Texas Gulf Coast)	8,228 MMSCFD
Williston Basin	194 MMSCFD
Appalachian Basin	68 MMSCFD
Los Angeles Basin	309 MMSCFD
Total Demand	8,799 MMSCFD

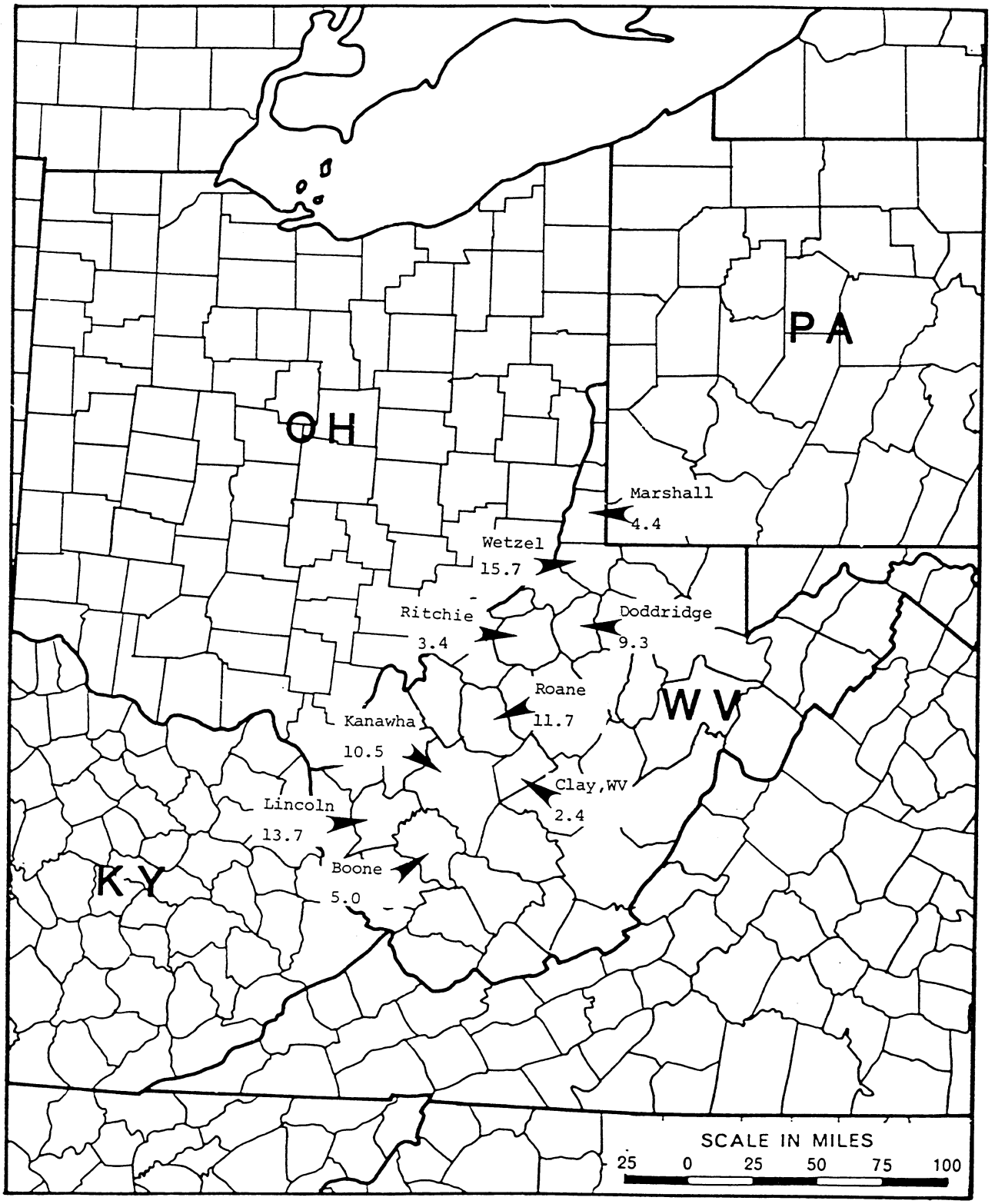

Exhibit 2-4: CO_2 Demand (MMSCFD) in the Appalachian Basin (Based on 15-Year Period)

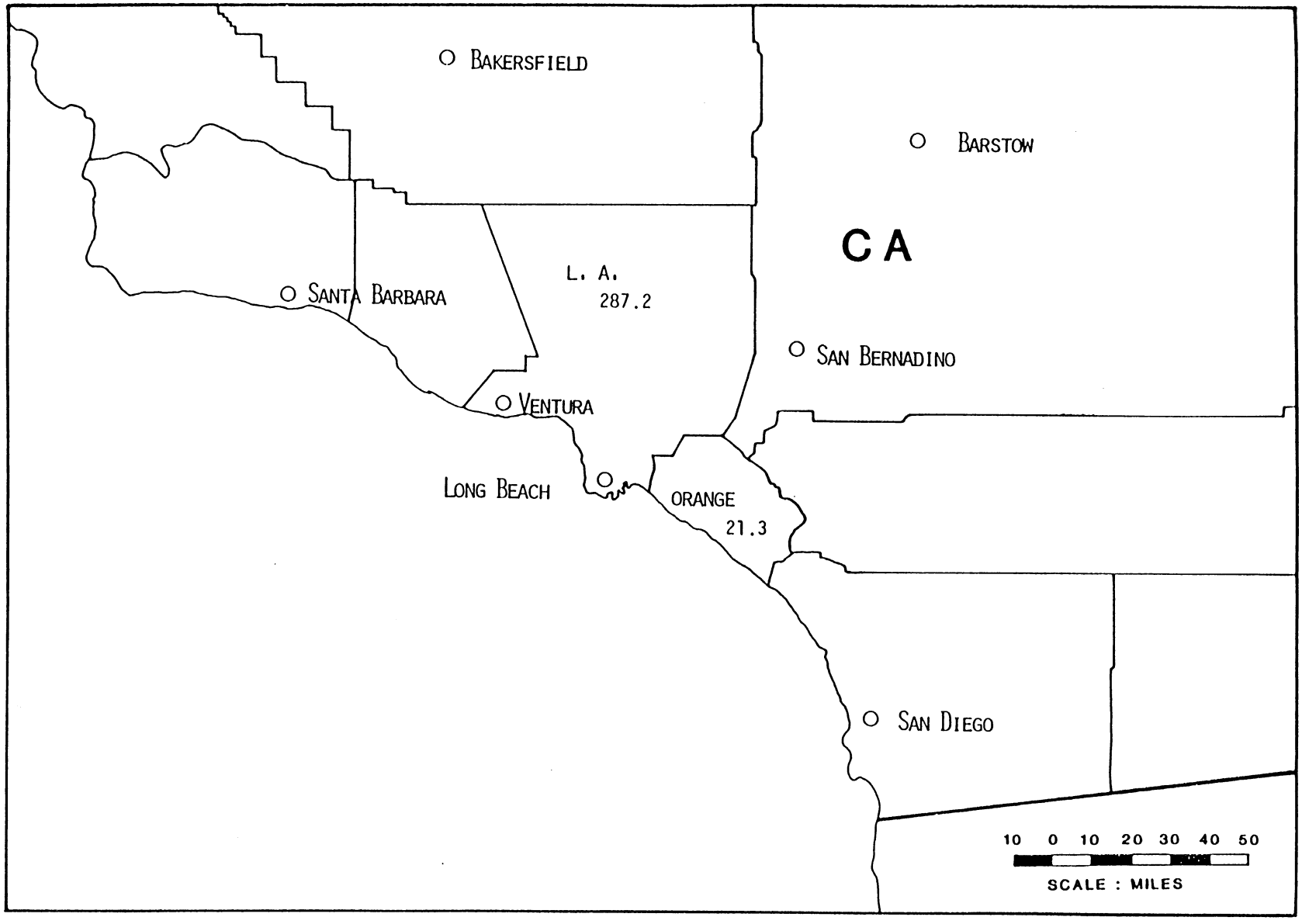

Exhibit 2-5: CO_2 Demand (MMSCFD) in the Los Angeles Basin (Based on 15-Year Period)

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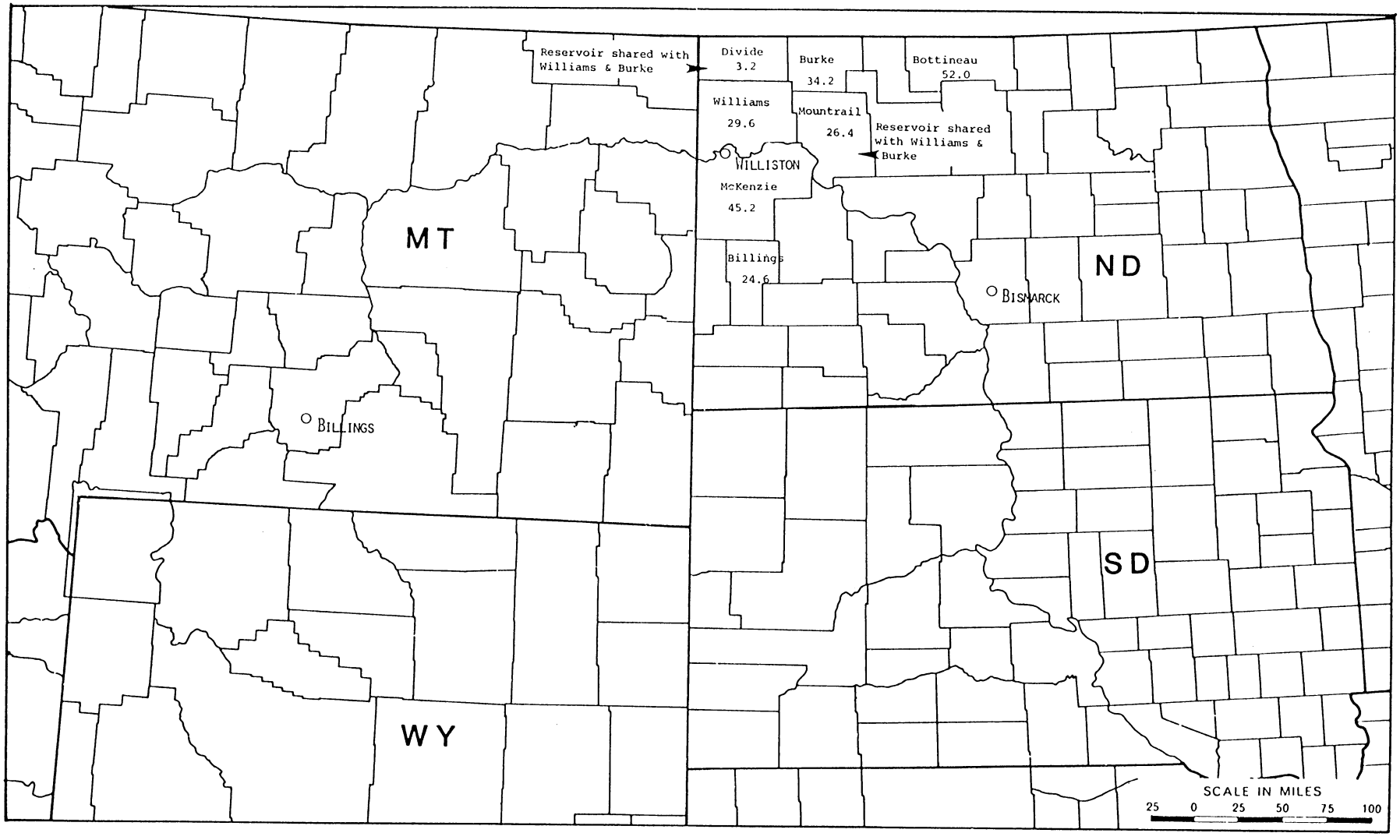

Exhibit 2-7: CO_2 Demand (MMSCFD) in the Williston Basin (Based on 15-Year Period)

3. BY-PRODUCT CO_2 SUPPLY SOURCES

3.1 INTRODUCTION

The term by-product CO_2 refers to any CO_2 incidentally produced from other than natural CO_2 sources. The sources considered in this study which produce CO_2 as an offgas are: fossil fuel power, cement, ammonia, refineries (FCCU regenerator off-gases and hydrogen plants); ethanol, ethylene oxide, and natural gas processing plants; and proposed synthetic natural gas (SNG) and alcohol plants. Since the demand for CO_2 for enhanced oil recovery is envisaged to be greater than known natural CO_2 reserves, by-product CO_2 sources are needed. For example, in west Texas where over 50% of the estimated oil recoverable by CO_2 is located, some 49×10^{12} SCF of CO_2 will ultimately be required if current projections are correct. Pullman Kellogg[41] has estimated that at most, only 18×10^{12} SCF of natural CO_2 reserves exist in and around west Texas -- 40% of the envisaged demand. The location and extent of major natural CO_2 reserves is shown on Exhibit 3-1. A detailed listing of these reserves is given in Appendix B.

3.2 POWER PLANTS

Power plants which generate large quantities of flue gas containing CO_2 are those which raise steam by the combustion of fossil fuels. From a knowledge of the quantity and quality of fuel consumed in over 700 fossil-fuel power plants (over 25 MW capacity) in the continental United States, calculations have been performed for each plant to indicate the quantity of CO_2 produced as well as the composition of the stack gas stream carrying the CO_2. Coal-fired, oil-fired, and gas-fired power plants have all been treated separately as outlined below. Exhibit 3-2 depicts the locations of the fossil-fuel power plants considered in this study.

3.2.1 Coal-Fired Power Plants

The quantity and quality of CO_2 generated in coal-fired power plants can vary widely depending upon the type of coal used. In particular, the amount of pollutants such as SO_2 and NO_x in the CO_2 stream could affect the optimum choice of a CO_2 recovery system. Each power plant has been evaluated

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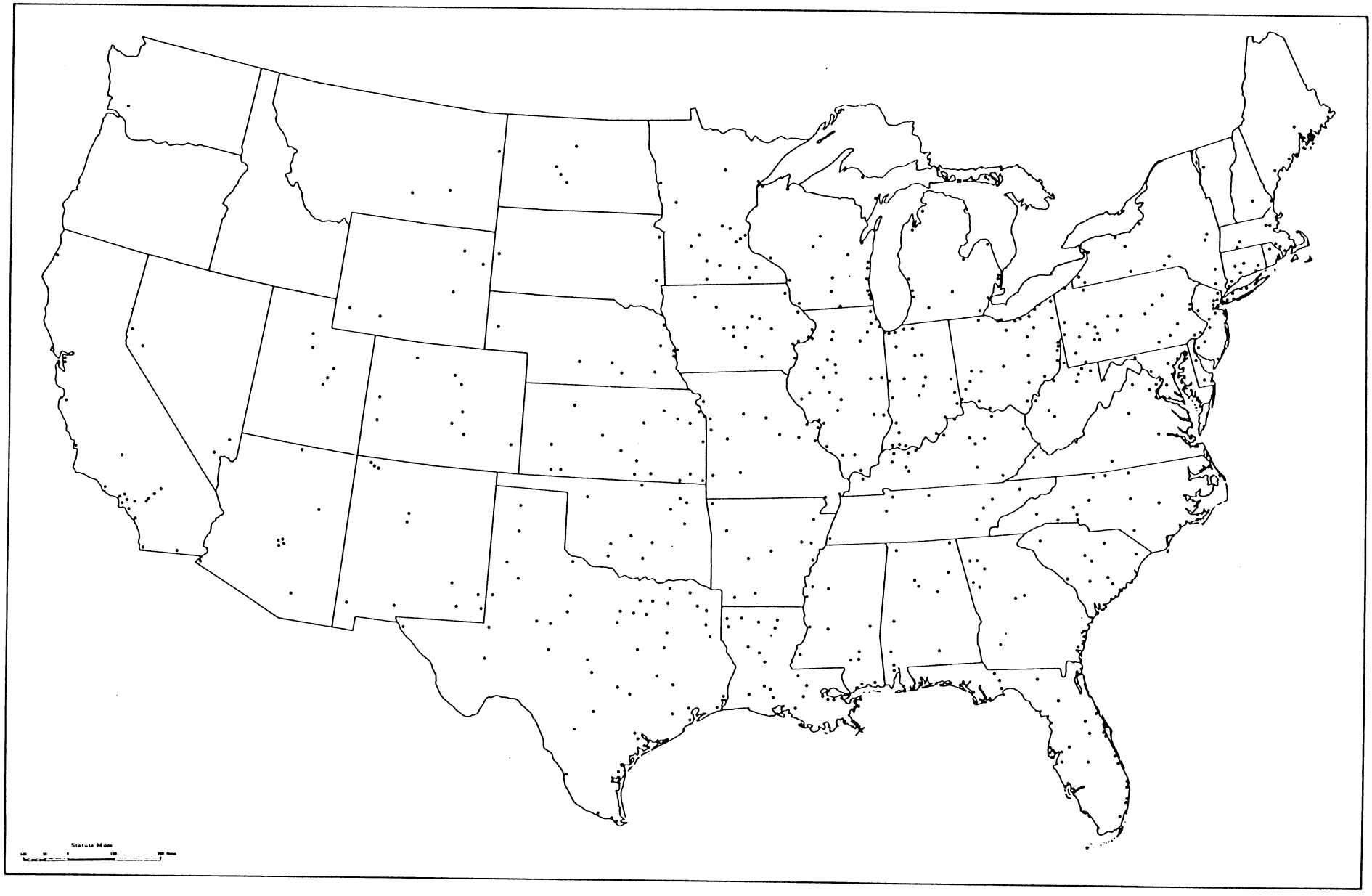


Exhibit 3-2: Location of Fossil Fuel Power Plants (>25 MW Size) in the United States

separately based on the quantity of coal burned and the coal's state-of-origin -- this information was obtained from the National Coal Association's Steam Electric Plant Factors.[31] All power plants were assumed to operate at 20% excess air, following discussions with representatives of PedCo Environmental, Inc.[36] An example calculation is included in the latter part of of this Section -- average compositions of coal for each state as used in the calculations were determined from the Keystone Coal Industry Manual.[28] The average proximate analyses of the various coals is given in Exhibit 3-3.

The average compositions were then used to calculate the stack gas composition and the quantity of CO_2 liberated when one ton of a given coal was burned. Exhibit 3-4 lists the calculated quantities and qualities of CO_2 for the important coals considered.

One other factor considered was the effect of flue gas desulfurization (FGD) equipment on the quantity and quality of CO_2 emitted. Due to EPA regulations and local limitations, the mass of sulfur that can be emitted per million Btu of heat released from the coal is restricted to 1.2 lb sulfur dioxide/MMBtu. In the case of high sulfur coals, the gaseous products of combustion cannot be released to the atmosphere without prior removal of at least part of the sulfur content - mostly in the form of sulfur dioxide. Several FGD systems have been proposed, but those that have proven most favorable are the scrubbing of the flue gases by either lime or limestone slurries. Exhibit 3-5 schematically shows the integration of a lime FGD system into a 500 MW model coal-fired power plant.[11] Normally, if no FGD were necessary, flue gas would pass directly from the electrostatic precipitors (ESP) to the atmosphere via a stack. The effects of both lime and limestone FGD systems on the quality of the flue gas from a hypothetical 500 MW coal-fired power plant burning 420,000 lb/hr. of 3.5% sulfur coal has been determined from EPRI's Lime FGD Systems Data Book[11] as shown below.

	Inlet Flue Gas to Scrubber (lb/hr)	Outlet Flue Gas from Typical Lime Scrubber (lb/hr)	Outlet Flue Gas from Typical Limestone Scrubber (lb/hr)
Ash	9,774	468	468
CO_2	941,600	939,930	957,940
HCT	130	---	---
N_2	3,745,500	3,745,500	3,745,500
O_2	324,500	323,930	322,712
SO_2	29,370	5620	5620
H_2O	257,700	496,300	496,300
Total	5,308,570	5,511,748	5,528,540

Exhibit 3-3: Average Proximate Analyses of Various Coals

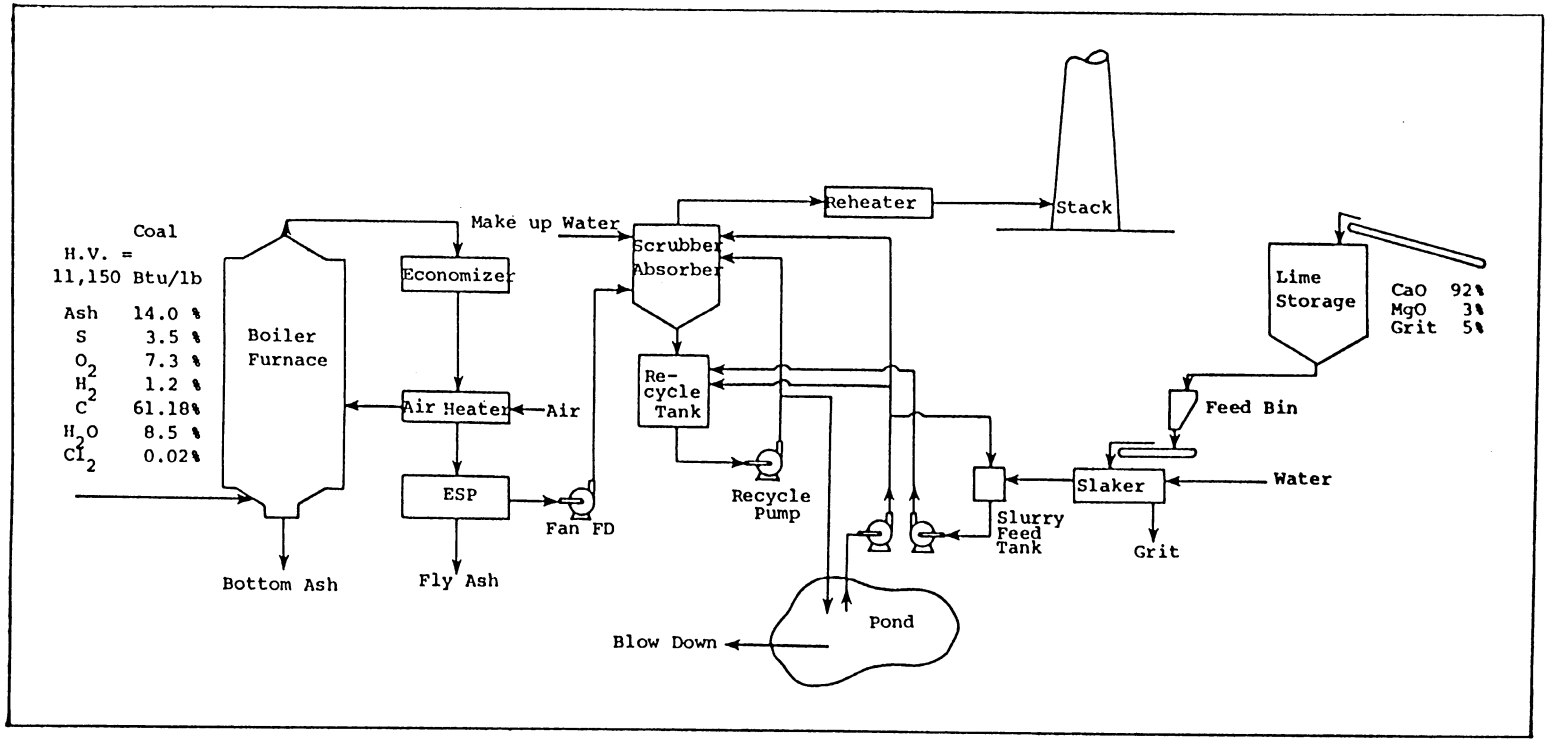
Coal's State/Region of Origin	Weight Percents				
	Ash	Volatile Matter	Sulfur	Water	Fixed Carbon
Alabama	8-10	31.0	1.7	2.3-3	58
Arizona	3.4-8.7	NA	0.4	9.7	NA
Arkansas	9.6	13.5	2	2.3	73
Colorado	6	31-40	0.5	12	39-69
Georgia	3.5	28	0.78	3.3	65
N.W. Illinois	10	33-44	3-5	18-21	75-78
S.E. Illinois	10	30-36	3-5	4-7	81-84
Indiana	11	36	2.7	12.3	40
Kansas	12.5	NA	3.3	6.5	NA
W. Kentucky	9-11	40	3.2	10	50
E. Kentucky	9	38	2.8	5	52
Louisiana	16.1	NA	0.64	30	NA
Maryland	9	18	1.5	2.5	72
Missouri	11.5	NA	4.3	11.1	NA
Montana	7	NA	0.6	NA	NA
New Mexico	12	35	0.8	13	45
N. Dakota (lignite)	6.2	26.7	0.6	37.9	29.2
Ohio	13	NA	3.5	NA	NA
Oklahoma	8	35	3.5	3	55
Pennsylvania	10	30	3.2	3	62
Tennessee	6.5	36	2	3	54
Texas (lignite)	13	30	1.1	3.3	27
Texas (bituminous)	15	31	3	11	40
Utah	7	40	0.7	5.0	50
Virginia	5	30	1	4	60
Washington	11	31	1.3	24	31
West Virginia	8	30	2	8	53
Wyoming	8	33	0.6	22	36

Exhibit 3-4: CO_2 Quantity and Quality Emitted from Coal-Fired Power Plants Burning Various Coals

Coal* Origin	CO_2 Produced per avg. ton of coal burned (SCF)	Average Composition of Stack Gas % Volume					
		CO_2	O_2	N_2	NO_x	SO_2	$H_2O(V)$
Alabama	39,400	14.3	3.4	75.9	0.31	0.15	5.9
Arizona	38,000	14.2	3.4	75.0	0.30	0.035	7.1
Arkansas	42,500	14.4	3.6	76.2	0.27	0.16	5.4
Colorado	36,700	14.1	3.3	74.6	0.31	0.045	7.7
Georgia	42,500	14.4	3.7	76.1	0.27	0.063	5.5
Illinois	42,300	14.1	3.4	74.9	0.22	0.26	7.1
Indiana	30,800	13.9	2.5	73.8	0.36	0.29	9.1
Kentucky	37,300	14.2	3.1	75.2	0.31	0.27	6.9
Maryland	43,100	14.4	3.6	76.2	0.27	0.12	5.4
New Mexico	33,600	14.0	3.0	74.1	0.34	0.078	8.5
North Dakota	23,400	12.9	1.7	68.3	0.44	0.078	17.0
Oklahoma	38,300	14.3	3.2	75.6	0.30	0.31	6.3
Pennsylvania	40,900	14.4	3.4	76.0	0.28	0.26	5.6
Tennessee	38,300	14.3	3.3	75.8	0.30	0.18	6.1
Texas	26,100	13.5	1.9	71.4	0.42	0.26	12.5
Utah	37,300	14.3	3.3	75.5	0.31	0.063	6.6
Virginia	40,200	14.4	3.4	75.9	0.29	0.084	6.0
Washington	25,000	13.4	1.9	70.8	0.43	0.16	13.4
West Virginia	37,300	14.2	3.2	75.1	0.31	0.18	7.0
Wyoming	27,700	13.6	2.3	71.8	0.39	0.069	11.9

* Average Composition of Coal Considered

Exhibit 3-5: Simplified Flow Diagram of a 500-MW Model Plant with FGD Unit



Source: Ref. 11, p. 2.3-17, Figure 2.3-12.

It can be seen that the quantity of CO_2 is hardly affected by either FGD system, but both systems are effective in severely reducing the ash and SO_2 content of the flue gas stream. However, the water content of the desulfurized flue gas is considerably higher than in the untreated flue gas. Overall, the quality of the CO_2 remains virtually unchanged although the temperature of the stack gas after FGD is 125°F, compared to approximately 285°F in cases where FGD is not required.

Appendix C lists the locations of all coal-fired power plants in the continental United States with generating capacities greater than 25 MW, and the quantity and quality of CO_2 emitted from each plant during an average day throughout the year (300 days per year). The EPA Utility FGD Survey[14] has been used to include information on any FGD system where it is known to be in operation. Exhibits 3-6, 3-7, 3-8, and 3-9 depict the locations of coal-fired power plants in each of the regions of interest and the volume of CO_2 emitted from each plant per operating day. Many plants use combinations of coal, oil, and gas to generate electricity, and the dominant fuel is indicated in the Exhibits. These details are given in the Steam Electric Plant Factors 1979[31] and the information has been used where practical in compiling Appendix C and Exhibits 3-6, 3-7, 3-8, and 3-9.

Sample Calculation

To calculate the quality and quantity of CO_2 generated by the combustion of one ton of coal, the ultimate coal analysis rather than the proximate analysis of Exhibit 3-3 is required. However, the ultimate analysis is not easily available. By studying the limited ultimate analysis data in the 1980 Keystone Coal Industry Manual,[28] the following method for approximating the ultimate analysis of each coal was formulated. The percentages are in weight percent.

C	(Fixed Carbon from Exhibit 3-3) + 1/2 (Volatile Matter from Exhibit 3-3)
H_2	Assumed 4%
N_2	Assumed 1.5%
O_2	Assumed 7%
S	From Exhibit 3-3
H_2O	From Exhibit 3-3
Ash	From Exhibit 3-3

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PAGE 35

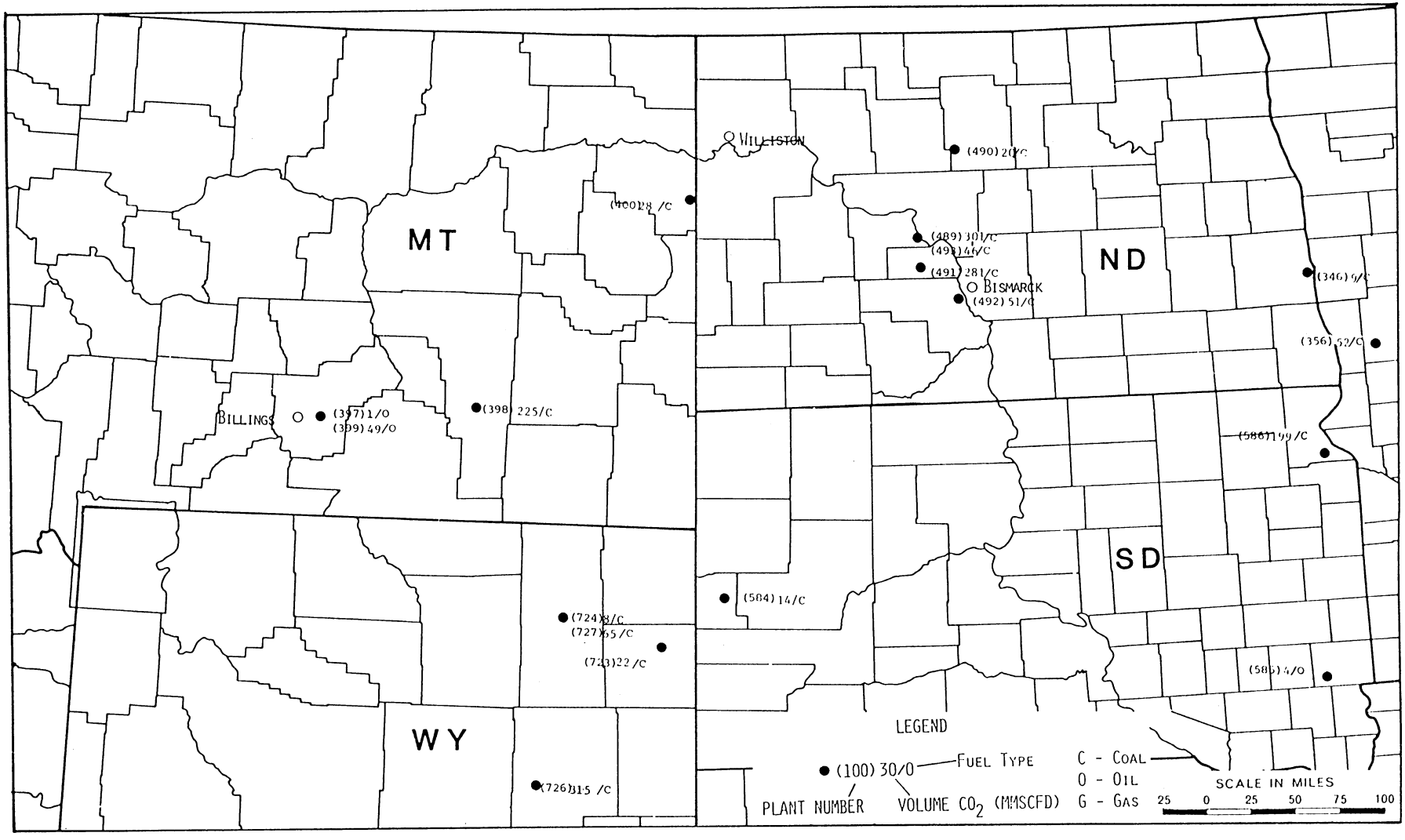


Exhibit 3-7: Carbon Dioxide Emitted from Power Plants in the Williston Basin

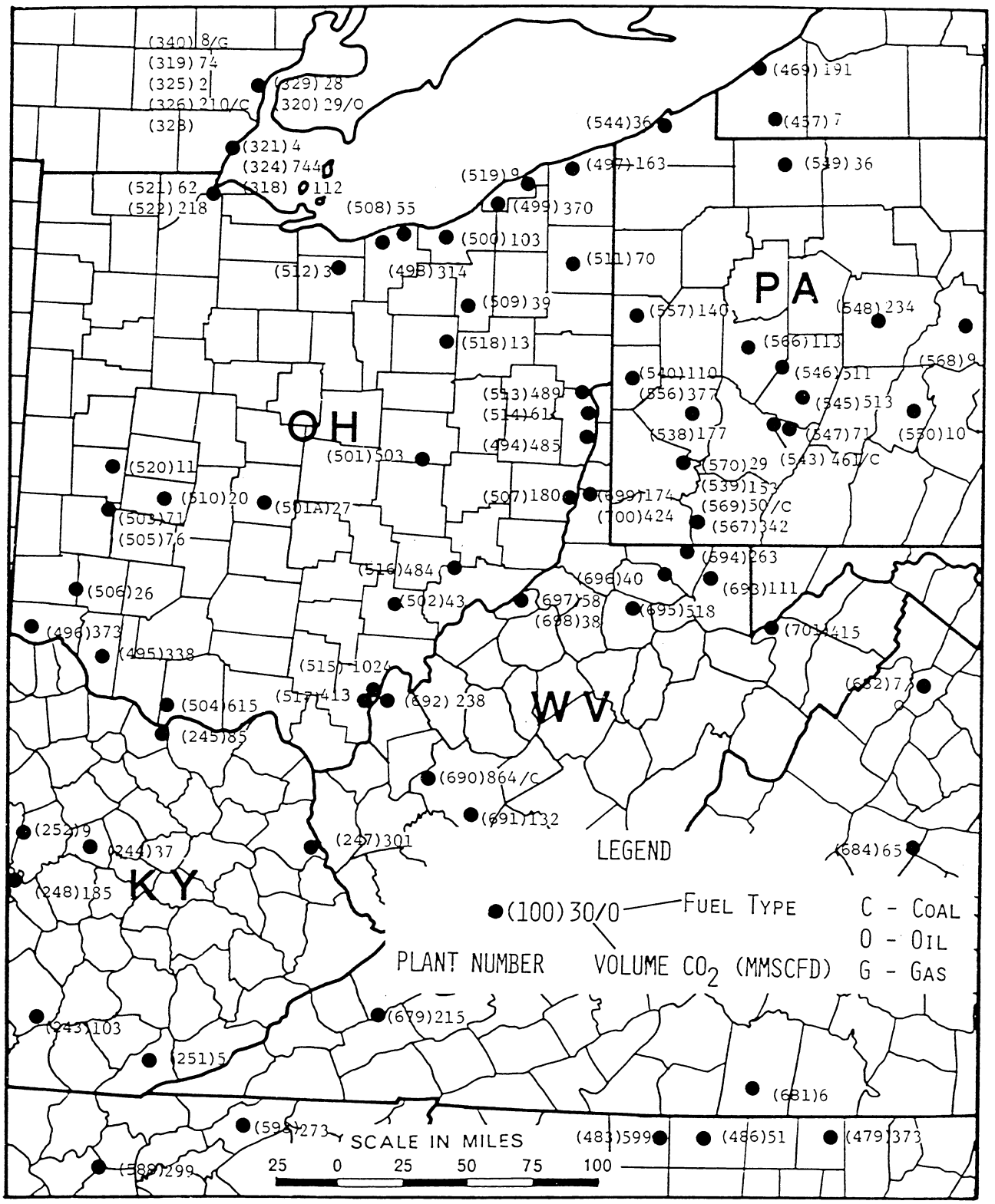


Exhibit 3-8: Carbon Dioxide Emitted from Power Plants in the Appalachian Basin

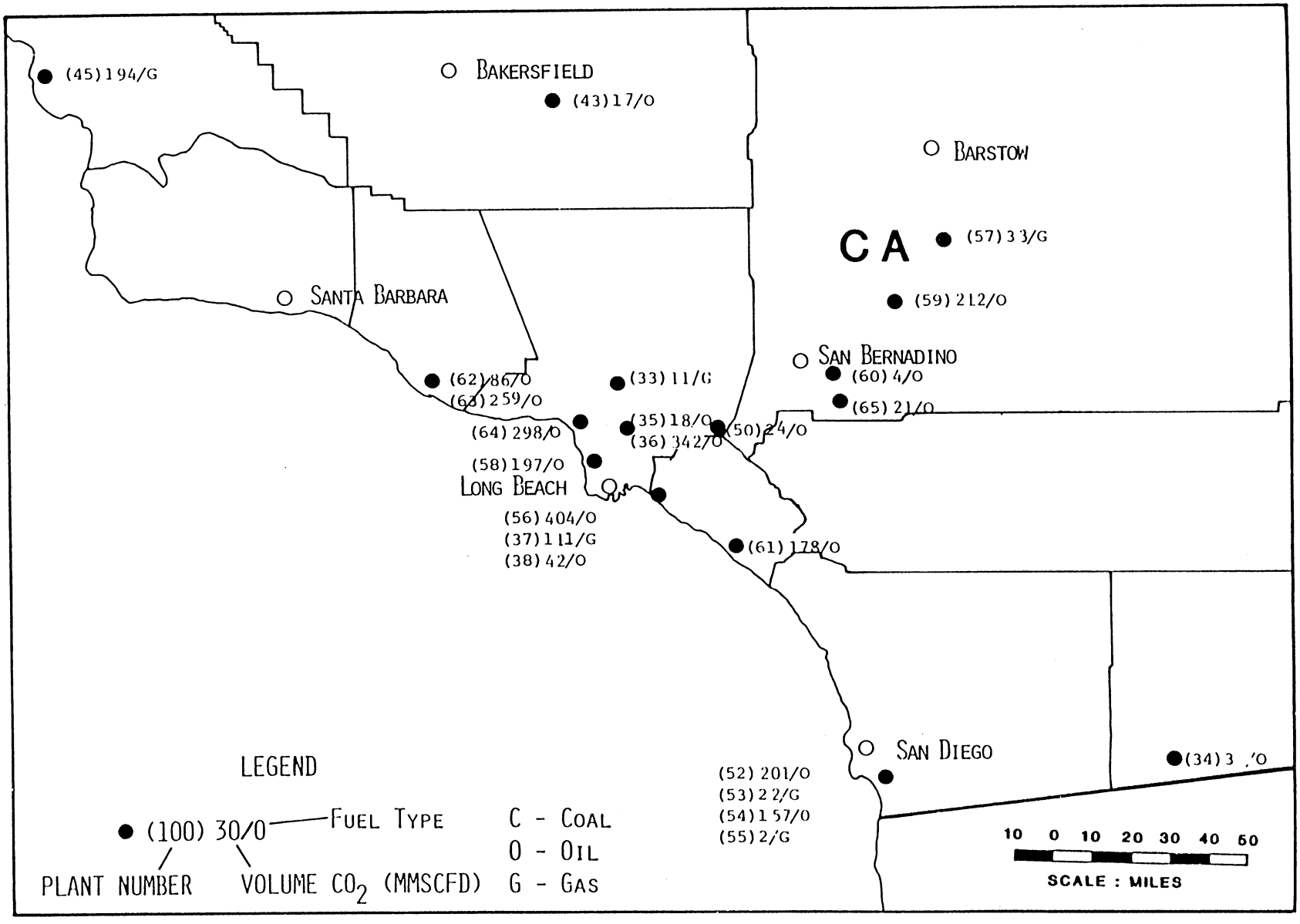


Exhibit 3-9: Carbon Dioxide Emitted from Power Plants in the Los Angeles Basin

Thus, the average ultimate analysis for Virginia coal becomes:

C	H_2	N_2	O_2	S	H_2O	Ash
75%	4%	1.5%	7%	1%	4%	5%

After discussion with Dr. J. Shang of DOE/METC, the typical carbon efficiency of coal-fired power plants was determined to be 85% -- that is, only 85% of all carbon in the coal is burned. Thus, 0.85 (0.75 x 2000) ÷ 12 lb moles of carbon (106.25 lb moles) are combusted when one ton (2000 lbs) of Virginia coal is burned. Thus, 106.25 lb moles of O_2 are consumed, and 106.25 lb moles of CO_2 are produced per ton of Virginia coal burned. Since one lb mole of a gas occupies 379 SCF at normal temperature and pressure (60°F, 1 atm), the combustion of one ton of Virginia coal produces 40,269 SCF of CO_2 as shown below.

(i) $C + O_2 \longrightarrow CO_2$

For Virginia coal:
0.85 (0.75x2000)/12
= 106.25 lb moles

106.25 lb moles = 40,269 SCF

106.25 lb moles = 40,269 SCF

Other reactions are:

(ii) $H_2 + 1/2\ O_2 \longrightarrow H_2O$

For Virginia coal:
(0.04x2000)/2
= 40 lb moles

20 lb moles

40 lb moles = 15,160 SCF

(iii) $N_2 + 3/2\ O_2 \longrightarrow 2NO_x$

For Virginia coal:
(0.015x2000)/28
= 1.07 lb moles

1.61 lb moles

2.14 lb moles = 811 SCF

(iv) $S + O_2 \longrightarrow SO_2$

For Virginia coal:
(0.01x2000)/32
= 0.625 lb moles

0.625 lb moles

0.625 lb moles = 237 SCF

All NO_x is assumed to come from the combustion of fuel nitrogen and not nitrogen from the air. From these four reactions the oxygen required per ton of coal can be calculated assuming 20% excess air as shown:

(lb moles of O_2 per ton of coal) =
1.2 [(lb moles of O_2 required for reaction (i))
+ (lb moles of O_2 for reaction (ii))
+ (lb moles of O_2 for reaction (iii)
+ (lb moles of O_2 for reaction (iv))
- (lb moles of O_2 in fuel)]

Thus, for Virginia coal:
(lb moles of O_2 per ton of coal) = 1.2 [(106.25 + 20 + 1.61 + 0.625) - (0.07 x 2000/32)]
= 1.2 [124.1]
= 148.9 lb moles

The volume of nitrogen that exits with the flue gas is then given by:

(SCF of N_2 in flue gas per ton of coal) = 379 (lb moles N_2 in air)
= 379 x (0.79/0.21) x (lb moles of O_2 per ton of coal)
= 379 x (0.79/0.21) x 148.9
= 212,296 SCF

The volume of oxygen that exits with the flue gas is approximately the excess oxygen supplied:

(SCF of O_2 in flue gas per ton of coal) = 379 x (1.2-1)
x [(lb moles of O_2 required reaction (i))
+ (lb moles of O_2 for reaction (ii))
+ (lb moles of O_2 for reaction (iii))
+ (lb moles of O_2 for reaction (iv))
- (lb moles of O_2 in fuel)]
= 379 x 0.2 x [124.1]
= 9407 SCF

The volume of water vapor that exits with the flue gas is given by:

(SCF of $H_2O(v)$ in flue gas per ton of coal) =

379 [(lb moles of $H_2O(v)$ formed by reaction (ii))

+ (lb moles of H_2O (v) in fuel)]

= 379 [40 + (0.04 x 2000/18)]

= 16,845 SCF

A table can now be devised showing the main gaseous components in the flue gas indicating the volume of each gas evolved when one ton of a particular coal is combusted with 20% excess air. The average composition of the stack gas on a percentage volume basis can then be computed.

Thus, for Virginia coal:

	SCF Per Ton of Coal	% Volume
CO_2	40,269	14.4
O_2	9,406	3.4
N_2	212,296	75.9
NO_x	811	0.29
SO_2	237	0.084
$H_2O(v)$	16,845	6.0
Total	279,864	100.074

(Total does not add to 100% due to rounding)

To determine the volume of CO_2 given off by a particular plant, the data from National Coal Association's Steam Electric Plant Factors 1979[31] were used to determine both the average daily consumption of coal in 1978 for each coal-fired power plant and the origin of that coal. Plants are assumed to operate for 300 days per year (approximately 80%). For example, the Appalachian Power Clinch River 712 MW coal-fired power plant was determined to consume 1,604,000 tons of Virginia coal in 1979. The volume of CO_2 emitted

per average operational day was then calculated from: (SCF of CO_2 emitted per average day) = (tons of coal, consumed per year/300) (SCF of CO_2 evolved per ton of coal)

Thus, for the Clinch River power plant:
(SCF of CO_2 emitted per day) = [1,604,000/300] (40,268) = 215.3×10^6 SCFD

3.2.2 Oil-Fired Power Plants

The quantity and quality of CO_2 generated in oil-fired power plants has been calculated on a plant-by-plant basis across the continental United States for all plants rated at capacities equal to or greater than 25 MW. Plants were located from the National Coal Association's Steam Electric Plant Factors 1979,[31] and the volume of fuel oil consumed per year was determined. An average fuel oil composition was assumed, and calculations were carried out using 15% excess air following discussions with representatives of PedCo Environmental, Inc.[36] The average fuel oil composition taken was the following:

	C	H_2	S	O_2	N_2
Weight percent:	85.5	11.5	1.6	0.7	0.7

Calculations indicated that the combustion of one barrel of this fuel oil would produce 8900 SCF of CO_2 as shown in the sample calculation. The calculated composition of the stack gas was determined to be:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
Volume percent:	12.3	2.6	75.0	0.086	0.086	9.9

Appendix C provides information on the locations and availability of CO_2 in MMSCFD and the flue gas composition for all oil-fired power plants in the continental United States with a generating capacity equal to or greater than 25 MW. Exhibits 3-6, 3-7, 3-8, and 3-9 depict the location of oil-fired power plants in each of the regions of interest along with the volume of CO_2 emitted from each plant per operating day. Note that many plants use combinations of coal, oil, and gas to generate electricity; the dominant fuel is shown in

Exhibits 3-6, 3-7, 3-8, and 3-9. These details are given in the Steam Electric Plant Factors 1979[31] and the information has been used where practical in compiling Appendix C and Exhibits 3-6, 3-7, 3-8, and 3-9.

Sample Calculation

One barrel of fuel oil weighs approximately 330 lbs (average of fuel oil #4 and #6). Thus, the composition of one barrel in various units can be determined:

	C	H_2	S	O_2	N_2
Weight percent:	85.5	11.5	1.6	0.7	0.7
Pounds per barrel:	282.15	37.95	5.28	2.31	2.31
Lb. Moles per barrel:	23.5	19.0	0.165	0.0722	0.0825

The reactions are very similar to those for coal combustion.

(i) $C + O_2 \longrightarrow CO_2$

per bbl:

23.5 lb moles — 23.5 lb moles — 23.5 lb moles
= 23.5 x 379 SCF
= 8910 SCF (approx)

(ii) $H_2 + 1/2\ O_2 \longrightarrow H_2O(v)$

per bbl:

19.0 lb moles — 9.5 lb moles — 19.0 lb moles
= 7201 SCF

(iii) $N_2 + 3/2\ O_2 \longrightarrow 2NO_x$

per bbl:

0.0825 lb moles — 0.124 lb moles — 0.165 lb moles
= 62.5 SCF

(iv) $S + O_2 \longrightarrow SO_2$

per bbl:

0.165 lb moles — 0.165 lb moles — 0.165 lb moles
62.5 SCF

A carbon efficiency of 100% is assumed. From these four reactions, the oxygen required per barrel of fuel oil can be calculated, assuming 15% excess air as shown:

$$(\text{lb moles of } O_2 \text{ per barrel of oil}) = 1.15\ [23.5 + 9.5 + 0.124 + 0.165 - 0.0722]$$
$$= 1.15\ [33.22]$$
$$= 38.2 \text{ lb moles}$$

The volume of nitrogen that exits with the flue gas is:

$$(\text{SCF of } N_2 \text{ in flue gas per barrel of oil}) = 379\ (\text{lb moles } N_2 \text{ in air})$$
$$= 379 \times (0.79/0.21) \times 38.2$$
$$= 54{,}464 \text{ SCF}$$

The volume of oxygen that exits with the flue gas is:

$$(\text{SCF of } O_2 \text{ in flue gas per barrel of oil}) = 379\ (1.15-1)\ [33.22]$$
$$= 1{,}888 \text{ SCF}$$

A table can now be constructed indicating the volume of each principal gas evolved when one barrel of fuel oil is combusted with 15% excess air. The average composition of the stack gas on a percentage volume basis can then be determined.

	SCF per barrel of fuel oil	% Volume
CO_2	8,910	12.3
O_2	1,888	2.6
N_2	54,464	75.0
NO_x	62.5	0.086
SO_2	62.5	0.086
$H_2O(v)$	7,201	9.9
Total	72,588	99.972

(Total does not add to 100% due to rounding)

To determine the volume given off by a particular plant, the National Coal Association's Steam Electric Plant Factors 1979[31] were used to determine the average daily consumption of oil assuming 300 operational days in a year (80%). The volume of CO_2 emitted per operational day can then be calculated as:

(SCF of CO_2 emitted per operational day) =
[(barrels of oil consumed per year)/300] x 8910

For example, the Kennedy plant in Jacksonville, Florida, is an oil-fired power plant that used approximately 1.8 MM bbl/year of oil in 1978. The volume of CO_2 emitted per average operational day was then calculated to be 53.4 MMSCFD.

3.2.3 Gas-Fired Power Plants

The quantity and quality of CO_2 generated in gas-fired power plants has been calculated on a plant-by-plant basis across the continental United States for all plants rated at generating capacities equal to or greater than 25 MW. Plant locations and the volume of natural gas consumed in 1978 were determined from the National Coal Association's Steam Electric Plant Factors 1979.[31] An average natural gas composition was assumed and calculations were carried out using 10% excess air following discussions with representatives of PedCo Environmental, Inc.[36] The following natural gas composition was assumed based on an arithmetic average of natural gas supplied in different states (Perry[37]).

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	CO_2	N_2	Other
Percent volume:	89.6	5.1	1.5	0.4	0.1	1.7	0.9	0.7

The calculations showed that the combustion of one MSCF of this natural gas would produce approximately 1100 SCF of CO_2. The calculated composition of the stack gas was determined to be:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
Volume percent:	9.1	1.7	72.1	--	--	17.0

Appendix C provides information on the locations, volume of CO_2 available, and average flue gas compositions for all gas-fired power plants in the continental United States with a generating capacity greater than 25 MW. Exhibits 3-6, 3-7, 3-8, and 3-9 depict the location of gas-fired power plants in each of the regions of interest along with the volume of CO_2 emitted from each plant per operating day. Note that many plants use combinations of coal, oil, and gas to generate electricity; the dominant fuel is shown in the Exhibits. These details are given in the Steam Electric Plant Factors 1979[31] and the information has been used where practical in compiling Appendix C and Exhibits 3-6, 3-7, 3-8, and 3-9.

Sample Calculation

The following reactions take place in the combustion of natural gas in a typical gas-fired power plant. It is assumed that the carbon efficiency of combustion is 100% and that the nitrogen supplied in the fuel appears in the gaseous combustion products still in the form of diatomic nitrogen molecules.

(i)	CH_4	+	$2O_2$	$\longrightarrow$	CO_2	+	$2H_2O$
per MSCF of natural gas	896 SCF		1792 SCF		896 SCF		1792 SCF
(ii)	C_2H_6	+	3 1/2 O_2	$\longrightarrow$	$2CO_2$	+	$3H_2O$
per MSCF of natural gas	51 SCF		178.5 SCF		102 SCF		153 SCF
(iii)	C_3H_8	+	$5O_2$	$\longrightarrow$	$3CO_2$	+	$4H_2O$
per MSCF of natural gas	15 SCF		75 SCF		45 SCF		60 SCF
(iv)	C_4H_{10}	+	6 1/2 O_2	$\longrightarrow$	$4CO_2$	+	$5H_2O$
per MSCF of natural gas	4 SCF		26 SCF		16 SCF		20 SCF
(v)	C_5H_{12}	+	$8O_2$	$\longrightarrow$	$5CO_2$	+	$6H_2O$
per MSCF of natural gas	1 SCF		8 SCF		5 SCF		6 SCF

Thus the volume of CO_2 produced when one MSCF of the assumed natural gas is combusted is given by:

(volume of CO_2 produced per MSCF of natural gas) = 896 + 102 + 45 + 16 + 5 + 17
= 1081 SCF
= 1100 SCF (approx.)

The oxygen required per MSCF of natural gas can be calculated assuming 10% excess air as:

(SCF of O_2 per MSCF of natural gas) = 1.10 (1792 + 178.5 + 75 + 26 + 8)
= 1.10 (2080)
= 2288 SCF

The volume of nitrogen that exits with the flue gas is:

(SCF of N_2 in flue gas per MSCF of natural gas) = (0.79/0.21) x 2288 + 9
= 8616 SCF

The volume of oxygen that exits with the flue gas is:

(SCF of O_2 in flue gas per MSCF of natural gas) = (1.10-1) (2080)
= 208 SCF

A table can now be compiled indicating the volume of each principal gas evolved when one MSCF of natural gas is combusted with 10% excess air.

	SCF per MSCF of natural gas	% Volume
CO_2	1081	9.1
O_2	208	1.7
N_2	8616	72.1
NO_x	--	--
SO_2	--	--
$H_2O(v)$	2031	17.0
Other	9	0.075
Total	11,943	99.975

(Total does not add to 100% due to rounding)

The average composition of the stack gas can then be determined on a percentage volume basis. To determine the volume of CO_2 given off by a particular plant, the National Coal Association's Steam Electric Plant Factors 1979[31] were used to determine the average daily consumption of natural gas assuming 300 operational days per year. The volume of CO_2 emitted per average operational day can then be calculated from:

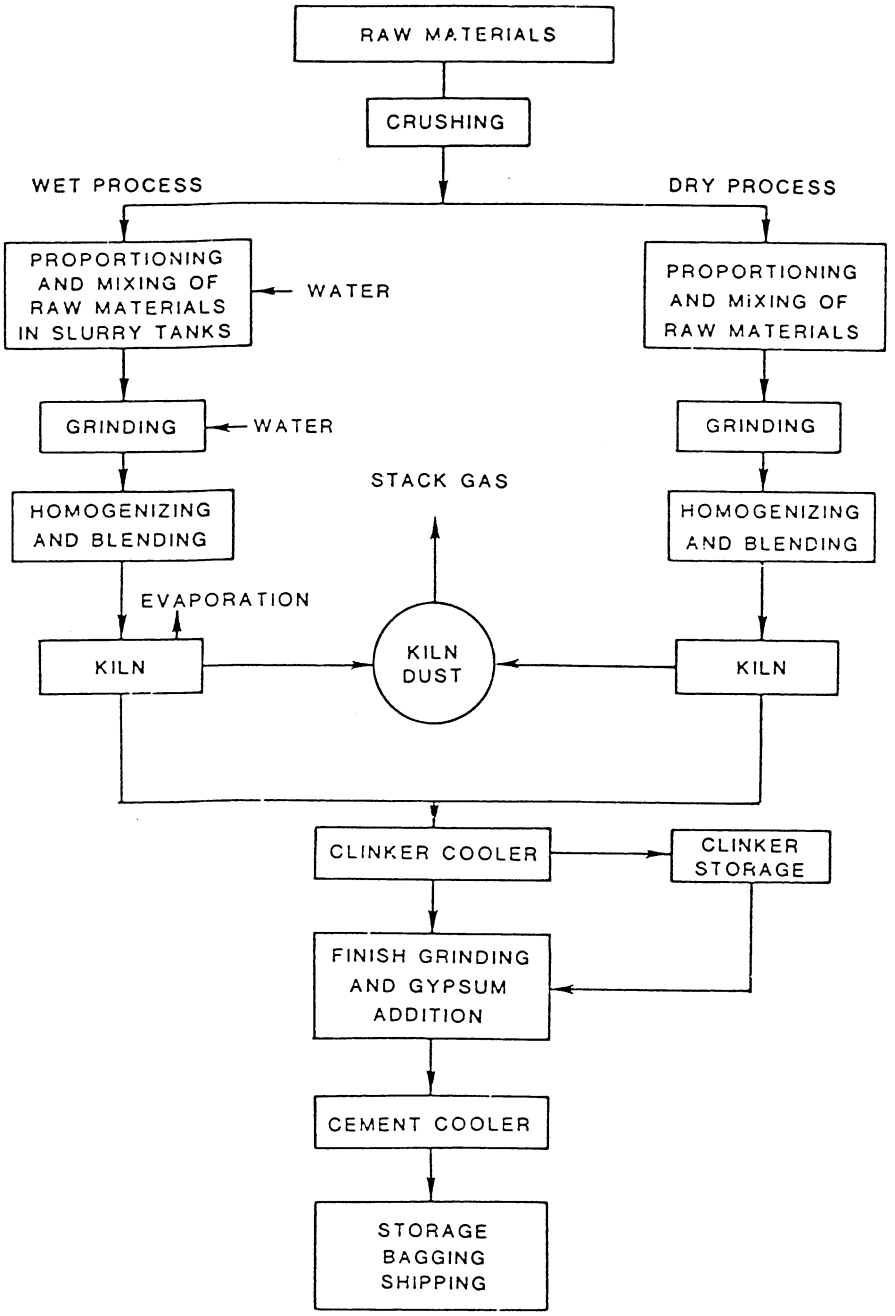
(SCF of CO_2 emitted per operational day) =
[(MSCF of natural gas consumed per year)/300] x 1081

For example, the Sommers gas-fired power plant in San Antonio, Texas, consumed 16,465 MMSCF of natural gas per year in 1978. The volume of CO_2 emitted per average operational day was then calculated to be 59.3 MMSCF.

3.3 CEMENT PLANTS

The process characteristics of cement plants are not as well understood as the layout of power plants. Thus, before discussing by-product CO_2 generation, the fundamentals of cement production will be briefly discussed. There are two major processes for making cement: a dry process, and a wet process. In the former, the raw materials (e.g., limestone, sand) are crushed, properly blended, and then fed to a kiln to form clinkers. Clinkers are produced by heating the raw materials and driving off CO_2 from the $CaCO_3$ in the feed material to leave CaO - the reaction being termed calcination. Finally, gypsum is added to the clinkers and the final mix is ground to form Portland Cement. In the wet process, the scheme is similar except that after proportioning the raw materials, water is added before grinding and the resulting slurry is then fed to the kiln. A process flow diagram for the manufacturing of Portland Cement is shown schematically in Exhibit 3-10. In terms of by-product CO_2 production, the fuel for the kiln is mixed with air at the lower end of the kiln where combustion then proceeds. The hot gaseous combustion products subsequently pass up the kiln in the opposite direction to the raw materials, heating the raw materials as they pass. The exhaust gas from the kiln, which contains a mix of combustion products and CO_2 from calcining, is then cleaned of particulates before being vented to the atmosphere via a stack. The temperature of the vented gas is normally in the

Exhibit 3-10: Flow Sheet for the Manufacture of Portland Cement



Source: U. S. Environmental Protection Agency, Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Cement Manufacturing Point Source Category: Report EPA 440/1-73/005, August 1973.

range of 300 to 400°F for both wet and dry processes. Normally, coal and/or natural gas are the fuels used to heat the kiln. One other important factor is that the cement industry, like other industries, has become considerably more fuel-efficient in the last few decades, and although this has been a gradual development, 1963 has been arbitrarily chosen as a cut-off date between the old and improved plant designs.[49]

From a knowledge of the quantity and type of fuel consumed[39] and the tonnage of cement produced, calculations of CO_2 quality and quantity have been made for each of the 149 cement plants operating in the continental United States. Information on plant locations, plant type, and production capacity was obtained from the U.S. Portland Cement Industry -- Plant Information Summary.[39] Plants were assumed to be operating at an average 80% of their rated capacities. It was determined that the quality of CO_2 produced was strongly dependent upon three factors: whether the wet or dry cement manufacturing process was employed; on the age of the plant; and on the type of fuel employed for heating. Detailed calculations have been performed for each possible combinatión and the results are presented in subsequent sections.

Appendix D lists the locations of all major cement plants in the continental United States along with the average quantity of CO_2 produced per operating day and the quality of the CO_2-bearing stream. Note that in some cases, coal and natural gas may both be used as fuel and where practical, Appendix D reflects this. Exhibit 3-11 depicts the locations of the major cement plants in the continental United States. Exhibits 3-12, 3-13, 3-14, and 3-15 depict the locations of all cement plants in each of the four regions of interest and the volume of CO_2 emitted from each plant per day assuming that the plants operated for 300 days per annum.

3.3.1 Pre-1963 Coal-Fired Wet Cement Plants

The quantity and quality of CO_2 liberated from pre-1963 coal-fired wet cement plants have been calculated on a plant-by-plant basis across the continental United States. The production of one ton of cement produces 18,800 SCF of CO_2 (see Sample Calculation), and the composition of the stack gas bearing this CO_2 is:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	21.0	1.7	39.6	0.17	0.09	37.5

Exhibit 3-11: Location of Cement Plants in the United States

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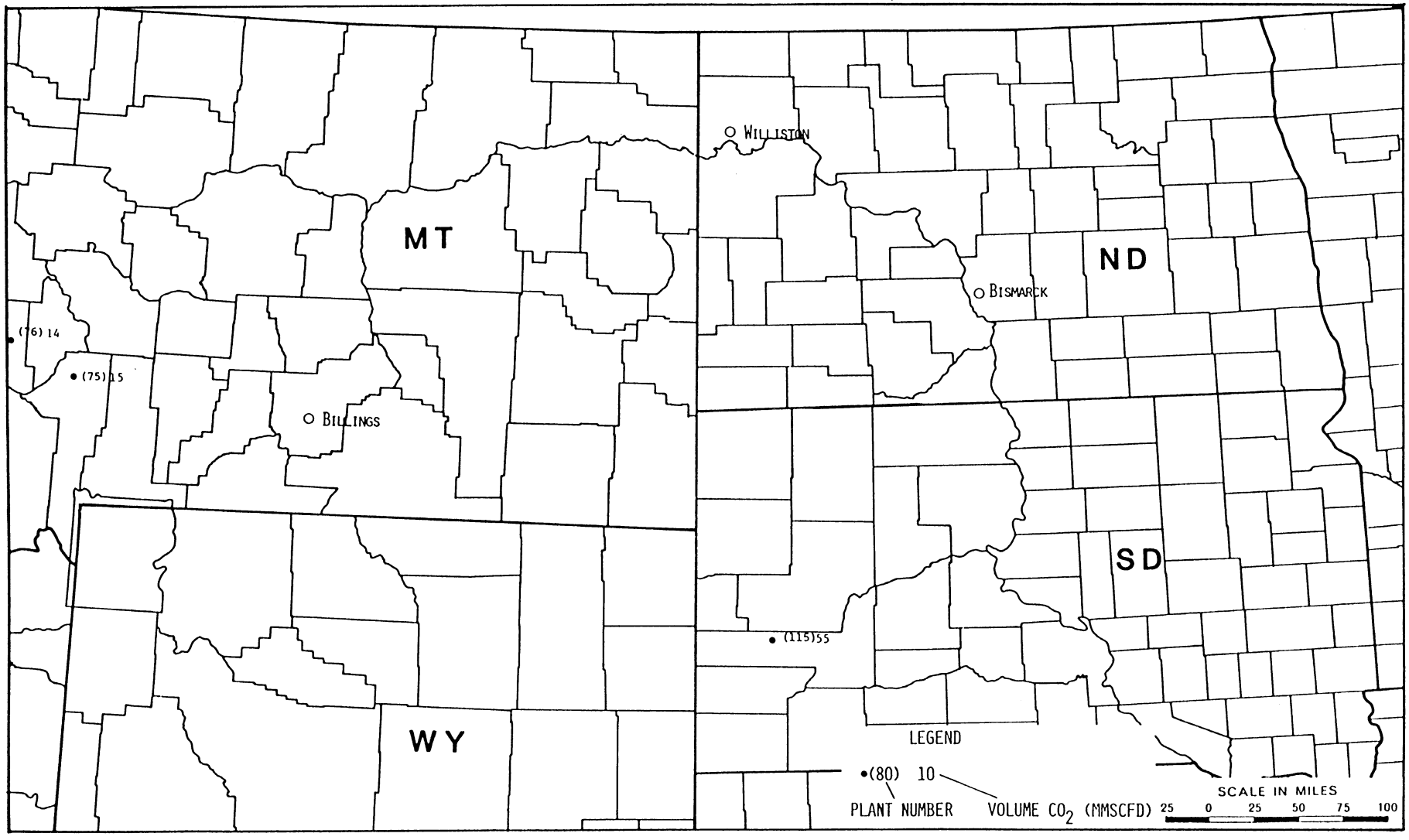


Exhibit 3-13: Carbon Dioxide Emitted from Cement Plants in the Williston Basin

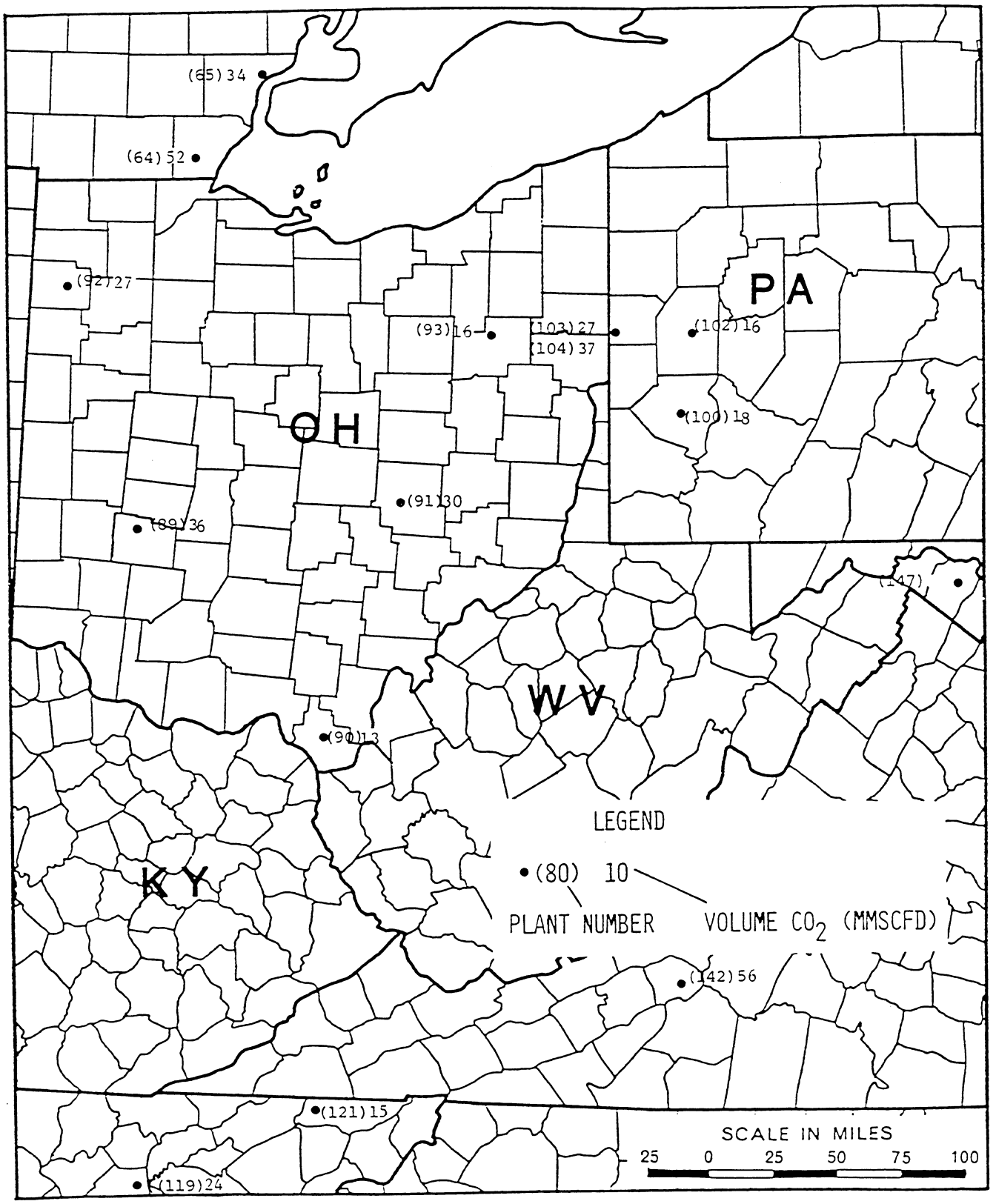


Exhibit 3-14: Carbon Dioxide Emitted from Cement Plants in the Appalachian Basin

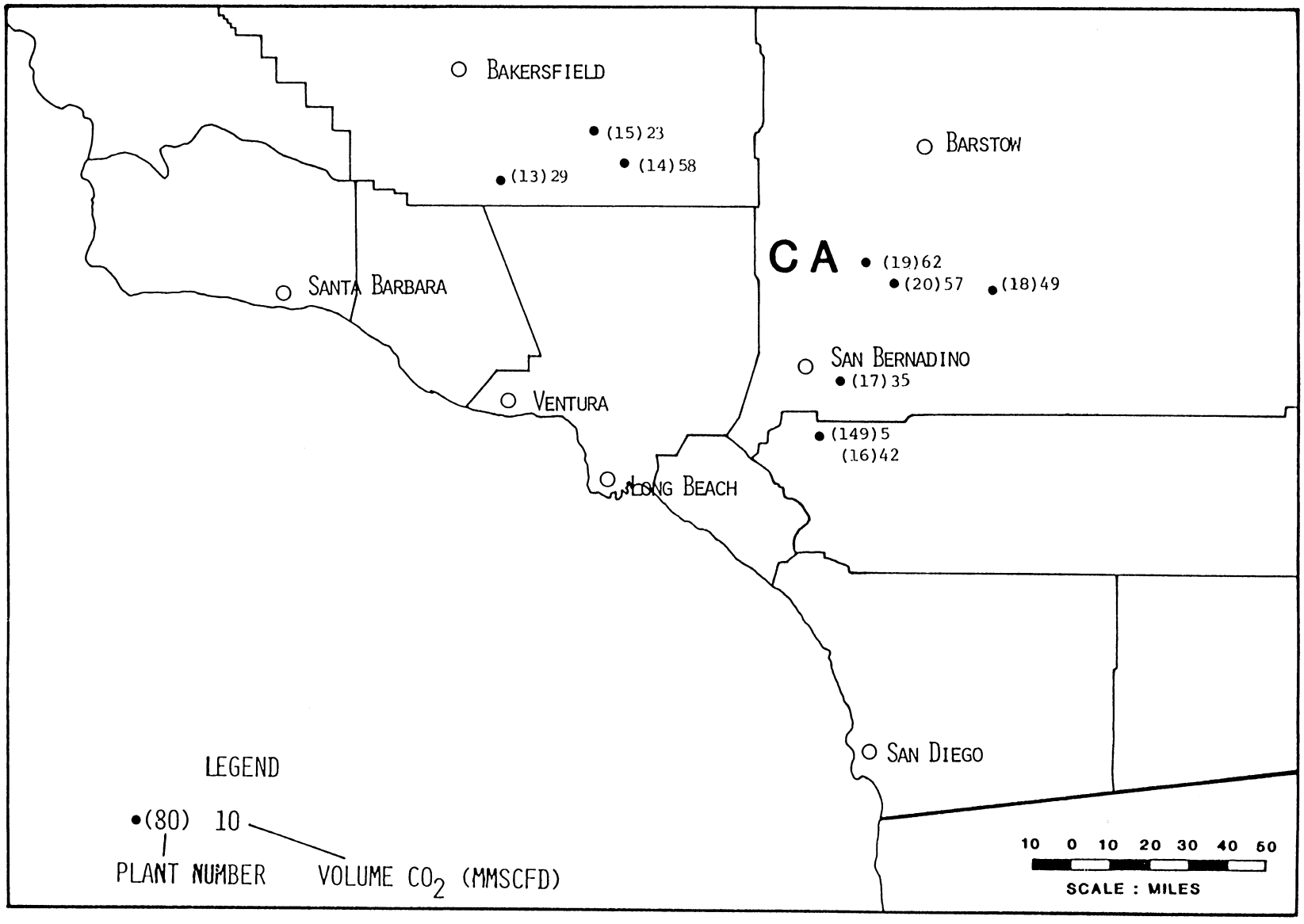


Exhibit 3-15: Carbon Dioxide Emitted from Cement Plants in the Los Angeles Basin

Sample Calculation

It was determined from Sittig's 1975 report[49] that in pre-1963 designed plants, 541 lbs of coal are burned in the production of one ton of cement. Thus, using a typical coal and calculations similar to those in Section 3.2.1, it can be determined that 9550 SCF of CO_2 will be formed from fuel combustion alone when one ton of cement is produced. The percentage composition of the gaseous combustion products is:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	14.2	3.2	75.1	0.31	0.18	7.0

This gas then mixes with the products of calcination. Most Portland Cement produced has the following approximate composition:

	CaO	SiO_2	Al_2O_3
weight percent	68.2	21.0	10.8
per ton	1364 lb	420 lb	216 lb

The amount of CO_2 produced by calcination in the production of one ton of cement can then be calculated from:

	$CaCO_3$	$\longrightarrow$	CaO	+	CO_2
Molecular	100		56		44
weight			1364 lb		(44/56) x 1364 lb
				=	44 x 1364 x 379/(56 x 44) SCF
				=	9230 SCF

Thus, the total amount of CO_2 liberated by the production of one ton of cement in a pre-1963 coal-fired wet cement plant is:

9550 + 9230 = 18780 = 18,800 SCF (approx.)

Through contacts with technical personnel at cement plants, the percentage composition of the gases given off in the kiln of a wet cement plant has been deduced to be:

	CO_2	H_2O	Air leaks etc.
percent volume	28.0	68.0	4.0

The resulting stack composition can then easily be determined to be approximately:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	21.0	1.7	39.6	0.17	0.09	37.5

To determine the daily volume of CO_2 given off by a particular plant, the plant capacity in terms of tons of cement per day is manipulated as follows: (Note the plant is assumed to operate for 300 days per year at 80% capacity)

(SCF of CO_2 emitted per average operating day) =
0.8 [(plant capacity)/300] x 18,800

For example, the Bonnes Springs cement plant of Lone Star Industries in Kansas has a capacity of 451,000 tons/yr, and it produces 22.6 MMSCFD of CO_2 per operating day.

3.3.2 Post - 1963 Coal-Fired Wet Cement Plants

The quantity and quality of CO_2 emitted from post-1963 coal-fired wet cement plants has been calculated on a plant-by-plant basis across the continental United States. The production of one ton of cement liberates approximiately 16,870 SCF of CO_2. The approximate stack gas composition is:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	25.8	1.6	37.2	0.16	0.09	35.2

Since Sittig[49] suggests that newer plants use 20% less fuel, only 433 lb of coal will be burned per ton of cement produced. Thus, approximately 7640 SCF of CO_2 comes from coal combustion and, as before, 9230 SCF from calcining per ton of cement. The calculations then proceed as in Section 3.3.1.

3.3.3 Pre - 1963 Gas Fired Wet Cement Plants

The production of one ton of cement in a pre-1963 gas-fired wet cement plant emits 16,900 SCF of CO_2. The stack gas composition has been calculated as:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	22.5	0.85	36.0	--	--	40.3

Sittig[49] suggests that approximately 7000 SCF of natural gas is required in these plants to produce one ton of cement. Thus, approximately 7,700 SCF of CO_2 comes from fuel combustion and, as before, 9230 SCF from calcining per ton of cement produced. The calculations then proceed as in Section 3.3.1.

3.3.4 Post - 1963 Gas-Fired Wet Cement Plants

Post-1963 gas-fired wet cement plants have been calculated as emitting approximately 15,300 SCF of CO_2 per ton of cement produced. The stack gas composition is:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	23.6	0.89	37.9	--	--	37.3

Since Sittig[49] has deemed the newest plants to be 20% more fuel efficient, only about 5,550 SCF of natural gas will be required per ton of produced cement. Thus, approximately 6050 SCF of CO_2 comes from the combustion of the natural gas and 9230 SCF from calcining. The calculations then proceed as in Section 3.3.1.

3.3.5 Oil-Fired Wet Cement Plants

Only three wet cement plants exist within the United States using oil as a major fuel. Little information is available on the volume of oil required to produce one ton of cement, and hence, no estimate of the amount of CO_2 generated from fuel combustion can be made. In the absence of data, these three plants have been assumed to behave as gas-fired wet cement plants of the same age.

3.3.6 Pre-1963 Coal-Fired Dry Cement Plants

Pre-1963 coal-fired dry cement plants have been determined to liberate approximately 18,800 SCF of CO_2 per ton of cement produced. The CO_2 bearing stream has the following composition:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	27.9	2.4	63.1	0.16	0.09	6.4

The calculations are very similar to those for pre-1963 coal-fired wet cement plants with 9550 SCF of CO_2 being evolved from coal combustion and 9230 SCF of CO_2 from calcining. The principal difference between the two types of plant is in the stack gas composition, since for the dry process little or no water is liberated from the raw material with the CO_2 produced by the calcination reaction.

3.3.7 Post-1963 Coal-Fired Dry Cement Plants

For post-1963 coal-fired dry cement plants, the CO_2 liberated per ton of cement produced is approximately 16,870 SCF with a stack gas composition of:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	29.3	2.3	61.9	0.14	0.08	6.3

Calculations are similar to those for post-1963 coal-fired wet cement plants except that no water evaporates into the effluent gas stream in the kiln.

3.3.8 Pre-1963 Gas-Fired Dry Cement Plants

Pre-1963 gas-fired dry cement plants generate approximately 16,930 SCF of CO_2 per ton of cement produced. An estimated stack gas composition is:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	25.4	1.6	61.6	--	--	11.2

Calculations are similar to those for pre-1963 gas-fired wet cement plants except that no water evaporates from the raw material.

3.3.9 Post-1963 Gas-Fired Dry Cement Plants

Post-1963 gas-fired dry cement plants liberate approximately 15,300 SCF of CO_2 per ton of cement produced. The stack gas composition can be approximated by:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	28.6	1.6	59.5	--	--	10.1

Calculations are similar to those for post-1963 gas-fired wet cement plants except that no water evaporates in the kiln.

3.3.10 Oil-Fired Dry Cement Plants

Only two dry cement plants exist within the continental United States which use oil as the primary fuel. No information is available either on the amount of oil required per ton of cement produced or on the volume of CO_2 produced from fuel combustion. In the absence of data, these two plants have been assumed to behave as gas-fired dry cement plants of similar age.

3.4 AMMONIA PLANTS

Ammonia is commerically produced by the fixation of nitrogen with hydrogen at high temperatures and pressures over a catalyst. The hydrogen is generally produced by steam reforming a desulfurized natural gas feedstock in nickel catalyst filled tubes.

(i) $$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

(ii) $$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Reaction (i) is the principal reforming reaction and reaction (ii) is a water-gas shift. The layout of a typical ammonia process is schematically shown in Exhibit 3-16.[8] The primary reforming step is followed by conversion of residual methane to hydrogen and oxides of carbon in a secondary reformer. Air is supplied to the secondary reformer in sufficient quantities to produce a raw synthesis gas containing a ratio of three moles of hydrogen to one mole of nitrogen. A subsequent shift converter removes CO from the gas stream by converting it to H_2 and CO_2 according to reaction (ii) above. Finally, before the hydrogen and nitrogen bearing stream can be passed to the ammonia converter, the CO_2 must be removed from the gas stream as it would readily poison the ammonia synthesis catalyst. The CO_2 is absorbed from the high pressure gas stream by a suitable high pressure CO_2 removal system. The stripped CO_2 is then either vented to the atmosphere or sold commercially for many applications including the soft drinks industry. It is this CO_2 that is of interest for enhanced oil recovery operations.

From a knowledge of the CO_2 absorption processess commonly employed in ammonia plants - Catacarb, Benfield, Giammarco-Vetrocoke, Sulfinol, Rectisol, Purisol, Fluor Economine - the composition of the CO_2 stream has been determined to be:

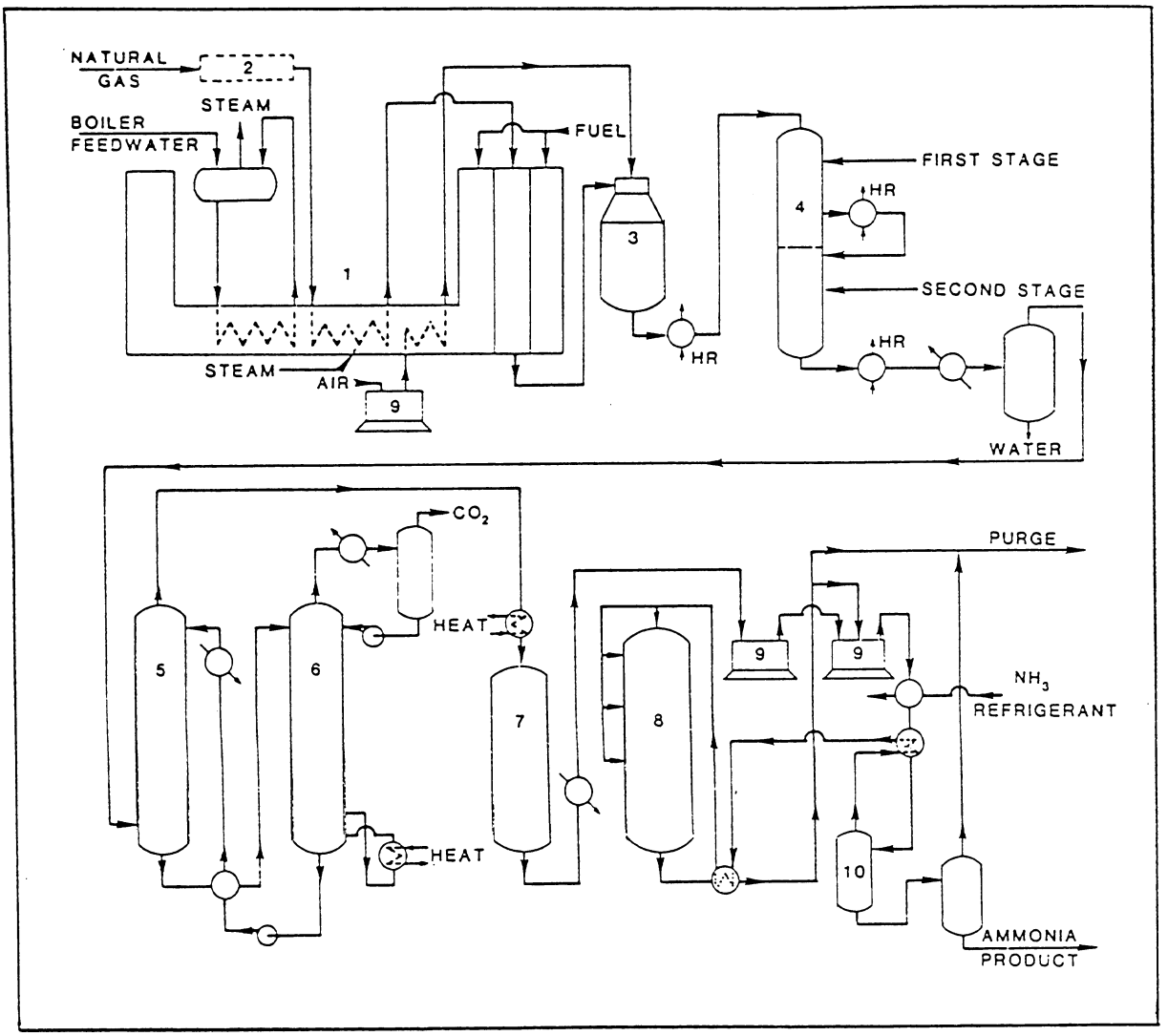
	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	97.5	--	0.02	--	--	2.4

The purified hydrogen-nitrogen mixture then passes to the ammonia converter where ammonia is synthesized over a promoted iron oxide catalyst at temperatures of 800-900°F and pressures of 150-240 atmospheres. The synthesis reaction is

(iii) $$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In terms of the amount of CO_2 produced per ton of NH_3 product, reactions i, ii, and iii suggest stoichiometrically that for every one SCF of NH_3 produced, 0.375 SCF of CO_2 will be evolved. Since hydrogen is recycled, most hydrogen eventually becomes ammonia and the stoichiometric ratios are a reasonable first approximation of what really occurs.

Exhibit 3-16: Ammonia Production Process



(1) Primary reformer; (2) Desulfurization; (3) Secondary reformer; (4) CO shift converter (in two stages); (5) CO_2 absorber; (6) CO_2 stripper; (7) Methanator; (8) NH_3 converter; (9) Compressor; (10) Separator. HR = heat recovery.

Source: Ref. 8, p. 111, Figure A-42, Peter A. Waldheim, M. W. Kellogg Company; Copyright (c) 1974 by McGraw -Hill, Inc. Used with the the permission of McGraw-Hill Book Company.

Thus:

$$1 \text{ SCF } NH_3 = 0.375 \text{ SCF } CO_2$$

$$(1 \times 17)/379 = 0.045 \text{ lb } NH_3 = 0.375 \text{ SCF } CO_2$$

$$1 \text{ ton } NH_3 = (2000 \times 0.375)/0.045 = 15{,}960 \text{ SCF } CO_2$$

Therefore, for every ton of ammonia produced the stoichiometry suggests that nearly 16,000 SCF of CO_2 is released. This value is approximate. Shreve suggests that in order to produce ammonia by the steam reforming of natural gas, 21,900 SCF of natural gas per ton of ammonia produced is required.[48] Based on these data, stochiometry of reactions (i) and (ii) suggest that for every ton of ammonia produced, nearly 22,000 SCF of CO_2 is released in practice. The actual amount of CO_2 released would vary based on the efficiency of the plant.

Appendix E is a list of ammonia plants based on data available in the 1981 Worldwide Petrochemical Directory[59] and the Chemical Economics Handbook.[51] Plants which were not on either list were checked to see whether they were still operating or perhaps had changed owners. Appendix E includes information both on the CO_2 being currently recovered and sold from each ammonia plant, and on the amount of CO_2 still available for purchase - these data were compiled using the Chemical Economics Handbook[51] and by directly contacting plant personnel. Appendix E does not include those plants which do not use steam reforming to produce hydrogen - a few plants produce ammonia from hydrogen generated from chlorine cells. No CO_2 is generated in these plants and hence they are of no interest. Exhibit 3-17 illustrates the locations of ammonia plants nationwide and Exhibits 3-18, 3-19, 3-20, and 3-21 depict the locations of ammonia plants in the four regions of interest and the CO_2 availability from each plant.

3.5 NATURAL GAS PROCESSING PLANTS

There are many deposits of natural gas which contain some CO_2. CO_2 can be separated from natural gas by any one of the number of acid gas removal processes (e.g., Selexol, Vetracoke, Sulfinol). CO_2 recovery processes from

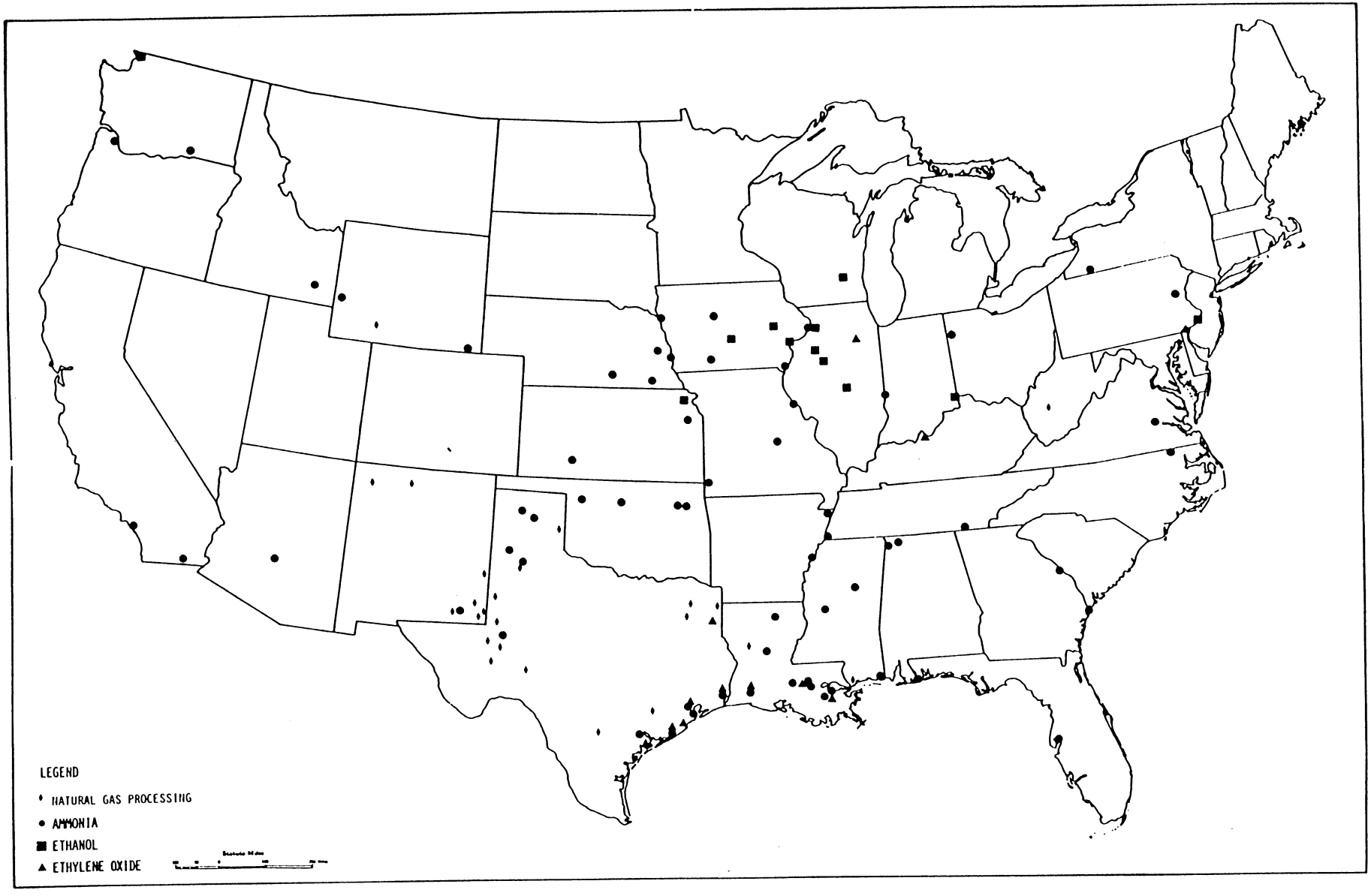


Exhibit 3-17: Location of Ammonia, Ethanol, Ethylene Oxide, and Natural Gas Processing Plants in the United States

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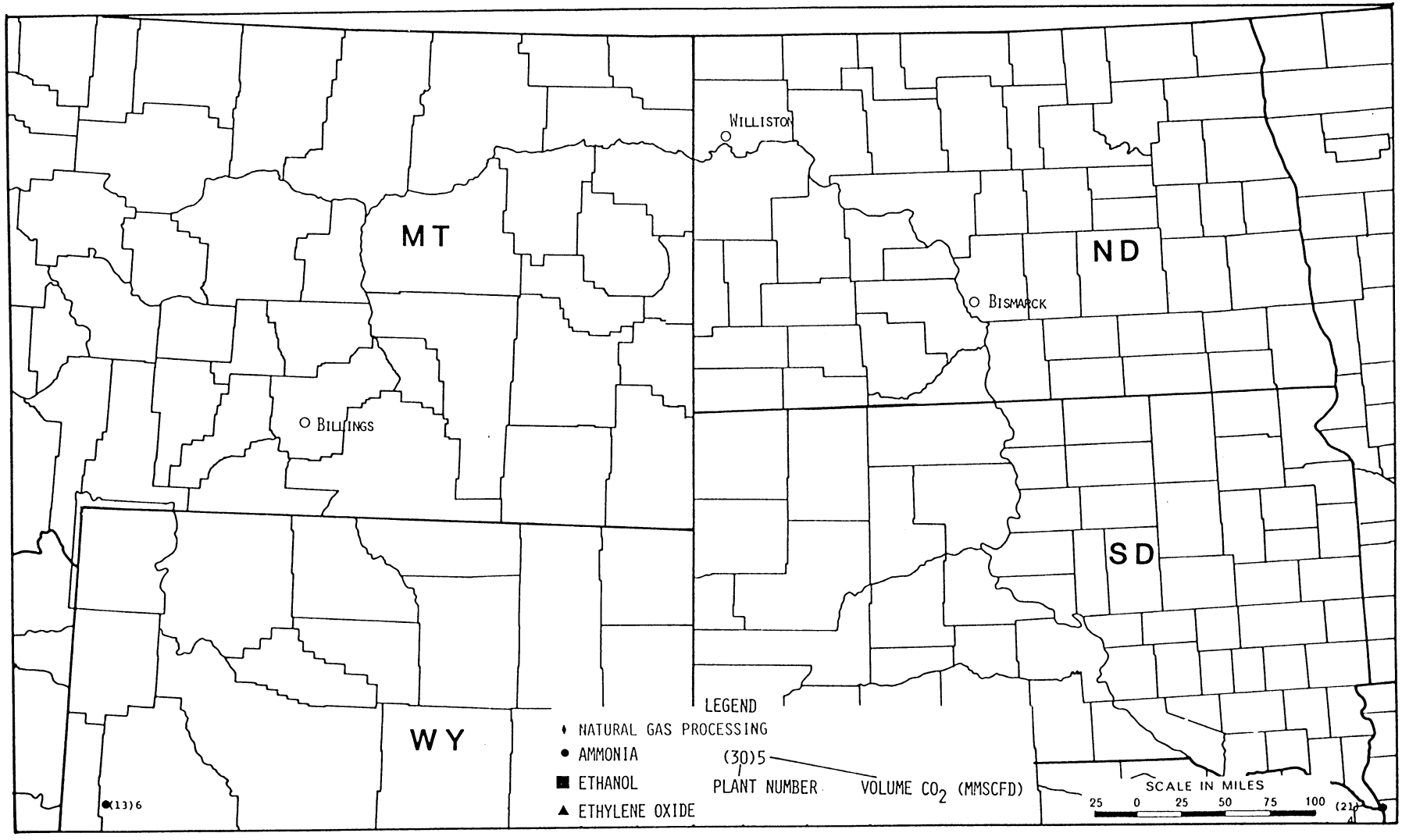


Exhibit 3-19: Carbon Dioxide Emitted from Ammonia, Ethanol, Ethylene Oxide, and Natural Gas Processing Plants in the Williston Basin

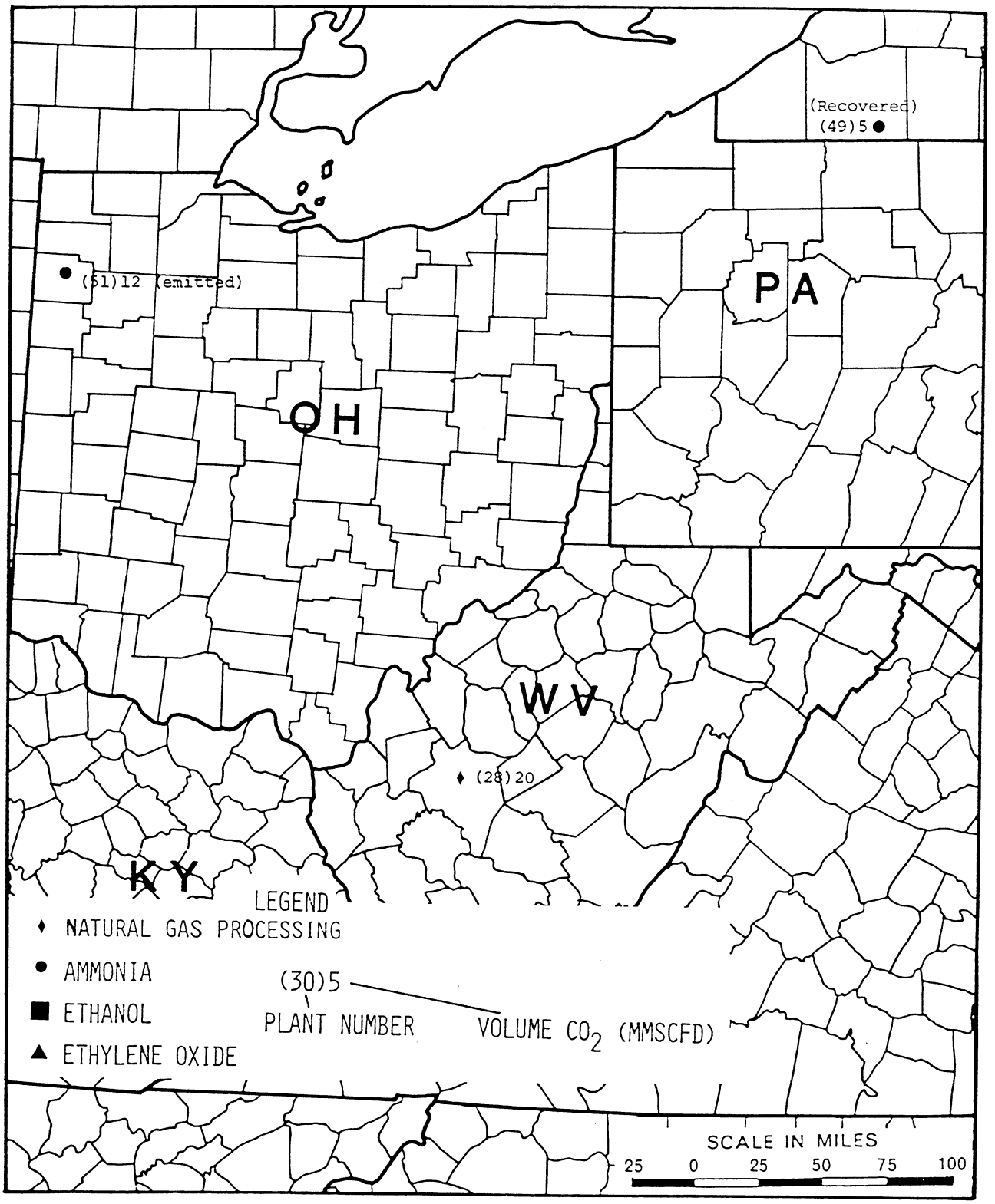


Exhibit 3-20: Carbon Dioxide Emitted from Ammonia, Ethanol, Ethylene Oxide, and Natural Gas Processing Plants in the Appalachian Basin

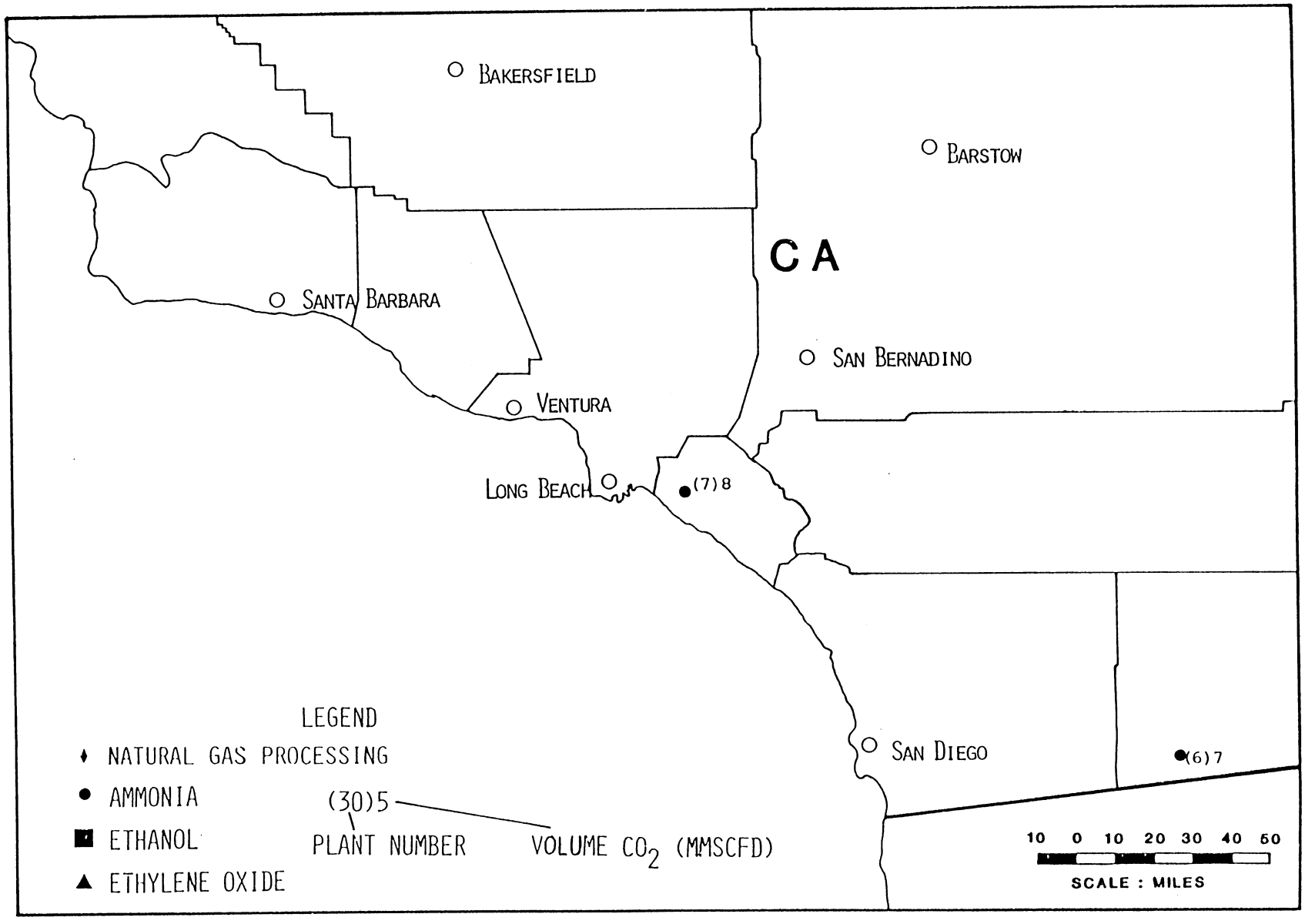


Exhibit 3-21: Carbon Dioxide Emitted from Ammonia, Ethanol, Ethylene Oxide, and Natural Gas Processing Plants in the Los Angeles Basin

such sources have been adequately discussed in SAI's study on Alternate Concepts for Supplying Carbon Dioxide for Enhanced Recovery Projects.[45] The location of natural gas processing plants and CO_2 availability in MMSCFD from such plants are provided in Appendix F.

3.6 GAS COMPRESSOR FLUE GAS

Gas compressor flue gas might provide CO_2 for some nearby reservoirs. The feasibility of recovering CO_2 from natural gas compressor stations for reservoirs in Louisiana was studied by researchers at the University of Southwestern Louisiana.[16] The recovery of CO_2 from compressor flue gas would resemble the recovery of CO_2 from low pressure, low purity, power plant stacks. Typical conditions for an exhaust gas for a 10,000 Hp gas-turbine compressor station are 900°F, 2% CO_2 and 144 MMSCFD exhaust gas. This could provide approximately 160 tons/day (2.72 MMSCFD) of CO_2. Typical conditions for an exhaust gas for a 20,000 Hp reciprocating gas engine compressor stations are 750°F, 4% CO_2, and 101 MMSCFD exhaust gas. This could provide approximately 220 tons/day (3.74 MMSCFD) of CO_2. Because of the very low CO_2 concentrations (2 to 4%) and because of the associated high costs ($2.79 to $4.18/MSCF in 1980 dollars for a turbine compressor station; and $3.82 to $4.92/MSCF in 1980 dollars for a reciprocating gas-engine compressor station), it was decided not to further study gas compressor flue gas. However, it is identified as a possible source of CO_2 if there is limited demand and if compressor stations are near (10 to 15 miles) the field of application.

3.7 FUEL ALCOHOL (ETHANOL) PLANTS

Most of the ethanol (ethyl alcohol) in the United States is produced by the fermentation of biomass. In this fermentation process, about 60 SCF of CO_2 is produced per gallon of ethanol, and the CO_2 released is essentially pure. A list of ethanol plants, their capacities and the availability of CO_2 in tons/day and MMSCFD are presented in Appendix G.

The CO_2 availability presented in Appendix G is based on an annual 300 days of operation and approximately 90% recovery. For example, a 1MM gal/yr ethanol plant would yield a CO_2 production of 60 MMSCF/yr; at 90% CO_2 recovery this would become 54 MMSCF/yr; at 17,000 SCF/ton CO_2 this is equivalent to

3176 tons/yr; for 300 days operation this is equivalent to 10.58 tons/day. For the calculations in Appendices G and K (see Section 3.10.2), approximately 10 tons/day of CO_2 or .17 MMSCFD of CO_2 for every million gal/yr of ethanol produced were assumed.

At the present time there are only a handful of relatively large alcohol producers, and they have been contacted to determine whether or not they presently recovery and sell CO_2 produced as the by-product of the fermentation process. The largest producer of fuel alcohol, Archer Daniels Midland, is planning to expand its capacity significantly in the next few years.[1] Archer estimates that it will produce 6,000 tons/day of CO_2 in the Illinois-Iowa area and has shown interest in supplying CO_2 for EOR.

3.8 ETHYLENE OXIDE PLANTS

The majority of the world's ethylene oxide is produced by the direct oxidation of ethylene by air or oxygen over a silver catalyst at pressures of 10 to 20 atmospheres and temperatures of 428 to 546°F. The principal reactions that occur in the process are:

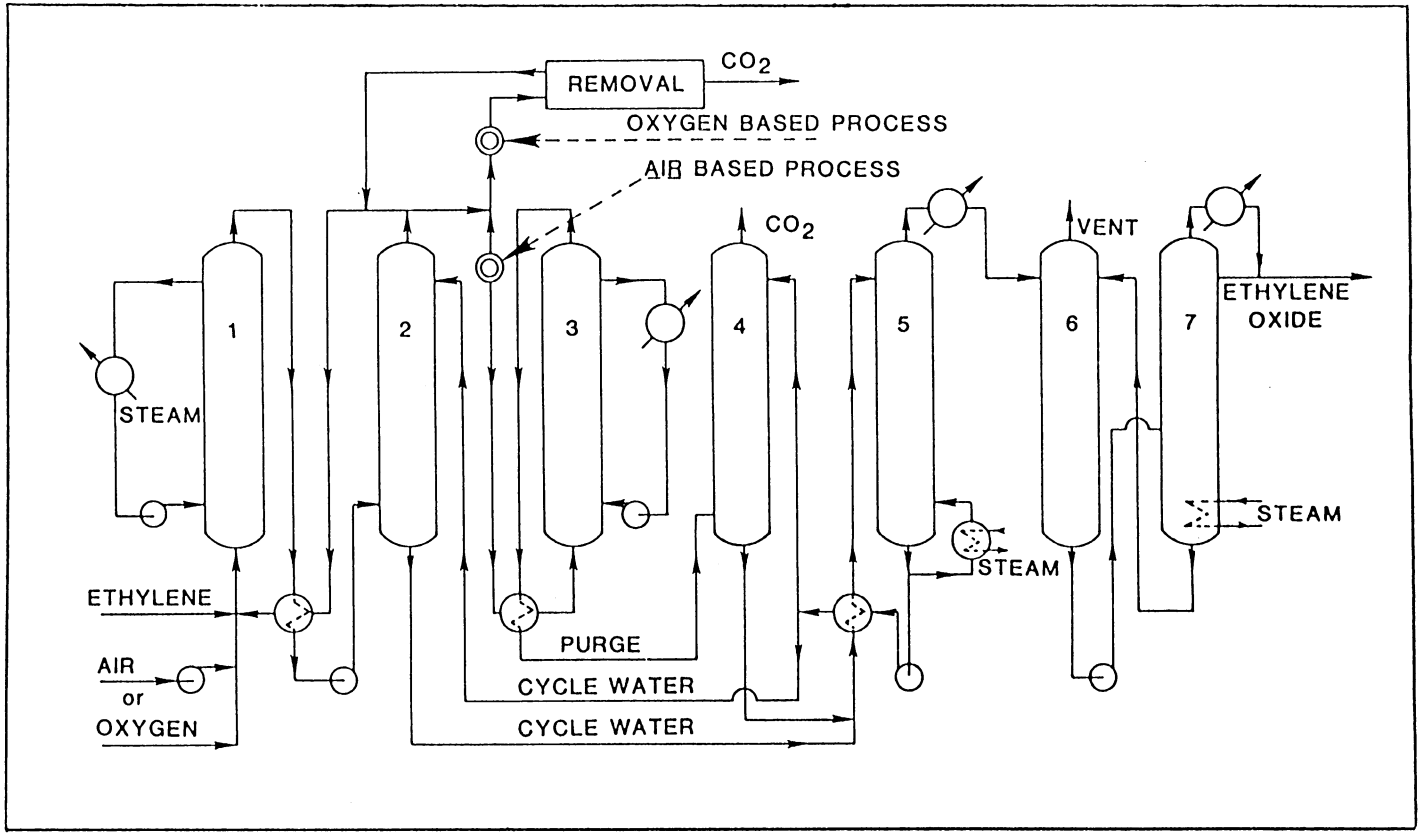
$$CH_2 = CH_2 + 1/2O_2 \longrightarrow CH_2 - CH_2 \text{ (O)}$$

$$CH_2 = CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

A schematic flow sheet of the process is given in Exhibit 3-22.[8] The gas leaving the main reactor passes to a scrubbing tower where the ethylene oxide is scrubbed with water. The unabsorbed ethylene and oxygen are partly recycled and partly conveyed to a second reactor where oxidation is completed. A second scrubber absorbs the ethylene oxide produced in the second reactor and the remaining ethylene free gas can be purged. This purged gas is a mixture of CO_2, nitrogen, and water vapor if air is the oxidizing agent; in the case of the newer, larger plants where pure oxygen is used, the purge is pure CO_2 in the presence of water vapor only. Much of this CO_2 is currently being marketed.

In an operation using oxygen, about 0.9 units of ethylene are consumed per unit of ethylene oxide produced. An air-based plant consumes about 1.0 unit of ethylene per unit of ethylene oxide produced.

Exhibit 3-22: Schematic Flow Sheet of Ethylene Oxide Production by Direct-Oxidation Route



(1) Main reactor; (2) Main absorber; (3) Purge reactor; (4) Purge Absorber; (5) Desorber for ethylene oxide; (6) Stripper for ethylene oxide; (7) Refiner for ethylene oxide.

Source: Ref. 8, p. 445, Figure E-27, Alvin S. Cohan, Scientific Design Company, Inc.; Copyright (c) 1974 by McGraw-Hill, Inc. Used with the permission of McGraw-Hill Book Company.

Thus, for a plant using oxygen, the reaction stoichiometry indicates that about 0.83 lbs of CO_2 is produced per pound of ethylene oxide produced. For a plant using air, the corresponding figure is 1.14 lbs of CO_2 per pound of ethylene oxide produced. These figures are only approximate; the actual production of carbon dioxide depends to a significant degree upon the control of the process at a specific plant.

Although the general configurations of oxygen-based plants and air-based plants are very similar, the waste offgas containing the carbon dioxide is emitted in different places. In an oxygen-based plant the carbon dioxide is emitted as a pure wet gas, having been scrubbed from a recycle gas in a CO_2 removal unit. Thus, the CO_2 stream is readily available from an oxygen-based plant and can be recovered without much difficulty. The carbon dioxide from an air-based unit is emitted from several places on the unit and is dilute. Collection of the carbon dioxide from this type of plant would be difficult to accomplish, particularly without interfering with the control of the unit.

Appendix H lists the fifteen major ethylene oxide plants in the continental United States which use pure oxygen as the oxidizing agent except where stated. The list was compiled both from the Chemical Economics Handbook[51] and by direct contact with plant personnel. The CO_2 generation capacity is included, and where possible, information is provided on the amount of CO_2 currently being recovered for resale and the amount of CO_2 still available. Exhibit 3-17 illustrates the locations of the pertinent ethylene oxide plants nationwide and Exhibits 3-18, 3-19, 3-20, and 3-21 depict plant locations in each of the four regions of interest along with the CO_2 availability from each plant.

3.9 REFINERIES

There are several operations occurring in refineries that vent CO_2 to the atmosphere. These operations have been identified from the Refinery Siting Workbook compiled by Mittelhauser Corporation for DOE.[30] They are:

- Hydrotreating
- Fluid Cat-Cracking Regenerator Unit
- Hydrogen Production Unit
- Sulfur Recovery Unit
- Steam Generation Plant

From discussions with Exxon representatives in Baytown, TX,[44] only the fluid cat-cracking regenerator unit and hydrogen plants within refineries were identified as sources of economically recoverable CO_2. Each source will be considered separately. Appendix I lists the major refineries in the continental United States along with the CO_2 emitted from fluid cat-cracking regenerators and hydrogen plants where applicable. Exhibit 3-23 depicts the locations of fluid cat-cracking units and hydrogen plants of interest nationwide.

3.9.1 Fluid Cat-Cracking Regenerator Units

Fluid catalytic cracking is a low pressure process which uses high temperatures in the presence of a catalyst to break or crack heavier, higher boiling petroleum fractions into lighter more valuable materials. A typical unit is shown in Exhibit 3-24.[30] The fresh feed is preheated, mixed with the regenerated catalyst, and is fed through the fresh feed riser to the reactor. The cracking process is carried out both in the riser and the reactor with the resulting hydrocarbon vapors passing onto the fractionator. The fractionator separates the cracked product into the various streams.

Due to the severity of the cracking operation conditions, the catalyst must be continuously regenerated to remove coke formed on the catalyst surface. The spent catalyst is discharged from the reactor. It is steam-stripped to remove entrained hydrocarbons, and is then fed to the regenerator. Air is fed to the regenerator and the coke is burned-off to form a mixture of CO and CO_2. This mixture passes out of the regenerator to a CO boiler where the remaining CO is burned to CO_2 before the whole gas stream is vented.

It was determined from discussions with Exxon representatives[44] that for every barrel of feedstock to the cat-cracker, some 205 SCF of CO_2 were evolved. Using data given by Smuggs,[50] the composition of the vented stack gas was determined to be:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	14.6	1.7	75.8	--	--	7.9

Appendix I lists CO_2 emissions from fluid cat-cracker regenerator units across the country. Exhibits 3-25, 3-26, 3-27, and 3-28 show the locations of

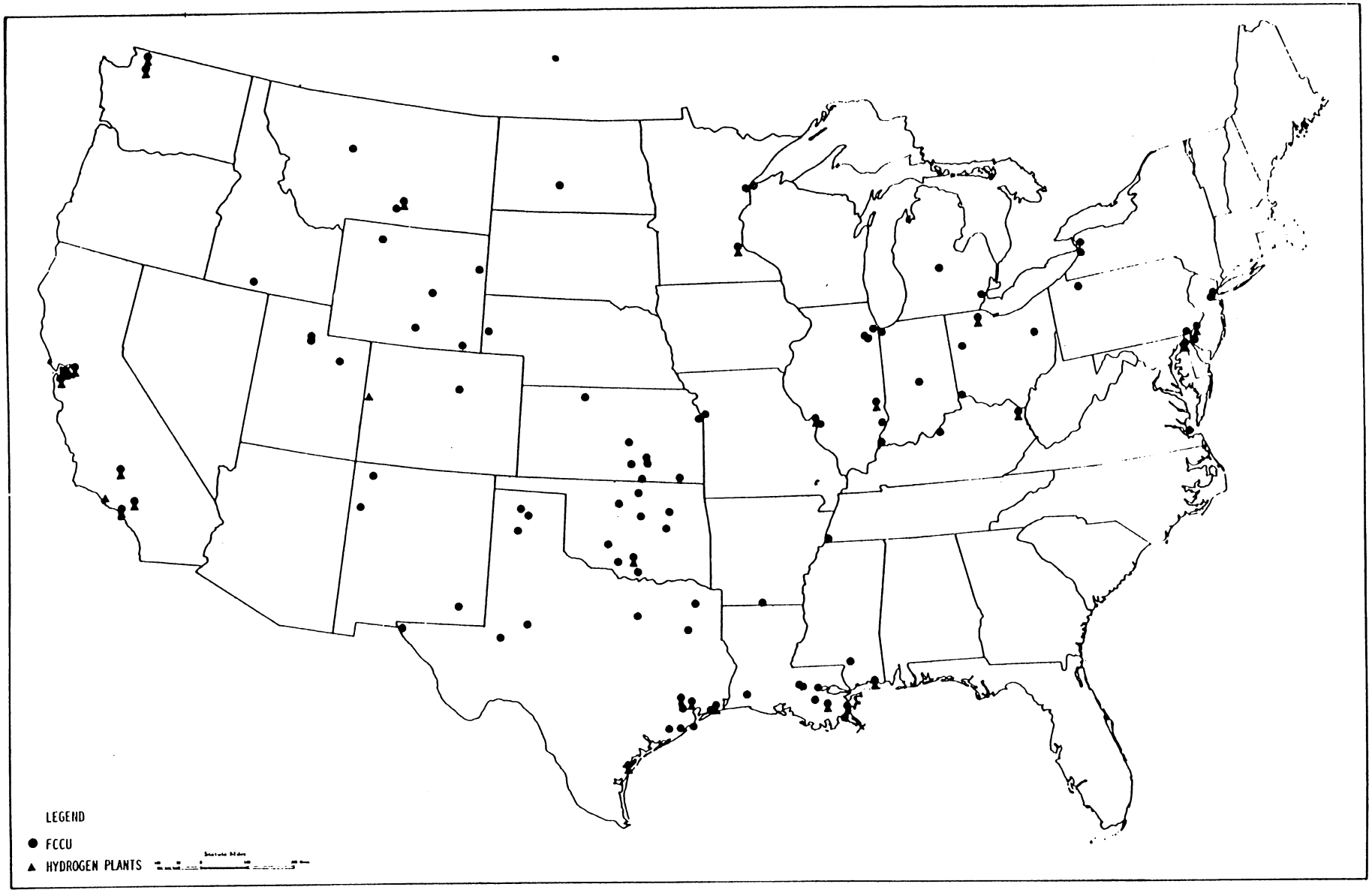
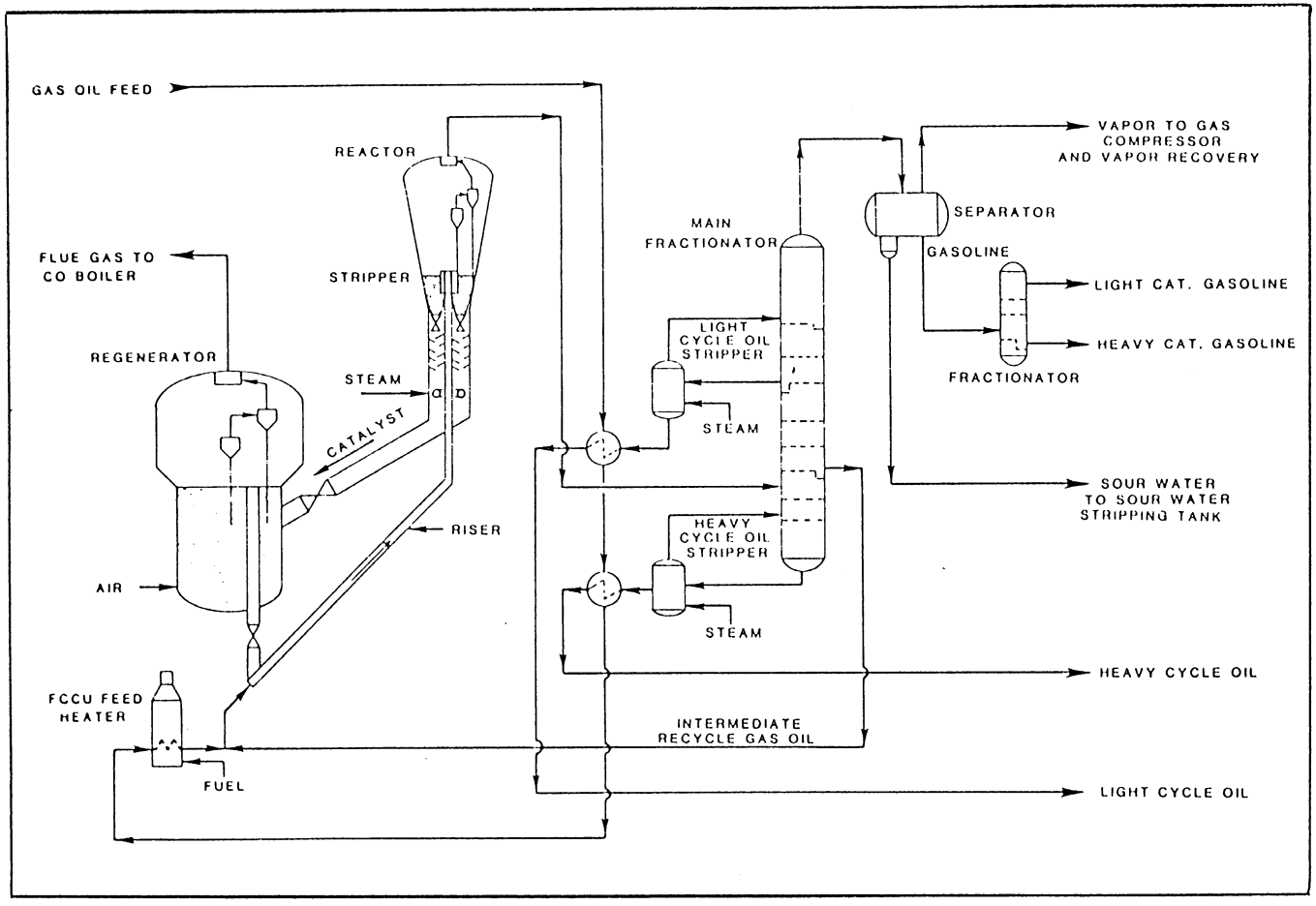


Exhibit 3-23: Location of FCCU (Refineries) and Hydrogen Plants in the United States

Exhibit 3-24: Flow Diagram for a Fluid Catalytic Cracking Unit



Source: Ref.30, p. 24, Figure 9.

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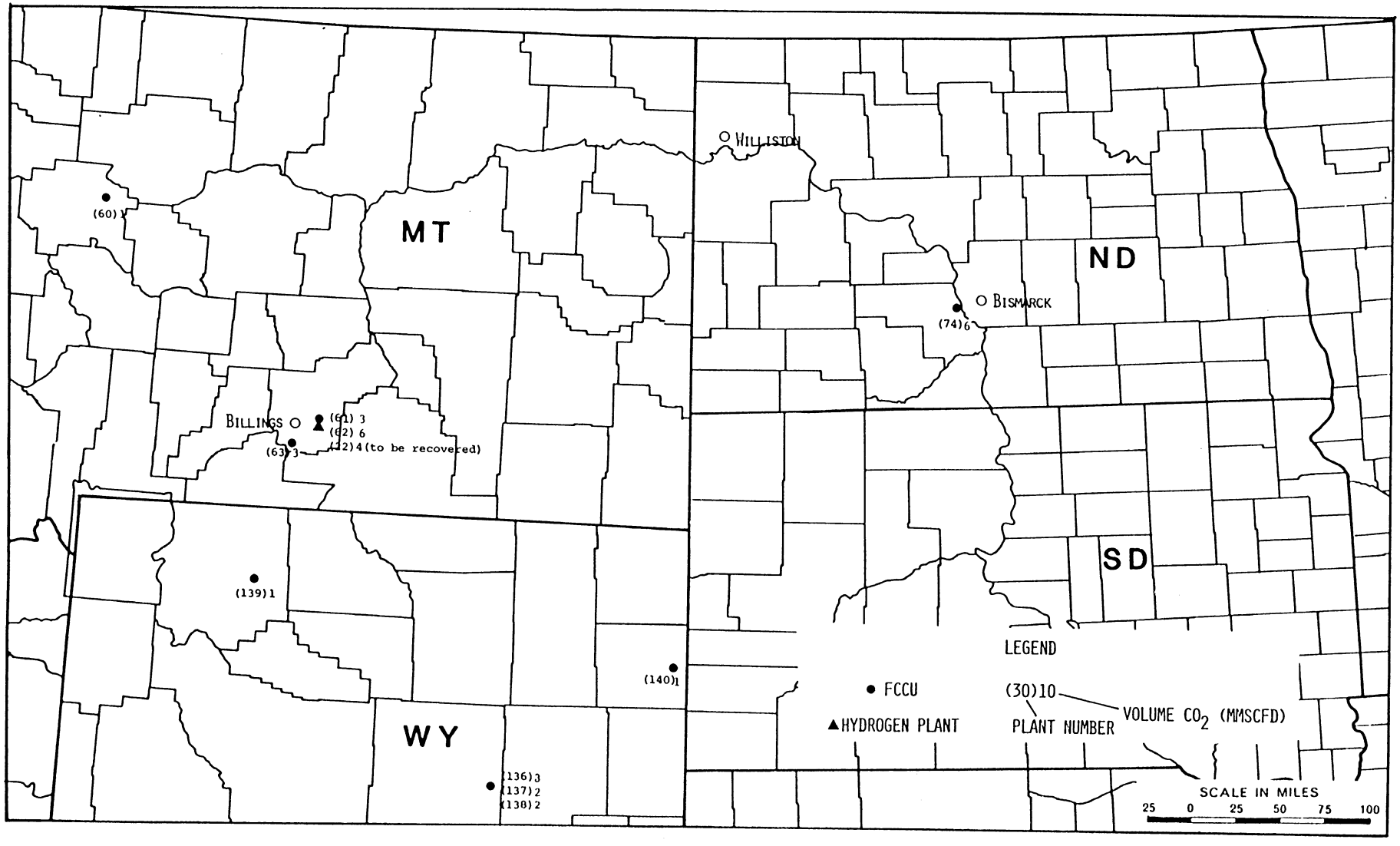


Exhibit 3-26: Carbon Dioxide Emitted from Refineries (FCCU) and Hydrogen Plants in the Williston Basin

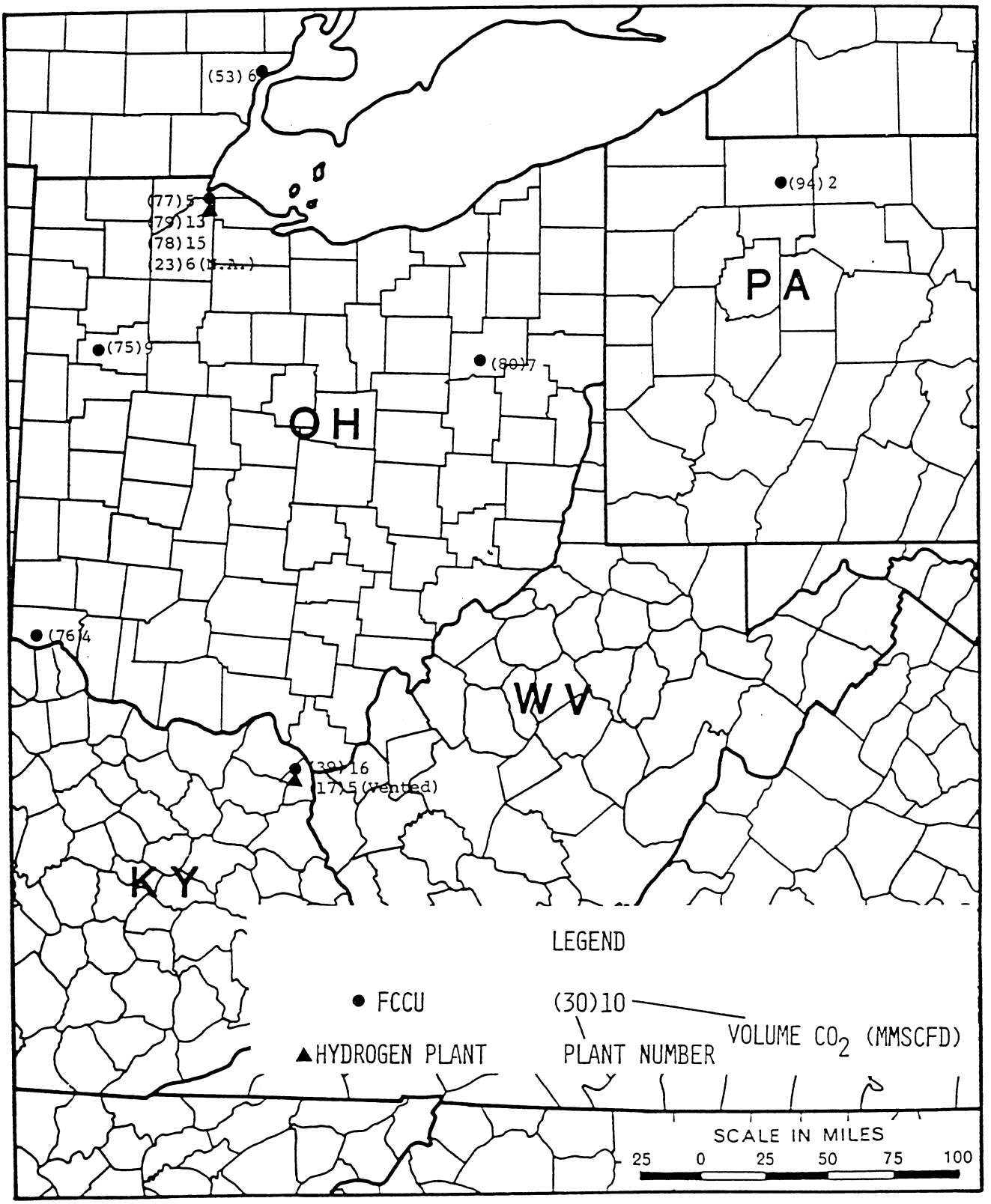


Exhibit 3-27: Carbon Dioxide Emitted from Refineries (FCCU) and Hydrogen Plants in the Appalachian Basin

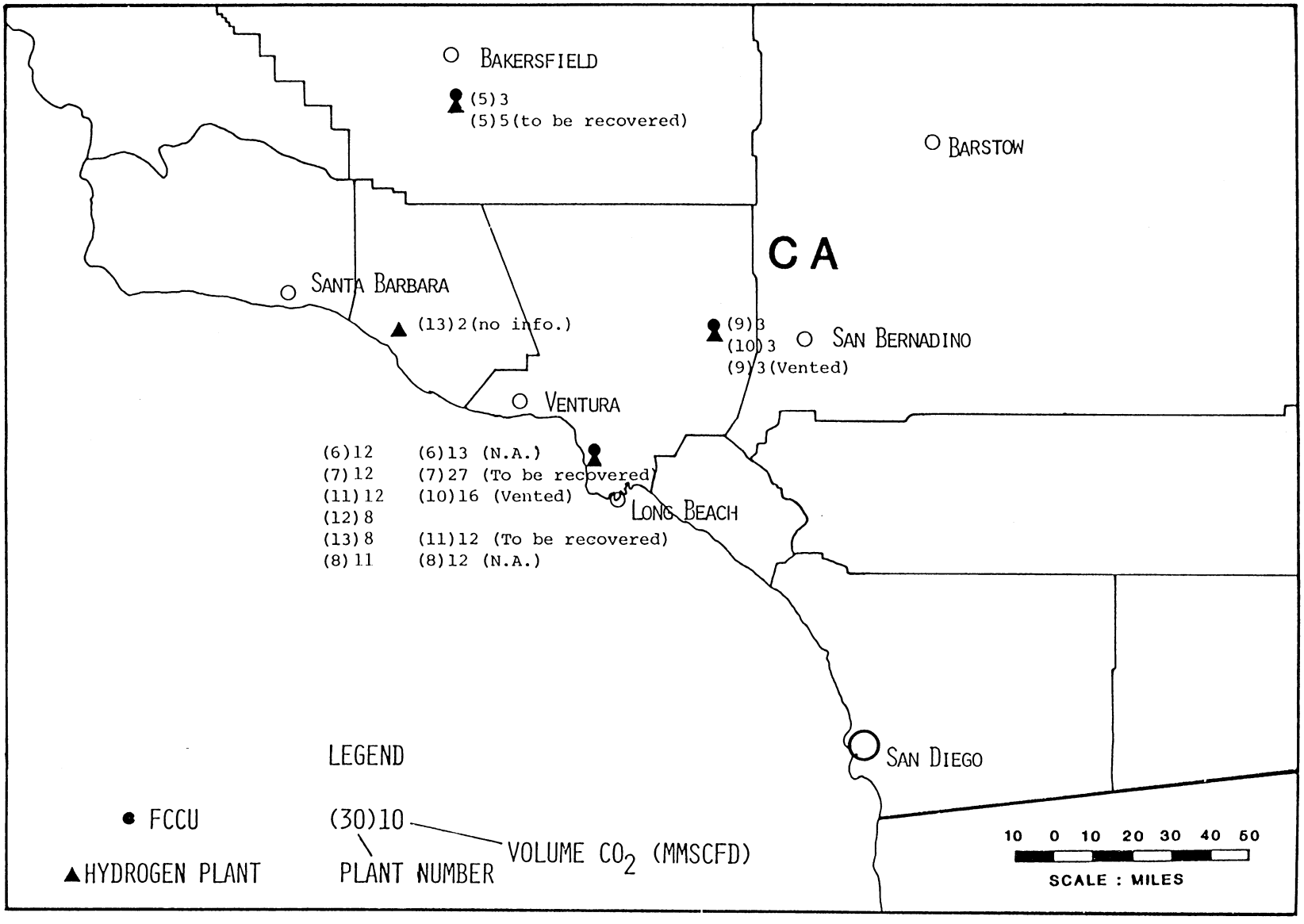


Exhibit 3-28: Carbon Dioxide Emitted from Refineries (FCCU) and Hydrogen Plants in the Los Angeles Basin

these units in the regions of interest along with the emissions of CO_2 from each plant per operating day. Plant locations and crude processing capacities were obtained from the Worldwide Directory of Refining and Gas Processing.[56]

3.9.2 Hydrogen Production Unit

Hydrogen is used as a reactant in many refinery units including hydrotreating, isomerization, and hydrocracking. Hydrogen is most widely produced by the steam reforming of available hydrocarbons such as natural gas, refinery fuel gas, propane, butane, or desulfurized light naptha. Not all refineries require separate hydrogen production units as hydrogen is also produced in the refinery as a by-product of the catalytic reforming process. When processing sour crudes, by-product hydrogen is usually not enough to satisfy the total refinery demand.

The production of hydrogen by steam reforming requires the following steps: sulfur removal; reforming; shift conversion; carbon dioxide absorption; and methanation. A flow sheet of a typical hydrogen production unit is given in Exhibit 3-29.[30] The overall conversion that occurs in the process is:

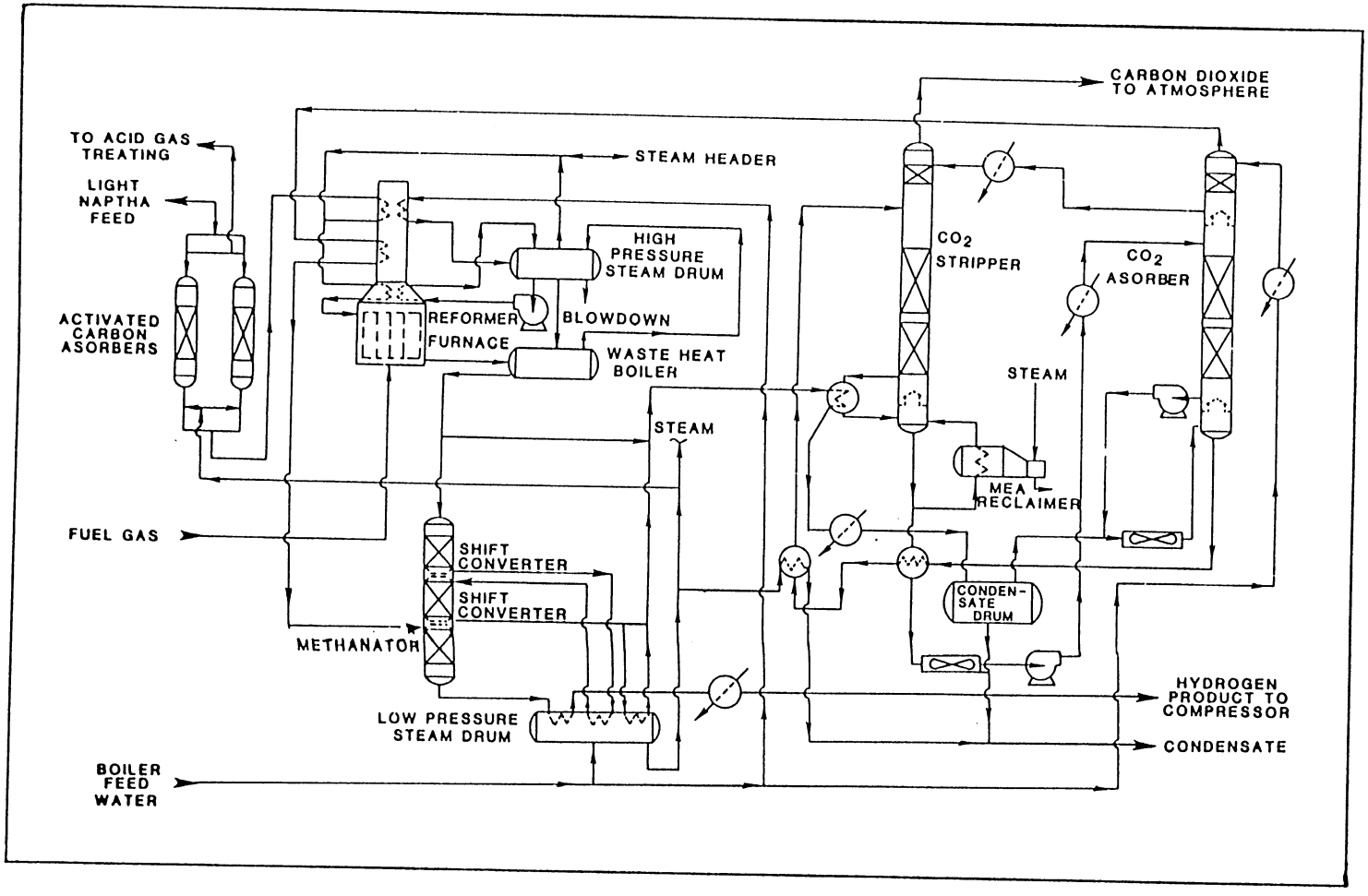
$$CH_4 + 2H_2O \longrightarrow 4H_2 + CO_2$$

Thus, to generate a high purity hydrogen product, CO_2 must be removed from the gas stream by a suitable CO_2 removal system analagous to that used in ammonia plants. Indeed, the production of hydrogen by this very method is the first step in ammonia synthesis. The removed CO_2 is then either vented to the atmosphere or sold after removing the moisture. The composition of the CO_2 stream is similar to that vented from ammonia plants:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	97.5	--	0.02	--	--	2.4

Stoichiometry suggests that for every 100 SCF of hydrogen produced, some 25 SCF of CO_2 will be evolved. This is true whether or not the reaction proceeds to completion, and these values were used as a primary estimate of CO_2 production volumes.

Exhibit 3-29: Flow Diagram for a Hydrogen Production Unit



Source: Ref. 30, p. 34, Figure 14.

Appendix I lists CO_2 generation capacities at refinery hydrogen plants across the continental United States. Where possible, information on the amount of CO_2 already recovered for resale has been included. Exhibits 3-25, 3-26, 3-27, and 3-28 show the locations of these units in the four regions of interest along with the emissions from each plant per operating day. Plant locations and hydrogen generation capacities were obtained from the Worldwide Directory of Refining and Gas Processing.[56]

3.10 FUTURE BY-PRODUCT CO_2 SOURCES

A number of plants are planned which will result in an increase in by-product CO_2 supply. Five particular types of plant have been investigated; future power plants, proposed fuel alcohol plants, proposed synthetic natural gas (SNG) plants, and proposed fluid cat-cracking units and hydrogen plants. Each will be considered separately.

3.10.1 Proposed Power Plants

Information has been obtained for all future fossil-fuel power plants envisaged to become operational by the end of 1988. The locations of these plants across the continental United States are depicted where known on Exhibit 3-30. Appendix J lists these plants, their planned locations, and the amount of CO_2 each is expected to emit per operational day. The envisaged quality of the CO_2 stream is also given. Calculations performed for future power plants were identical to those outlined for existing plants in Section 3.2. Exhibits 3-31, 3-32, 3-33, and 3-34 illustrate the proposed locations of future power plants and the magnitude of CO_2 released per plant, per day in each of the four regions of interest.

3.10.2 Proposed Fuel Alcohol (Ethanol) Plants

It is difficult to develop a relatively complete, up-to-date list of ethanol plants because of the intense interest at the grass-roots level in producing ethanol for fuel purposes. Many of the proposed projects involve plants of small capacity. To keep the list manageable and to consider only those sources likely to be cost-effective in recovering the CO_2, only projects

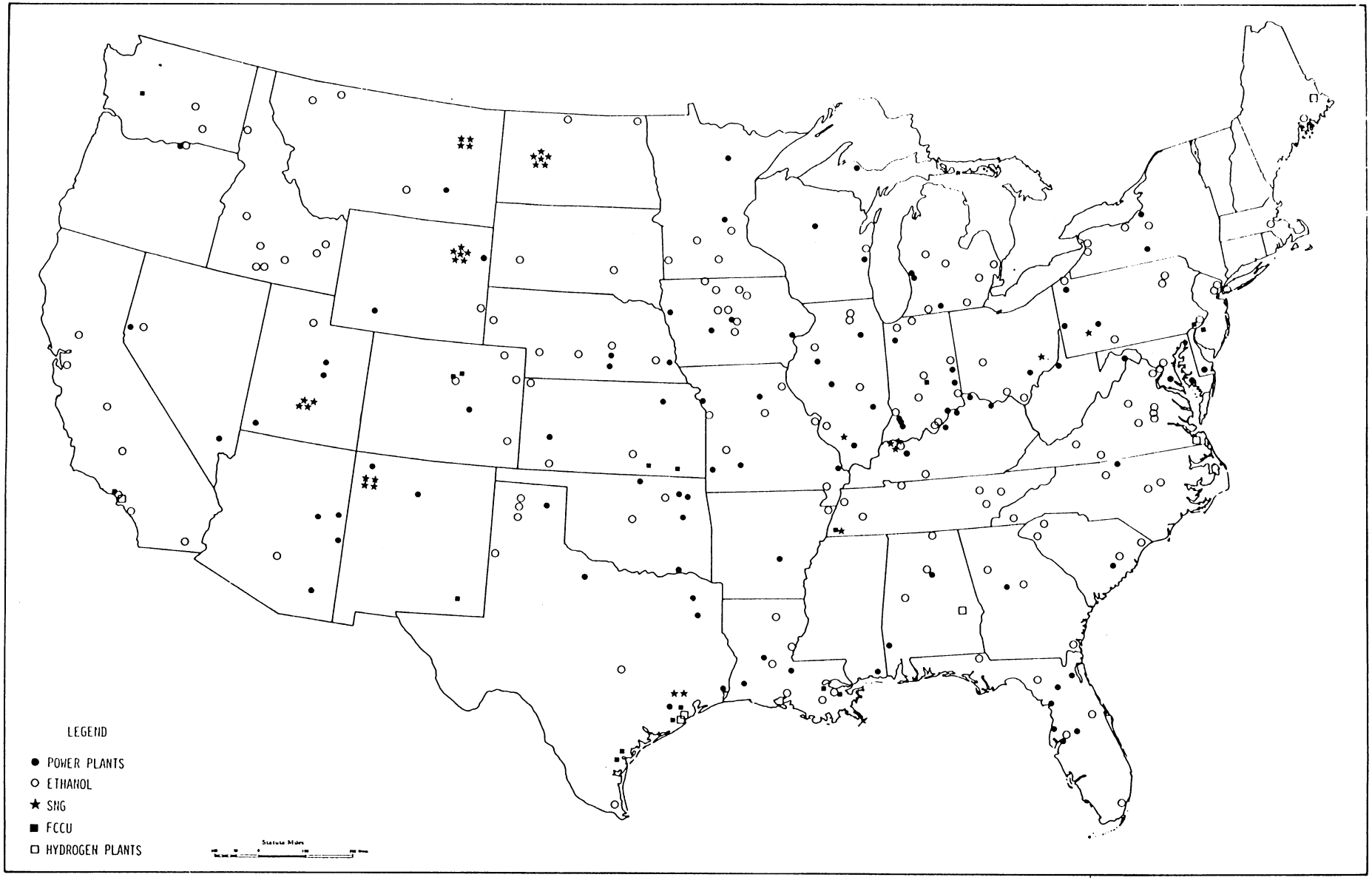


Exhibit 3-30: Location of Future Plants Emitting Carbon Dioxide in the United States

INSERT MAP

EXHIBIT 3-31

Pg 82

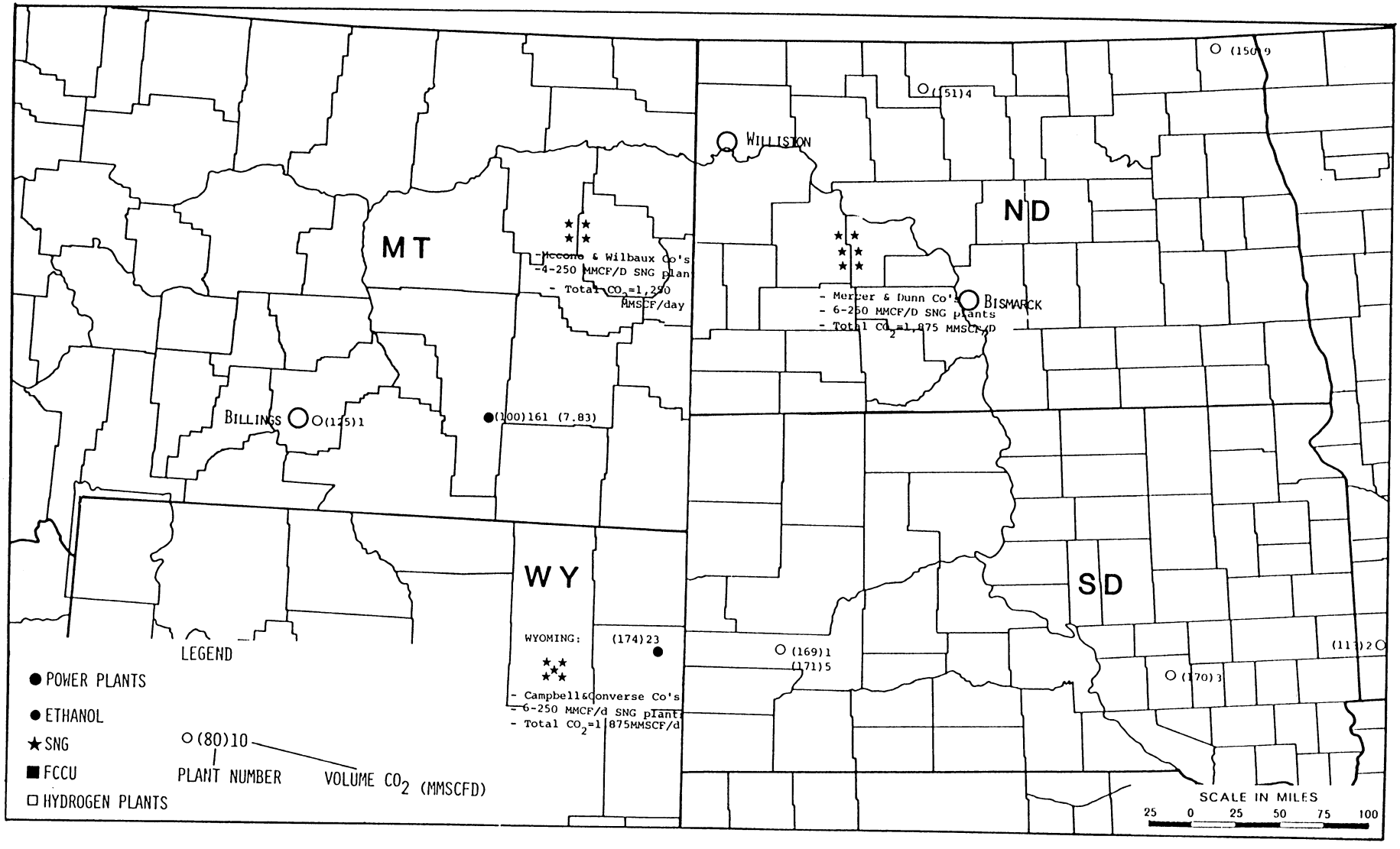


Exhibit 3-32: Potential Carbon Dioxide Emissions from Proposed Plants in the Williston Basin

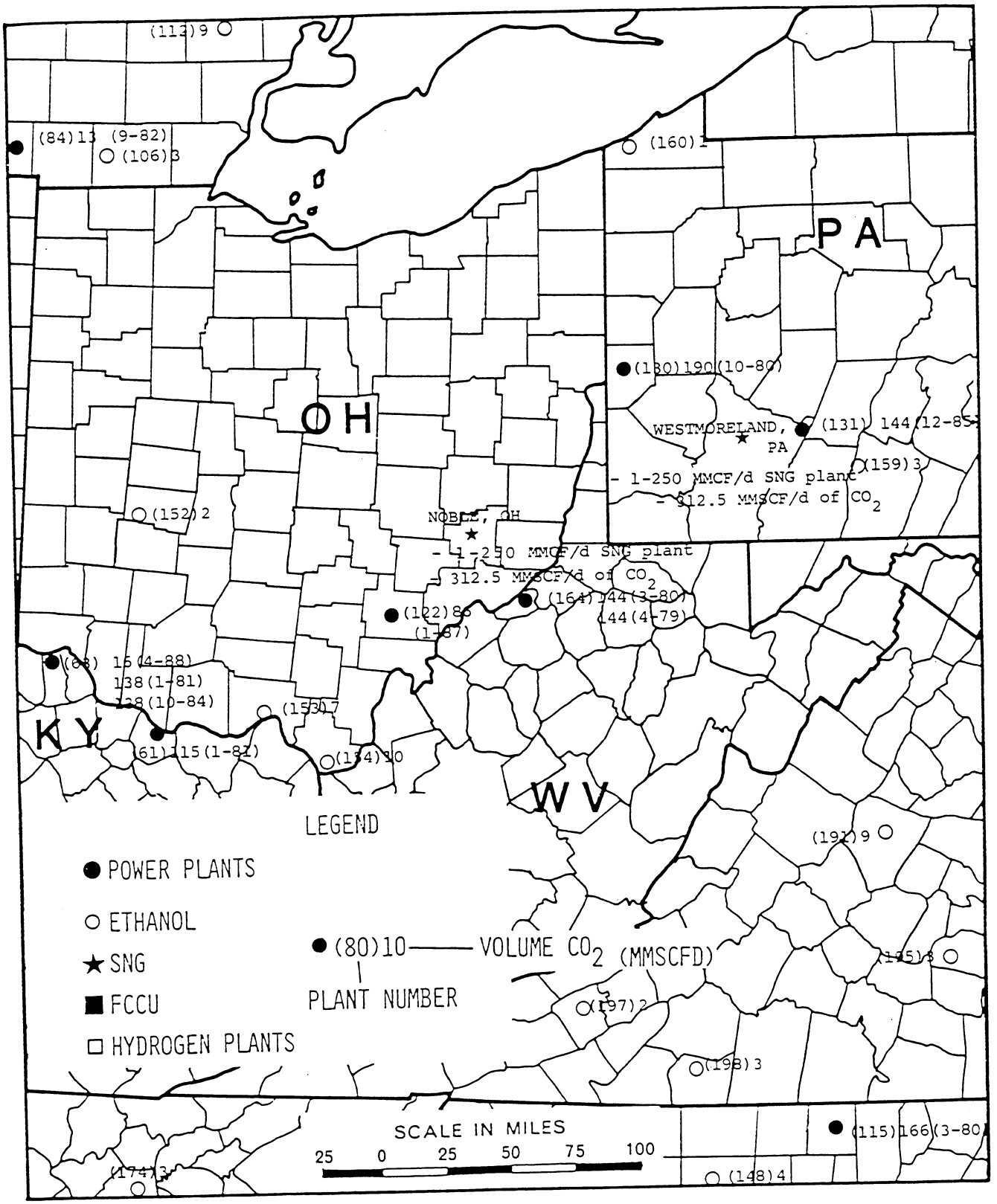


Exhibit 3-33: Potential Carbon Dioxide Emissions from Proposed Plants in the Appalachian Basin

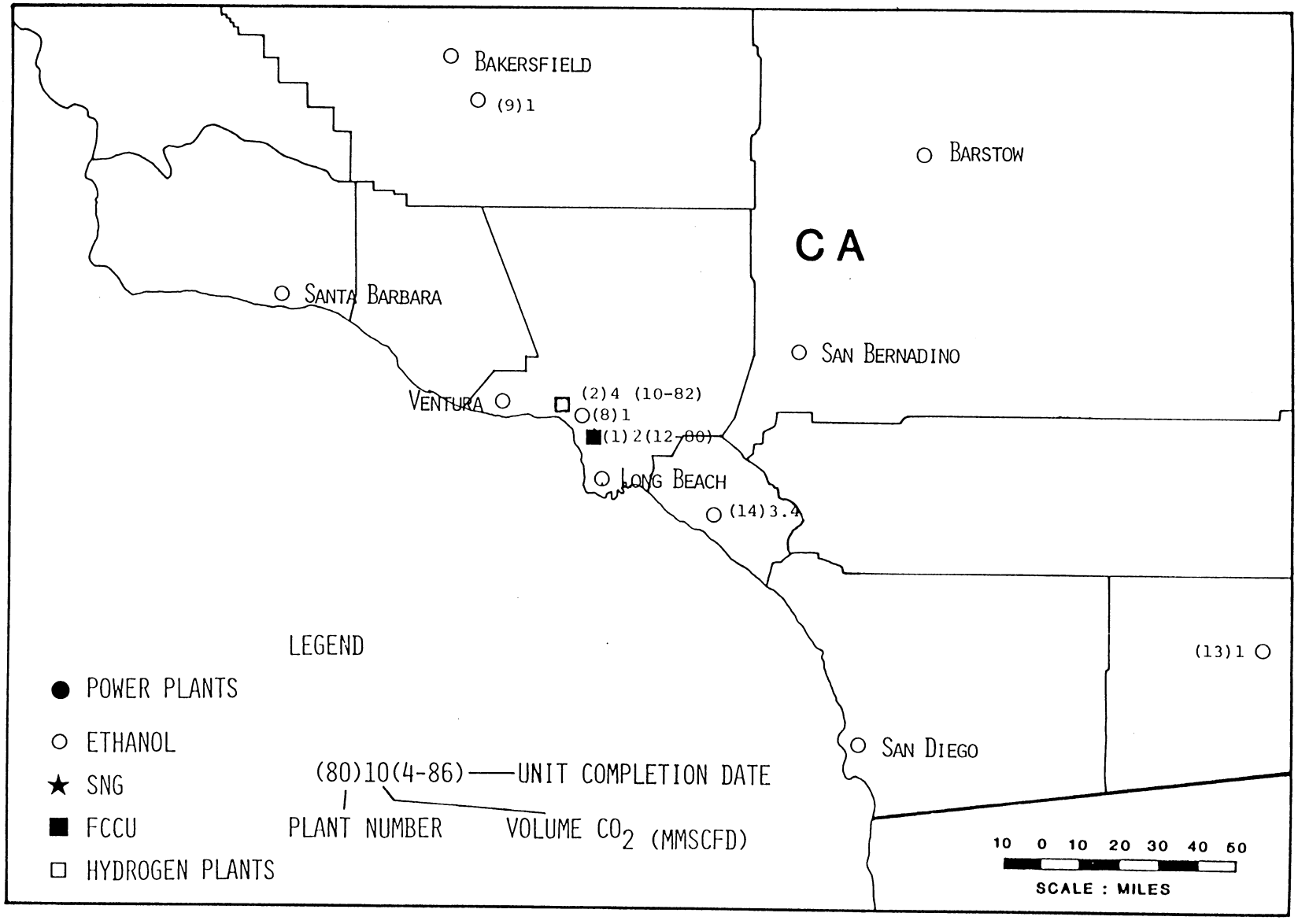


Exhibit 3-34: Potential Carbon Dioxide Emissions from Proposed Plants in the Los Angeles Basin

with a capacity of over 5,000,000 gal/yr (a CO_2 generation rate of 50 tons/day or 0.86 MMSCFD) were included.

Additional information on potential future alcohol production facilities is available in a recent report by Davy McKee Corporation,[9] on the potential of converting idle capacity in distilleries, breweries, sugar beets, corn wet milling, sugar cane, cheese whey, potato by-products, and citrus waste. Data from this report have been analyzed.

Appendix K lists proposed fuel alcohol (ethanol) plants. Estimates of CO_2 availability have been made where possible. Exhibit 3-30 depicts the locations of the proposed alcohol plants nationwide and Exhibits 3-31, 3-32, 3-33, and 3-34 illustrate the plant locations in each of the four regions of interest.

3.10.3 Proposed SNG Plants

The feasibility of using CO_2 produced from the proposed high-Btu coal gasification plants for enhanced oil recovery is the sole topic of a study by MITRE Corporation[29] for the American Gas Association. The report concludes that if all 33 proposed SNG plants are completed by the year 2000, a total of about 100 trillion cubic feet of CO_2 would be available over a 30-year period. These plants are envisaged to meet 76% of the total demand for CO_2 for use in enhanced oil recovery by the year 2000.

It is apparent that if these proposed plants are actually constructed, their CO_2 output could completely change the complexion of the enhanced oil recovery CO_2 supply-demand situation.

Appendix L lists the proposed locations of the plants along with the envisaged daily CO_2 output. Approximately 1.25 SCF of CO_2 is liberated for every one SCF of SNG produced. The by-product gas stream is high in CO_2 as shown below:

	CO_2	O_2	H_2	NO_x	Combined S	$H_2O(v)$	CO	HC
percent volume	90.2	0.1	4.5	5.3×10^{-4}	1.9×10^{-3}	3.7	0.03	1.5

Exhibit 3-30 illustrates the locations of the plants nationwide and Exhibits 3-31, 3-32, 3-33, and 3-34 depict the locations of these plants and daily CO_2 production figures in each of the four regions of interest.

3.10.4 Proposed Fluid Cat-Cracking Units and Hydrogen Plants

A number of fluid cat-cracking units and hydrogen plants have been proposed or are actually under construction. The quantity and quality of CO_2 liberated from these plants can be determined from Section 3.6 once the capacities of the proposed plants are known. Appendix M is a list of newly constructed or proposed fluid cat-crackers and hydrogen plants along with their CO_2 generation capacities. These plants were located from the 1981 Worldwide Petrochemical Directory.[59]

4. REGIONAL CARBON DIOXIDE SUPPLY/DEMAND BALANCE

The predicted ultimate calendar-day demand for carbon dioxide in the four main basins considered in Appendix A of this study is shown below, with the demand based on 300 days injection per year being shown in brackets.

Basin	CO_2 Demand (MMSCFD) Calendar Day	300 Days/yr.
Permian Basin (and Texas Gulf Coast):	8,228	(10,011)
Williston Basin	194	(236)
Appalachian Basin	68	(83)
Los Angeles Basin	309	(376)
Total	8,799	(10,706)

4.1 TOTAL CARBON DIOXIDE SUPPLY

The carbon dioxide supply from natural and by-product sources identified in Section 3 is shown below (using 60% recovery from coal-fired power and cement plants, and 90% recovery from other power and cement plants and FCCU). (Note that all data in the Appendices and the rest of this Section are based on spreading the actual output in 1978 over 300 operational days).

Source	Daily Supply (MMSCFD)
Natural CO_2	1,350
Power Plants	54,608
Cement Plants	2,649
Ammonia Plants	716
Ethylene Oxide Plants	59
Ethanol Plants	14
Natural Gas Processing	255
Hydrogen Plants	368
Fluid Catalytic Cracker Unit Regenerator	834
Total	60,853

These figures, and the ones in the remainder of this Section, do not take into account the minimum economic size for the plants, as this depends on distance to the nearest demand point.

It is apparent that currently known naturally occurring high purity carbon dioxide sources can provide less than 15% of the total CO_2 demand. The total supply from by-product sources is more than sufficient to meet the demand, but the economically available supply is much less, due to the costs of transporting CO_2 over large distances (see Section 6).

4.2 REGIONAL CARBON DIOXIDE SUPPLY

In order to obtain a better estimate of the available carbon dioxide supply for each of the four main basins, only those sources within each of the regions identified in Exhibit 2-2 were considered. These regions are subjective, but were drawn to include all major sources within approximately 500 miles (Permian Basin) or 250 miles (other three basins) from the center of demand.

The total supply available from each type of source in each of the four regions is shown in Exhibit 4-1. The locations of the individual sources are shown in Exhibits 4-2, 4-3, 4-4, and 4-5. Full details on any of these sources can be obtained from Appendices B through M, which are organized by State and County. Exhibit 4-6 lists CO_2 by-product source plants in each of the four basins by identification number. These numbers are used in Appendices C through I.

The different sources are divided into low- and high-purity CO_2 as follows:

Low Purity	High Purity
Power plants	Natural Sources
Cement Plants	Natural Gas Processing Plants
Refinery FCCU	Ethylene Oxide Plants
	Ethanol Plants
	Ammonia Plants
	SNG Plants

Exhibit 4-1: Regional CO_2 Availability (MMSCFD) by Type of Source

SOURCE	PERMIAN BASIN	WILLISTON BASIN	APPALACHIAN BASIN	LOS ANGELES BASIN
Natural	1,350*		17	
By-Product Plants				
Power Plants	10,066	887	7,732	2,405
Cement Plants	524	33	172	216
Ammonia Plants	196	4	12	17
Ethylene Oxide Plants	43	---	---	---
Ethanol Plants	17	---	---	---
Natural Gas Processing	235	---	20	---
Hydrogen Plants	52	4	5	21
Refineries (FFCU)	331	18	47	48
Total By-Product	11,464	946	7,988	2,707
Proposed Plants				
SNG Plants	3,125	5,000	625	---
Power Plants	5,683	379	1,771	---
Ethanol Plants	71	23	23	4
Ethylene Oxide Plants	---	---	---	---
Refineries (FFCU)	53	---	---	3
Hydrogen Plants	41	---	---	4
Total Proposed	8,973	5,402	2,419	11

* Includes natural CO_2 from Jackson Dome area

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EXHIBIT A-2

PAGE 9

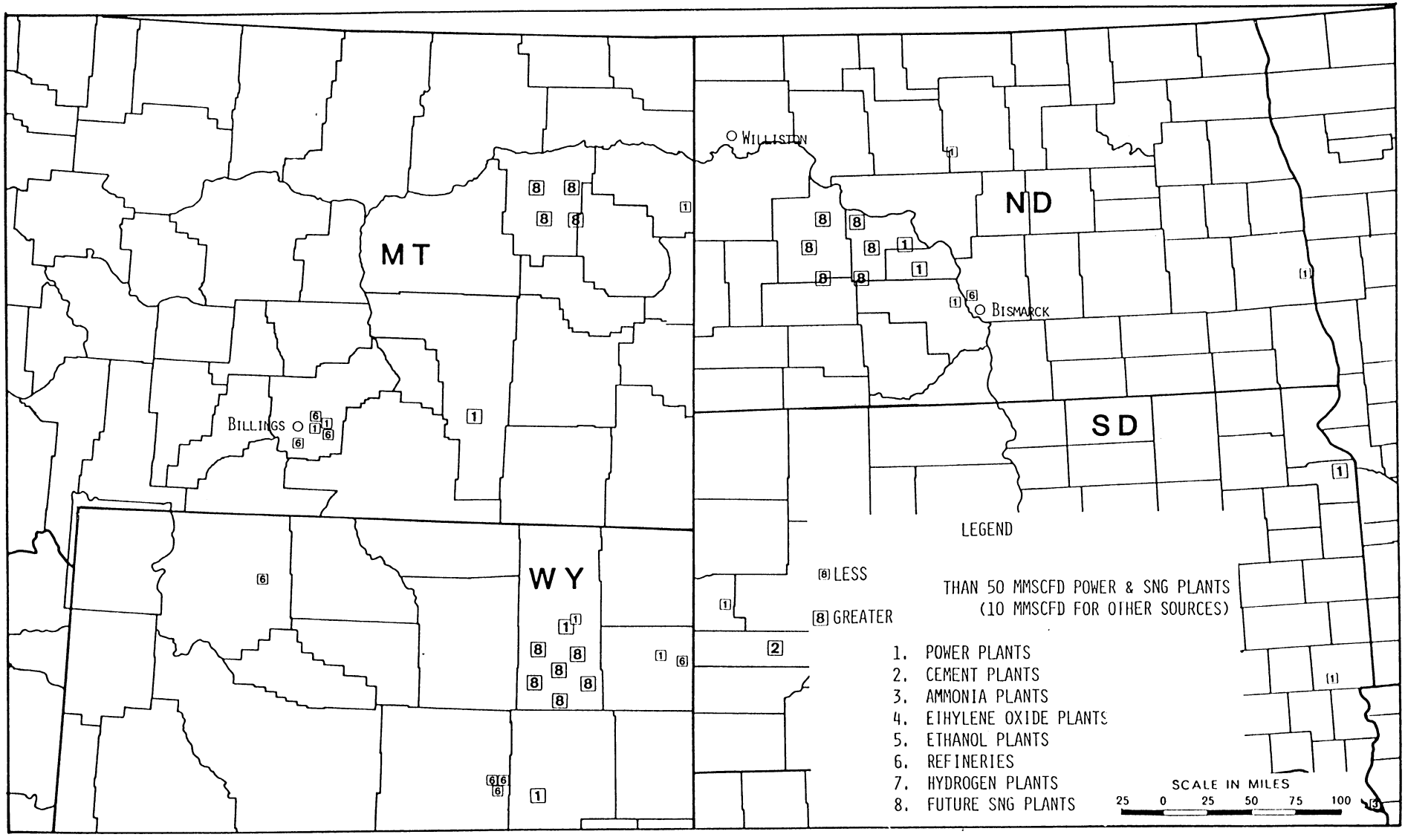


Exhibit 4-3: Carbon Dioxide Sources in the Williston Basin

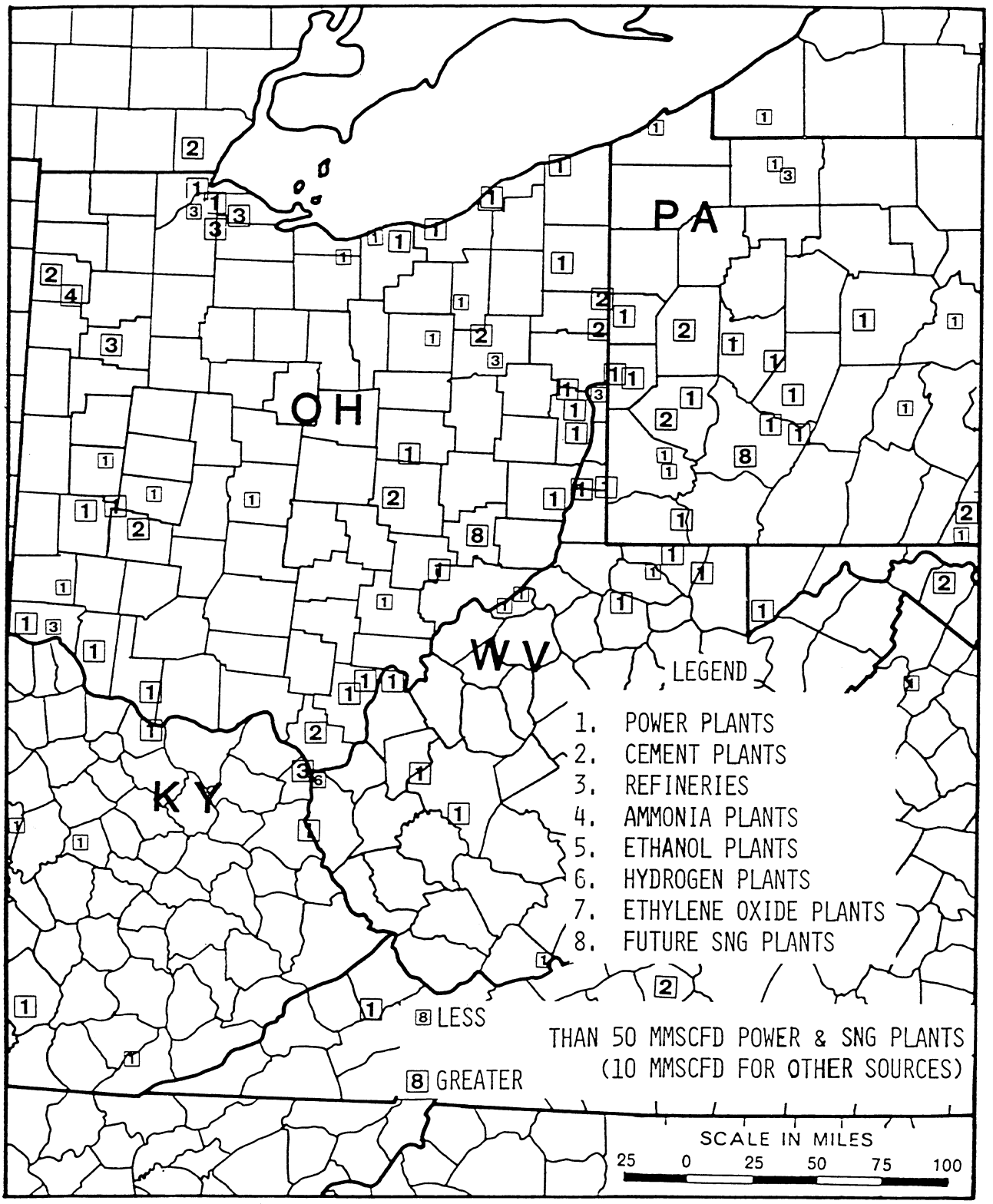


Exhibit 4-4: Carbon Dioxide Sources in the Appalachian Basin

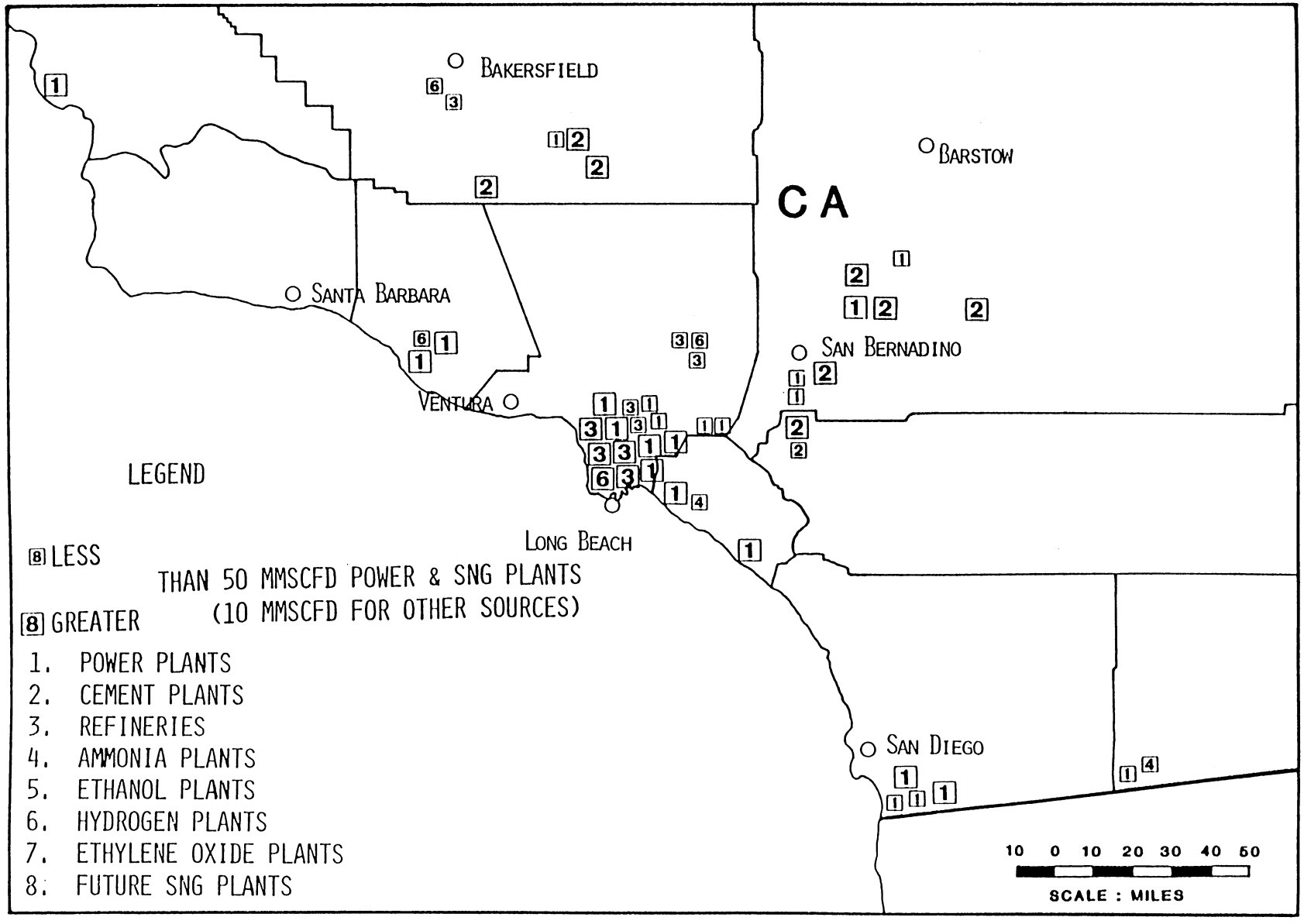


Exhibit 4-5: Carbon Dioxide Sources in the Los Angeles Basin

Exhibit 4-6: CO_2 By-Product Source Plant Numbers* in the Four Major Regions

Williston Basin

Plant Number

Power
397
399
398
400
489
493
491
492
490
584
585
586
723
724
727
726

Cement
115

Ammonia
21

FCCU
61
62
63
74
136
137
138
140

Appalachian Basin

Plant Number

Power	Power	FCCU
243	546	39
244	547	75
245	543	76
247	549	77
248	550	78
251	548	79
252	557	80
295	566	94
494	567	
513	568	
514	569	
497	539	
498	680	
508	690	
500	691	
501	692	
501A	693	
502	694	
503	695	
505	696	
504	697	
506	698	
507	699	
509	700	
510	701	
511		
512		
495		
496		
515		
517		
516		
518		
519		
499		
520		
521		
522		
538		
570		
540		
556		
544		
545		

Hydrogen
17

Cement
60
89
90
91
92
93
100
102
103
104
147

Ammonia
51

Los Angeles Basin

Power	FCCU
33	5
38	6
35	7
36	8
56	9
37	10
50	11
51	12
58	13
64	
43	
52	
53	
55	
54	
57	
59	
60	
65	
61	
62	
63	
34	
45	

Hydrogen
9
10
13

Cement
13
14
15
16
17
18
19
20
149

Ammonia
3
6
7

Permian Basin

Plant Number

Power	Power	Power	Power	Cement	Ammonia	FCCU
12	267	535	632	11	64	89
15	275	534	633	25	65	90
21	277	536	634	49	66	96
20	283	537	646	50	67	97
19	284	595	636	51	68	98
23	285	596	637	52	69	99
24	379	597	638	53		100
25	380	598	639	69		101
26	381	659	614	78		102
31	382	664	641	80		103
66	384	600	642	94		104
67	387	607A	643	95		105
75	385	600A	644	96		106
68	386	601	645	122		107
69	383	602	648	123		108
71	388	603	647	124		109
72	389	604	635	125		110
73	390	607	649	126		111
73A	391	606	650	127		112
74	433	605	652	128		113
77	436	608	654	129		114
219	443	640	653	130		115
220	435	610	651	131		116
221	434	611	655	132		117
222	437	612	656	133		118
223	438	613	657	134		119
224	445	609	658	135		120
225	439	616	660	136		121
226	440	617	661	137		122
227	441	615	662	138		123
228	442	618	663	139		
229	444	619	599	152		
231	446	620	665	153		
230	523	621	666			
232	524	622	667			
233	525	623	668			
234	526	624	669			
235	528	625	670			
236	527	626	671			
237	529	629	672			
238	530	630				
239	531	627				
240	532	628				
263	533	631				

Ethanol
10

Ethylene Oxide
6
10
11
12
13

FCCU
1
15
30
31
32
33
34
35
36
37
38
41
42
59
69
70
71
81
82
83
84
85
86
87
88

Ammonia
30
42
52
54
55
60
61
62
63

Cement
8
10

Hydrogen
24
26
27
28

*NOTE: The plant numbers in this Exhibit refer to plant identification numbers in Appendices C through I.

4.2.1 Permian Basin

The projected CO_2 requirement (based on 300 days injection per year) is 10,011 MMSCFD. The potential supply is summarized below.

Source	Number of Plants	Average Size (MMSCFD)	Maximum Size (MMSCFD)	Total
1. Natural				1,150
2. Power Plants	172	47	420	10,066
3. Cement Plants	35	15	33	524
4. FCCU	55	7	30	331
5. Ammonia Plants	12	16	53	196
6. Ethylene Oxide Plants	4	11	24	43
7. Hydrogen Plants	4	13	19	52
8. Natural Gas Processing	26	9	140	235

The CO_2 supply from existing high purity sources is only 1676 MMSCFD. There are sufficient power plants in this region to make up the difference, but this would require the majority of the power plants in the region to be retro-fitted.

A promising alternative is the use of on-site generation by the wet air oxidation process (see Section 7). Another potentially large source is SNG plants; however, the near future of these plants is uncertain due to opposition by environmentalists and a lack of commitment by industry or Government.

4.2.2 Williston Basin

The projected CO_2 requirement is 236 MMSCFD. The potential supply is summarized below.

Source	Number of Plants	Average Size (MMSCFD)	Maximum Size (MMSCFD)	Total
1. Power Plants	16	55	172	887
2. Cement Plants	1	33	33	33
3. FCCU	8	2	4	18
4. Ammonia Plants	1	4	4	4
5. Hydrogen Plants	1	4	4	4

There are only two high purity CO_2 sources currently in this region. The potential demand would have to be met either primarily from power plants, or by on-site generation. Given the proximity to large coal reserves, this latter approach appears promising. Alternatively, the SNG plant proposed for Mercer County, ND, could supply all the required CO_2.

4.2.3 Appalachian Basin

The projected CO_2 demand is only 83 MMSCFD. The available supply is shown below:

Source	Number of Plants	Average Size (MMSCFD)	Maximum Size (MMSCFD)	Total
1. Power Plants	69	112	559	7,732
2. Cement Plants	11	16	27	172
3. FCCU	8	6	11	47
4. Ammonia Plants	1	12	12	12
5. Hydrogen Plants	1	5	5	5
6. Natural Gas Processing	1	20	20	20
7. Natural				17

As for the other basins, there is insufficient high purity CO_2 available from existing sources. However, there are several natural CO_2 sources in West Virginia, but information on these is limited. There is an abundance of power plants available in this area, but the demand could also be met entirely from cement plants or refineries.

4.2.4 Los Angeles Basin

The projected CO_2 demand is 376 MMSCFD. The supply details are as follows:

Source	Number of Plants	Average Size (MMSCFD)	Maximum Size (MMSCFD)	Total
1. Power Plants	24	67	220	2,405
2. Cement Plants	9	24	37	216
3. FCCU	9	5	8	48
4. Ammonia Plants	3	6	8	17
5. Hydrogen Plants	2	7	15	21

Again, low purity sources are required to satisfy the potential demand. Either power plants or cement plants could supply the bulk of this demand.

On-site generation is not as attractive as in the other basins, due to the distance from commercial coal deposits, and the higher coal cost involved.

5. TECHNO-ECONOMIC ANALYSIS OF VARIOUS CO_2 RECOVERY SYSTEMS

5.1 INTRODUCTION

There are nearly 30 available processes for the removal of acid gases from gas streams and each process claims to have a special solvent with certain advantages. This is irrespective of whether the solvent is a completely new compound or a familiar solvent with a few extra additives. A list of pertinent processes is given in Exhibit 5-1. The processes are in two definite groups: (1) those employing a chemical solvent -- those which chemically absorb the acid gas: and (2) those employing physical solvents -- those which physically absorb the acid gas. The choice of the correct solvent is important since the amount of solvent and solvent circulation rates normally determine the size of equipment required; hence, the choice substantially affects the overall cost of acid-gas recovery.

Solvent selection is normally based on the temperature of the feed gas and the partial pressure of acid gas in the feed gas stream. Exhibit 5-2 lists gas stream temperatures, CO_2 partial pressures, and total pressures for each of the by-product CO_2 supply sources considered in Section 3. The CO_2-bearing gas streams from ammonia plants, hydrogen plants, ethylene oxide plants, proposed SNG plants, and alcohol plants would not require CO_2 recovery systems since the gas streams in these cases are essentially pure CO_2 with little water vapor -- compression and drying is all that would be required to make these particular gas streams suitable for enhanced oil recovery operations.

The economics of CO_2 recovery are most strongly influenced by the partial pressure of the CO_2 in the feed gas stream. If CO_2 partial pressures are low, then physical solvents can be eliminated, because compression of the gas for physical solvent absorption makes this mode of CO_2 recovery too expensive. If the CO_2 partial pressures are high, then physical solvents are normally the best choice. This is shown quantitatively in Exhibit 5-3.[53] The five by-product CO_2 streams (see Exhibit 5-2) that require a CO_2 recovery system have CO_2 partial pressures ranging from 1.3 to 4.3 psi in the CO_2 feed stream. Thus, Exhibit 5-3 clearly indicates that chemical solvents will be the only solvents suitable for the present five by-product streams and in particular amines will be one of the best choices. Note that the partial pressures of

<u>Chemical Solvents</u>	
Amines:	Monoethanolamine, Diethanolamine, Triethanolamine, Diisopropylamine, Diglycolamine
Activated hot potassium carbonate:	Benfield, Vetrocoke, Catacarb, Lurgi, Vacuum Carbonate
Others:	Stretford, Scott, Tripotassium Phosphate, Ammonia, Copper Liquor, Alkazid, Ferrox, Manchester, Konox, Sulfox, Seaboard, Thylox, Sodium Phenolate
<u>Physical Solvents</u>	Fluor, Purisol, Rectisol, Selexol, Sulfinol (really a mixed chemical-physical solvent), Water

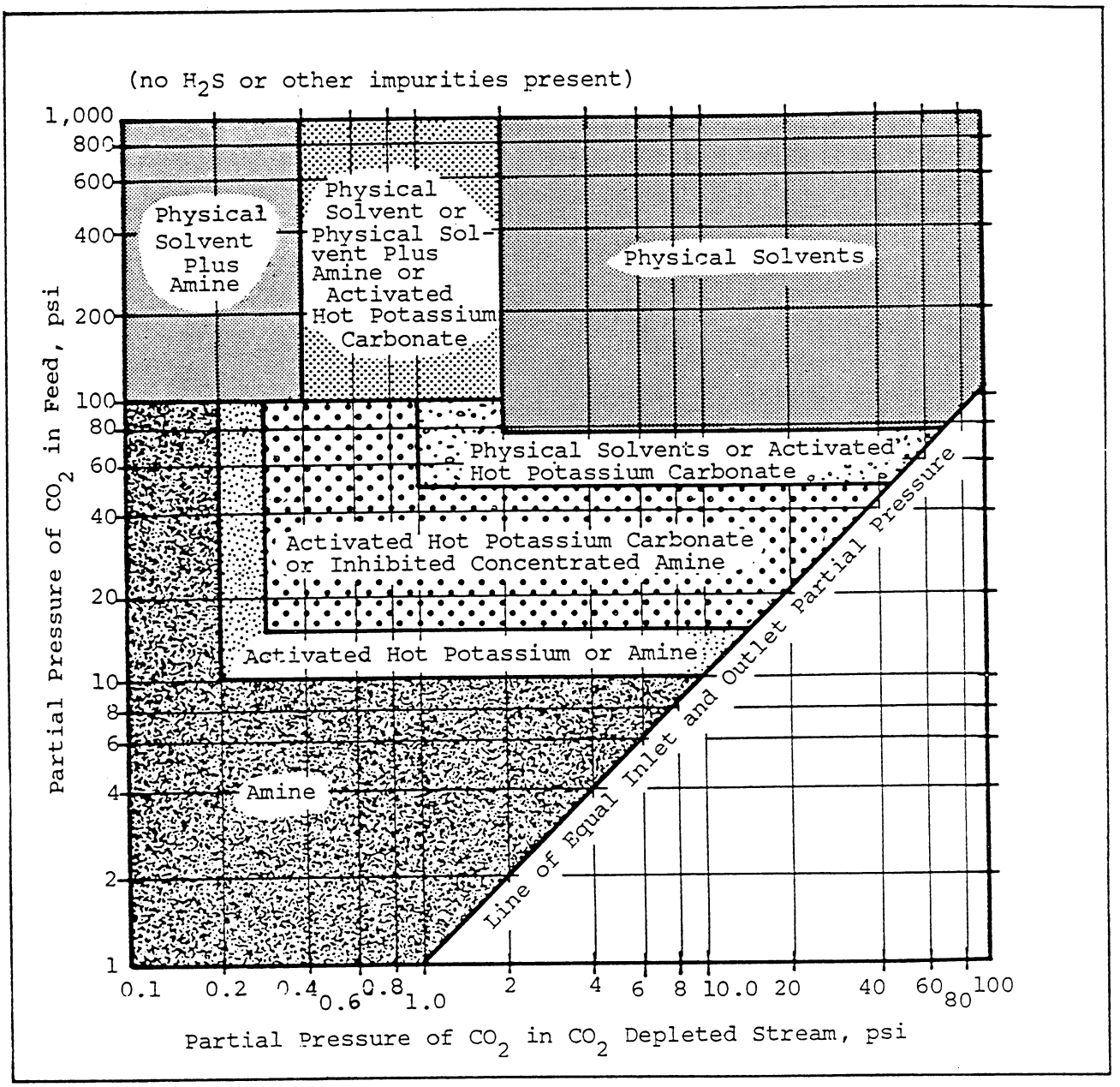
Exhibit 5-1: Available Gas Treatment Processes

Source	Gas Temperature (^{o}F)	CO_2 Partial Pressure (psi)	Total Pressure (psia)
Power Plants			
after FGD:	125	1.3 - 2.1	14.7
with no FGD:	285	1.3 - 2.1	14.7
Cement Plants			
wet process:	300-400	3.1 - 3.8	14.7
dry process:	300-400	3.7 - 4.3	14.7
Oil Refineries			
FCCU Regenerator:	150	2.1	14.7
Hydrogen Plant*:	240	18.5	19
Ammonia Plants*	240	18.5	19
Ethylene Oxide Plants*	240	18.5	19
Alcohol Plants*	about 70	14.3	14.7
Proposed SNG Plants*	about 80	22.3	about 24.7

*These plants would not require a CO_2 recovery system since the by-product gas stream is essentially pure CO_2

Exhibit 5-2: Temperature, CO_2 Partial Pressure, and Total Pressure of By-Product Streams Bearing CO_2 (These gas streams would be the feed gas to a CO_2 Recovery System)

Exhibit 5-3: The Optimum CO_2 Recovery System Based on CO_2 Partial Pressures



Source: Ref. 53, p. 17, Figure 1; Copyright (c) 1979 The Petroleum Publishing Company; used with the permission of Pennwell Books.

CO_2 in the CO_2-depleted streams must necessarily be lower than the CO_2 partial pressures in the feed streams, since CO_2 itself is being recovered.

As a result of this preliminary analysis, it was decided to carry out detailed techno-economic analyses for processes using two chemical solvents, monoethanolamine (MEA) and potassium carbonate (K_2CO_3). Most suggested installations have chosen a MEA process for by-product recovery, and this is the most popular process in the United States for natural gas purification. However, Pappano, Sears, and Parr[35] indicated that a K_2CO_3 process may have particular advantages, especially when recovering CO_2 from gas streams bearing both CO_2 and SO_2. The stack gases from coal-fired power plants and cement plants tend to contain CO_2 in the presence of small quantities of SO_2.

5.2 THE BASIC MEA PROCESS

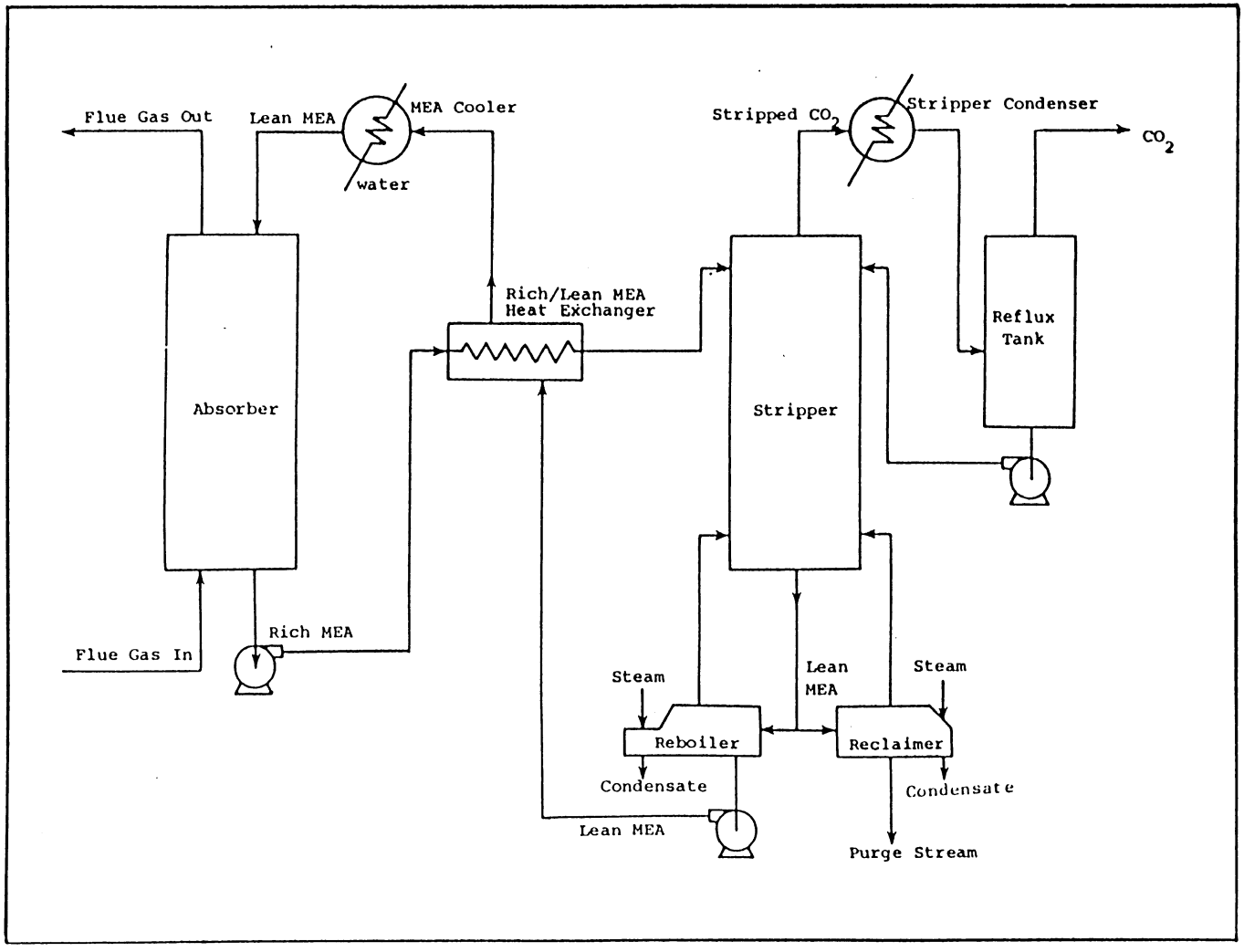
The development of alkanolamines for the absorption of acid gases is credited to R. R. Bottoms,[5] who in 1930 patented triethanolamine (TEA) for use in early natural gas treating plants. The development of other alkanolamines followed, such as monoethanolamine (MEA) and diethanolamine (DEA). Due to their reactivity and availability at low cost, MEA and DEA especially have become prominent in the gas-sweetening industry. The structural formula of MEA is $HO\text{-}CH_2\text{-}CH_2\text{-}NH_2$. The hydroxyl group serves to reduce the vapor pressure and increase the water solubility, while the amino group furnishes the alkalinity required in water solutions to absorb acid gases. In gas sweetening, two moles of MEA are capable of chemically absorbing one mole of CO_2 to form the amine salt of a substituted carbamic acid.

$$2\ RNH_2 + CO_2 \rightleftharpoons RNHCOONH_3R$$

The reaction can be easily reversed by simply heating the reaction products.

A simplified process flow diagram for CO_2 recovery using MEA is shown in Exhibit 5-4. The process scheme varies little regardless of the strength of the MEA solution employed. Ten to thirty weight percent MEA solutions are typical. The two main pieces of equipment are the absorber column - normally either a packed bed or a plate tower, and the stripper column - normally a plate tower.

Exhibit 5-4: Simplified Flow Diagram for the MEA Process



The CO_2-bearing gas stream enters at the bottom of the absorber column and flows upward through the absorber in intimate counter-current contact with the aqueous amine solution. The depleted gas stream leaves the top of the absorber and is vented to the atmosphere. This stream may need to be heated for plume rise. The rich amine solution laden with CO_2 flows from the bottom of the absorber and passes through the amine-amine heat exchanger and then to the top of the stripper column. The solution is boiled at the bottom of the stripper by heating the aqueous solution in the reboiler, and steam (primarily) then rises upward in counter-current contact with the rich amine solution. The CO_2 is stripped out of the amine solution, and the CO_2 gas rises to the top of the stripper with the steam. After condensing the majority of the steam from the CO_2-steam mixture, a rich CO_2 stream is produced. This stream requires only further drying and compression before the CO_2 is ready for use in enhanced oil recovery. At the bottom of the stripper the amine solution (now lean in CO_2) is pumped through the amine-amine heat exchanger and then through a water or air-cooled exchanger before being introduced at the top of the absorber column. A detailed process flowsheet is given in Section 5.5 including an outline of the detailed process design calculations.

A number of general operating problems are encountered when running MEA plants. These problems can be broadly categorized as: corrosion, solution degradation, and foaming. Each will be considered separately.

Corrosion occurs because an acid gas is being treated in an aqueous environment, and will be the most severe at places where the highest concentrations of CO_2 encounter the highest temperatures. These points will include the amine-amine heat exchanger, the stripping column, and the reboiler. Stress corrosion is also prevalent in amine systems. It is generally associated with residual stresses which result from localized heating during vessel construction such as welds in absorbers, strippers, and piping. The stress relieving of all major equipment is advised to help alleviate stress corrosion.

Solution degradation can occur for a number of reasons, such as the entrainment of solids, sulfur pickup, and the formation of dissolved salts. To recover much of the fouled solution about three percent of the solution circulation rate is taken for most by-product streams as a side stream just before the reboiler. This side stream passes to an amine reclaimer where the

water and amine are distilled from the fouled solution and then returned to the bottom of the stripper column. The reclaimer is discussed in greater detail in Section 5.5.

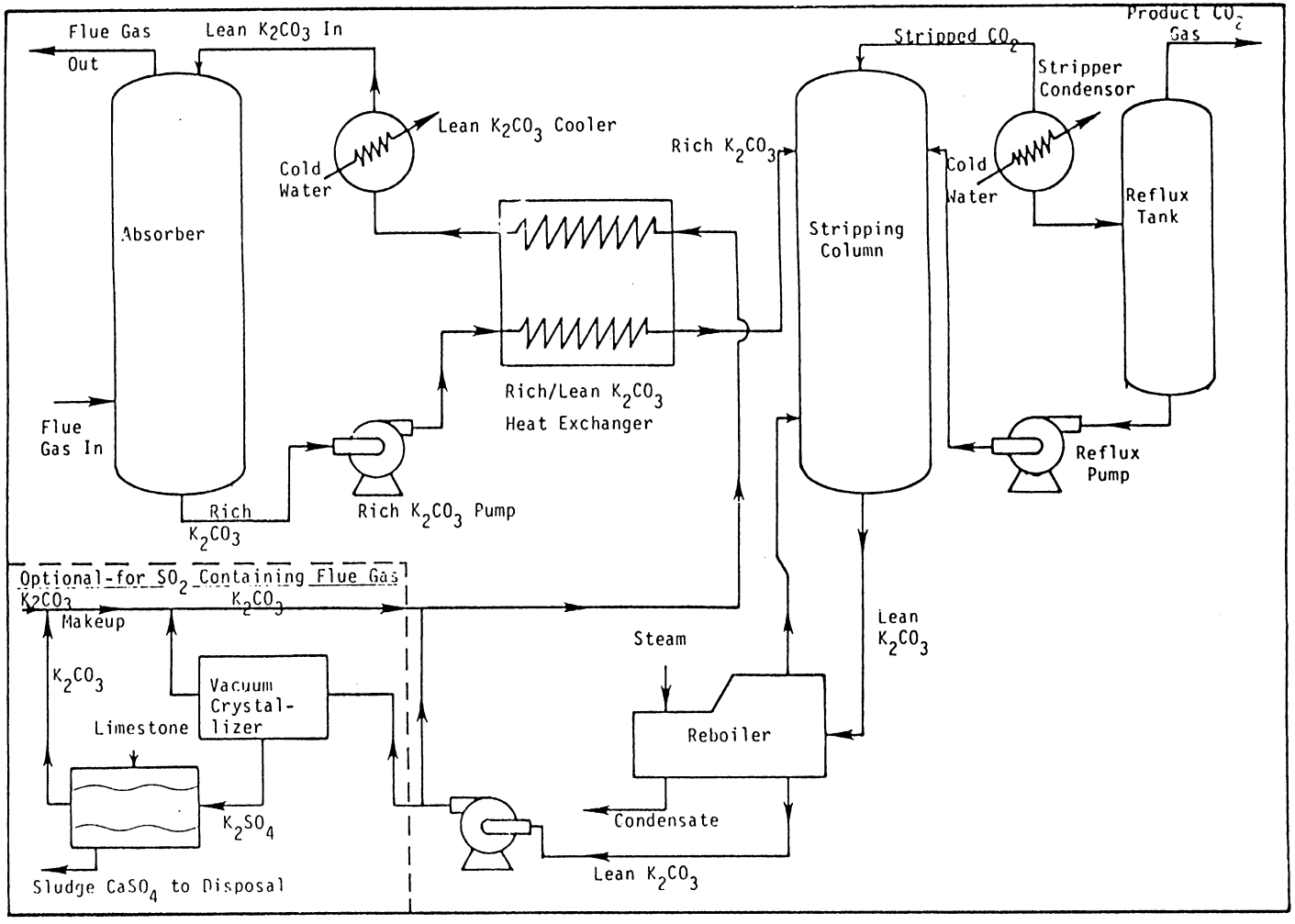
Foaming in the amine CO_2 recovery process can cause a severe reduction in gas throughput, a reduction in the amount of CO_2 absorbed, and a significant increase in amine loss. The foaming problem can be caused by suspended solids, amine degradation products, and almost any foreign material. The use of an amine reclaimer combined with proper solution filtration is known to help solve many foaming problems.

5.3 THE BASIC POTASSIUM CARBONATE PROCESS

The fact that potassium carbonate can be used to remove CO_2 from a mixture of gases has been known for many years. Kohl and Riesenfeld[24] mention a German patent granted in 1904 which described a process for absorbing CO_2 in a hot solution of potassium carbonate, followed by stripping the solution through pressure reduction without additional heating. This process was developed in the United States by the U.S. Bureau of Mines in Bruceton, PA, as part of an early program on synthetic fuels from coal. It was further developed as the Benfield process by Benson and Field, who conducted much of the original work at the U.S. Bureau of mines. Many improvements have subsequently been made, including the development of additives to the aqueous potassium carbonate solution, which results in substantial lowering of capital and operating costs and higher treated gas purity.[4] The hot potassium carbonate process was developed to remove CO_2 from synthesis gas at high CO_2 partial pressures. This process is in commercial operation for acid-gas removal from high pressure streams such as those in ammonia plants, natural gas processing plants, and hydrogen plants. It has been suggested that the process, appropriately modified, could be economic compared to MEA for recovery of CO_2 from power plants, especially when sulfur is present.[46]

There is a similarity between the process flows for the potassium carbonate and amine processes. A schematic flow diagram for a potassium carbonate system is presented in Exhibit 5-5. In a hot potassium carbonate system the absorber operates at higher temperatures, which saves in the amount of heat exchange surface area needed; thus, reducing the number and size of heat exchangers between the absorber and the stripper. In the present

Exhibit 5-5: Simplified Flow Diagram for Activated Hot Potassium Carbonate Process



modification, the absorber is at a lower temperature and more heat exchange surface is required. The higher temperature in the absorber also increases the solubility of potassium bicarbonate (a product after the CO_2 is absorbed in K_2CO_3) in solution. This permits the use of a concentrated potassium carbonate solution and increases the carrying capacity for acid gases per gallon of solution.

An alternative is to utilize a process akin to the vacuum carbonate process.[24] This process would eliminate the rich/lean K_2CO_3 heat exchanger and would operate the stripping column at reduced pressures. This change would increase the stripper column diameter, but would decrease steam regeneration requirements. Either alternative could operate down to 0.4 psia outlet-CO_2 partial pressure, according to present conventional commercial system practice.

The reactions that occur can be represented by the following overall reactions:

<u>CO_2 absorption:</u>

$$K_2CO_3 + H_2O + CO_2 \rightleftharpoons 2KHCO_3 \qquad (1)$$

This reaction proceeds in two steps:

$$K_2CO_3 + H_2O \rightleftharpoons KOH + KHCO_3 \qquad (1A)$$

$$KOH + CO_2 \rightleftharpoons KHCO_3 \qquad (1B)$$

The $KHCO_3$ produced by the above reactions can be regenerated to K_2CO_3 in the stripper at higher temperatures. As the above reactions are slow and limit CO_2 absorption rates at low partial pressures, activators have been incorporated to increase absorption rates by initial reaction with the dissolving CO_2 (e.g., Benfield, Catacarb). This increase in absorption activity is important for a K_2CO_3-based process. The activator-CO_2 product then reacts with the alkaline potassium carbonate solution. Sears[46] shows data for ethylaminoethanol (EAE) as an activator for absorption for low-CO_2-partial-pressure gases.

SO_2 absorption:

In the presence of oxygen, SO_2 reacts with K_2CO_3 which can be represented by:

$$K_2CO_3 + SO_2 + 1/2\ O_2 + H_2O \longrightarrow K_2\ SO_4 + H_2O + CO_2 \quad (2)$$

This reaction proceeds in the following steps:

$$SO_2 + H_2O \longrightarrow H_2SO_3 \quad (2A)$$

$$H_2SO_3 + 1/2\ O_2 \longrightarrow H_2SO_4 \quad (2B)$$

$$H_2\ SO_4 + K_2CO_3 \longrightarrow K_2SO_4 + H_2O + CO_2 \quad (2C)$$

The K_2SO_4 produced by the above reactions cannot be regenerated in the stripper and will reduce the capacity for SO_2 and CO_2 absorption unless K_2SO_4 is separated from the K_2CO_3 solution. Cooling of the solution causes solidification of K_2SO_4 in a crystallizer through which a purge solution is passed after stripping and before being sent to the absorber. The sulfate ($SO_4^=$) can be precipitated but sulfite ($SO_3^=$) can not be readily precipitated; therefore, it is desirable that minimum sulfite be present in the solution. Approximately 0.2 wt% of $K_2Cr_2O_7$ (or other additive) is added as a corrosion inhibitor and oxidizing agent for sulfite to sulfate.[46]

Reaction with CO_2 gives two parts of potassium bicarbonate for each part of potassium carbonate reacted. Reaction with SO_2 in the presence of oxygen gives one part of potassium sulfate for each part of potassium carbonate reacted.

As shown in Exhibit 5-5, the process flow diagram varies a little (addition of crystallizer and K_2SO_4 regenerator) if the flue gas contains SO_2. Twenty to forty weight percent K_2CO_3 solutions are typically used to absorb acid gas from the input gas stream. The two main pieces of equipment are: the absorber column - normally either a packed bed or a plate tower; and the stripper column - normally a plate tower.

The CO_2-bearing stream enters at the bottom of the absorber column and flows upward through the absorber in intimate counter-current contact with lean potassium carbonate solution entering from the top of the absorber. The

depleted gas stream leaves the top of the absorber and is vented to the atmosphere after water wash to recover any entrapped potassium carbonate solution. Plume reheat may be required on the depleted gas. The rich potassium carbonate solution laden with CO_2 flows from the bottom of the absorber, passes through the rich-lean K_2CO_3 heat exchanger, and is then sent to the feed plate of the stripper column. Steam is produced at the bottom of the stripper by heating the aqueous potassium carbonate solution in the reboiler, and the steam then rises upward in counter-current contact with the rich K_2CO_3 solution. The heat strips the CO_2 from the rich potassium carbonate solution ($2KHCO_3 \xrightarrow{heat} K_2CO_3 + H_2O + CO_2$), and the CO_2 gas rises to the top of the stripper with the steam. The majority of the steam is condensed and returned to the stripper through the reflux tank via the reflux pump. The uncondensed portion of the CO_2-rich gas stream is a product gas and requires only further drying and compression before the CO_2 is ready for use in enhanced oil recovery. At the bottom of the stripper the potassium carbonate solution, now lean in CO_2 after passing through the reboiler, is pumped to the top of the absorber through the rich/lean K_2CO_3 heat exchanger and the lean K_2CO_3 cooler.

A number of general operating problems are encountered in the operation of a K_2CO_3 plant. These problems are broadly categorized as: corrosion, stress corrosion, vapor locking of pumps, and solution degradation. Such problems and possible solutions are briefly discussed below.

Pilot plant studies conducted by the Bureau of Mines encountered severe corrosion of carbon steel in several areas.[26] Corrosion will be most severe at places where the conversion to bicarbonate is high and where carbon dioxide and steam are released. Successful corrosion inhibitors include arsenic, vanadium salts, and dichromates. Stainless steel is recommended for reboiler tubes, control valves, and solution pumps. The absorber and strippers, whether using trays or packing, can be made of carbon steel (in reducing environments). However, the stripper should be lined with corrosion-resistant material such as plastic or gunnite. Stress corrosion is expected because potassium carbonate is an electrolyte which readily attacks; thus, requiring stress relieving of welds and vessels.

Vapor locking of pumps could be a problem, specifically for the lean potassium carbonate pump where regenerated solution leaving the stripper is at its saturation temperature and may partially vaporize in suction, resulting in vibration and excessive wear of pump impellers. This problem can be solved by proper pump design for low pressure operations and by adding a single stage slow-speed booster pump to serve as a feed pump for the high pressure pumps in case of high pressure requirements in the absorber.

5.4 COMPARATIVE ANALYSIS FOR MEA AND K_2CO_3 PROCESSES

The two most likely processes for absorption of CO_2 from flue gas are appropriate modifications of MEA and activated potassium carbonate systems. The factors to be considered in the choice of a system are discussed in the following sections.

5.4.1 MEA Processes

- The capacity and absorption rate for CO_2 by aqueous MEA solutions decrease rapidly with impurity buildup. As impurities such as sulfites and sulfates increase, two moles of MEA are reacted per mole of SO_x; thus, reducing the capacity for CO_2 absorption. Degradation products are a direct loss of MEA as oxidation proceeds; thus, less MEA is left to react. Since this is a kinetically controlled process, this decreases the absorption rate. In addition, the presence of these products increases the equilibrium CO_2 vapor pressure,[46] raising the absorption back pressure, and decreasing the absorption rate.

- The energy requirements for regeneration increase with impurity concentration. As the concentration of amine sulfide (and probably amine sulfur oxides) increases, the amount of heat required to regenerate the CO_2 increases. This occurs because the regenerator now must be run at higher reflux conditions and temperatures to assure driving off enough acid gas to lower the back pressure to easily absorb CO_2. The water vapor/CO_2 ratio increases, with the consequent need for more regeneration steam.

  In order to reduce the back pressure, a purification scheme is suggested which involves reboiling off MEA to leave only fouled amine products, followed by Na_2CO_3 addition or simultaneous addition for Na product precipitation. This is the accepted procedure; but rapid impurity build-up would cause high steam use in this secondary reboiler.

- Corrosion with MEA is severe in oxidizing atmospheres. Stainless steel is recommended for the hottest points, including the reboiler. Presence of CO_2 and O_2 increases the severity of corrosion. Corrosion would appear to be enhanced in SO_2-rich streams, as more stringent regeneration conditions would be expected (see above).

- In general the MEA process would be preferred in cases where degradation, sulfur oxides, and other impurities are limited.

5.4.2 Activated K_2CO_3 Process

- The effect on absorption capacity and rate with impurities is less than with MEA. Only one mole of capacity is lost per mole of sulfur oxides. Oxidative degradation is not present. As the absorption rate is controlled by the activator which is not as readily affected by impurities, the absorption rate is more readily maintained.

- Removal of SO_x is feasible. The sulfites can be oxidized to sulfates. These sulfates and natural sulfates can be precipitated out as K_2SO_4 to small levels by vacuum crystallization. The concentrated K_2SO_4 can now be handled by a double-alkali scheme to recycle the potassium ions.

- Corrosion with K_2CO_3 is severe in oxidizing atmospheres. Stainless steel is recommended for many of the same points as for the MEA process. As some of the oxidative degradation products in MEA systems are not present in K_2CO_3 systems, and as the amine/ ammonia attacks on nickel/monel/copper are not present, this corrosion is slightly less than in pure MEA systems, but stress corrosion may be worse.

- On balance, the activated potassium carbonate system can be used both where SO_x and other impurities are present and where they are not present.

5.4.3 Design Factors

The absorption rate in pure environments is five to ten times more rapid with MEA than with K_2CO_3 (activated) at 1 atm.[46] The energy requirements are slightly higher with MEA than with K_2CO_3. The MEA process is readily adapted for SO_2 impurity-free flue gases, but the K_2CO_3 process should be considered further.

In SO_2 impurity-present flue gases, the absorption rate in MEA and activated K_2CO_3 are roughly the same for high contamination levels.[46] The energy requirements for regeneration are higher but in roughly the same ratio as for sulfur-free gases. As corrosion-resistance and foaming problems are

less in K_2CO_3 systems, K_2CO_3 processes must be considered for SO_2-present flue gases. The precipitation problems are, however, more difficult. For both process solutions, increasing impurities and sulfur oxides in the flue gases cause increasing operation problems.

It will be assumed that the same fuel will be used for regeneration-steam production as at the original CO_2 source site. The major present emission standards are for SO_2 and particulates. The particulates levels vary, but generally are equivalent to 99.5% reduction at a typical coal-fired power plant. The present SO_2 levels indicate a SO_2-level equivalent to that obtained burning 0.7% sulfur coal (1.2 lb SO_2 per million Btu). As about 20 to 40% of the energy used (in a power plant) to generate the CO_2 is required for compression-regeneration steam, the effects of this regeneration flue gas stream must be considered.

If the feed is a 3 wt% S fuel, the total SO_2 removal accomplished must be 77%. As reheat by use of the regenerator flue gas for plume rise of the total flue gas is suggested, the SO_2 regulations cannot be met by just mixing scrubbed main flue gas and unscrubbed regenerator flue gas. Some of the secondary flue gas must be scrubbed. If the feed is a 1 wt% S fuel, mixing of unscrubbed main gas and unscrubbed secondary flue gas for plume rise reasons may be acceptable by environmental sulfur standards.

5.4.3.1 MEA Processes

The percent recovery of CO_2 without chlorine and sulfur contaminants will be determined by net marginal costs for the last percent recovery. The important parameters will be the CO_2 driving force for absorption and the energy expenditure to regenerate the CO_2 to allow small driving forces.

As MEA is usually recommended for this type of flue gas, the standard operating procedures for absorption of CO_2 in natural-gas or hydrogen plants provide good guidelines. The presence of oxygen will increase amine degradation and the size of the slip stream needed to be purified, but will not basically disturb the absorption. The purification is accomplished by a secondary reboiler to regenerate good MEA, while degraded and fouled material is precipitated by addition of an alkali salt. This salt could be either Na_2CO_3 or K_2CO_3, the latter being more expensive per pound but more effective.

Absorption of CO_2 in MEA can be readily accomplished at $\geq$ 90% in the absorption tower itself. Ultimate absorption may depend on some slip stream being available for reheating, as otherwise the exit gas from a power plant stack will settle in the vicinity of the power plant with condensation. This is assumed to be unacceptable. The flue gas from the regenerator should provide the required reheat for the plume. Thus, a conservative estimate of 90% absorption will be taken.

The steam requirements are estimated to be approximately 100 to 130 lb steam/mole CO_2. Absorption at 125 to 150°F will help keep amine vapor emissions low, while regeneration at 200 to 250°F will be satisfactory. The ultimate absorption capability for MEA with a P_{CO_2} limit of 2 psia is 0.55 mole CO_2/mole MEA. A satisfactory driving force is obtained at 0.4 mole CO_2/mole MEA, and a loading of 20 to 30 wt% MEA. The regeneration required to have the lean MEA available with VP_{CO_2} < 0.1 psia at absorption temperature is only 0.4 mole CO_2/mole MEA. Thus, the major factor in purification during regeneration is heat exchange/ pumping requirements versus size of stripping tower. For these estimates, a broad minimum can be expected at 0.05 to 0.1 mole CO_2/mole MEA. Typical MEA operating limits in reducing gas are generally above this point.

If sulfur oxides are present, these contaminants must be removed by increasing the secondary-reboiler slip stream. High-SO_2 flue gases could increase the purge rate to 8 to 10% of the MEA absorption solution in the stripper,and steam requirements by 25% over the case of no sulfur oxides in the flue gas.

5.4.3.2 Potassium Carbonate Processes

For the K_2CO_3 (activated) processes, the percent absorption is determined by several factors: allowed contamination buildup as determined by purification procedures, equilibrium vapor pressure restrictions on allowable CO_2 partial pressures, and total sulfur and particulate emissions to the air allowed from the sites, which must include the regeneration of carbon dioxide.

In flue gases from low-S fuels, K_2SO_3/K_2SO_4 concentrations must be kept small to obtain absorption. This can be accomplished by cooling a 20 to 30 wt% initial K_2CO_3 solution, with 2 wt% K_2SO_4 to 77°F. This allows crystallization of the sulfate to 1 wt% K_2SO_4 in the crystallizer. Crystallization

at 0^oC allows for smaller K_2SO_4 levels, but would require refrigeration (which will be assumed to be too costly). In order to absorb 90% of the CO_2 in the flue gas to be scrubbed, essentially all the SO_2 will be absorbed. With no sulfur in the fuel, a crystallizer/purifier is not needed.The VP_{CO_2} out must be reduced from an inlet 2 psia to an outlet 0.22 psia (with change in molar flow rate). A reasonable equilibrium CO_2 pressure for the solution would then be 0.1 psia to have a reasonable driving force for absorption. This requires the stripped solution at a conversion of K_2CO_3 to $KHCO_3$ to be approximately 10% for absorption at 125 to 158^oF. The maximum conversion at VP_{CO_2} < 2psia is approximately 40%. For a CO_2 regenerator at 230^oF, the steam estimate is 90 to 100 lb steam/mole CO_2. If the absorber temperature is lowered to 125^oF and regeneration is accomplished with vacuum regeneration, the steam estimate is around 70 to 90 lb/steam per mole CO_2, as the ultimate K_2CO_3-$KHCO_3$ conversion can be raised, and the H_2O - CO_2 ratio at the feed plate is reduced, lowering steam requirements. In summary, apparently 90% CO_2 absorption can be accomplished with good steam economy with no SO_x in the feed gas or low sulfur fuels.

From TVA/FGD data with high SO_x flue gases, control is usually accomplished by 90% SO_2 absorption of 80% of the flue gas, with a 20% flue gas by-pass for plume rise. For high sulfur fuel ($\geq$ 3.5% S), use of a 20% by-pass or regenerator flue gas for plume rise would lead to violation of SO_2 environmental standards. With a lower rise in the absorber temperature, regenerator steam and flue gas are required. However, less CO_2 can be absorbed because of higher CO_2 equilibrium vapor pressures in the solution. Presently, extrapolation of published equilibrium data on H_2S - CO_2 - solutions to SO_2 - CO_2 - solutions is required for these preliminary designs, as well as a design for operation of a K_2SO_4 crystallization unit. It is recommended that a more conservative approach be followed. A conservative design would be 60% CO_2 removed from flue gas with SO_2.

5.4.3.3 Comparison of K_2CO_3 and MEA Systems Chemistry

Exhibit 5-6 presents a listing of conditions for lean and rich solutions for absorption and stripping of CO_2 by the MEA and K_2CO_3 processes. Included is a comparison of heat transfer coefficients, materials of construction, and steam requirements per recovered pound-mole CO_2. Note that the basic design

Exhibit 5-6: Parameters Used in the Design of CO_2 from By-Product Flue Gases with Aqueous MEA and Activated K_2CO_3 Solutions

CONSERVATIVE DESIGN		
	Parameter Values	
Parameter	MEA Solution	K_2CO_3 Solution
Concentration	20 wt% MEA	20 wt% K_2CO_3
Lean Loading	0.10 mole CO_2/ mole MEA	0.10 mole CO_2/mole K_2CO_3
Rich Loading	0.41 mole CO_2/ mole MEA	0.50 mole CO_2/mole K_2CO_3
Absorber Temperature	140°F	125-135°F
Stripper-Reboiler Temperature . .	235-245°F	200-215°F
Reclaimer Temperature	260°F	N.A.
Gas Conditioning	Filter Water Wash	Filter
Heat Transfer Coefficients:		
Solution-Solution.	110 Btu/hr ft^2 °F	145 Btu/hr ft^2 °F
Condenser-Water.	110 Btu/hr ft^2 °F	175 Btu/hr ft^2 °F
Cooler, Solution-Water . . .	130 Btu/hr ft^2 °F	140 Btu/hr ft^2 °F
Reboiler	110 Btu/hr ft^2 °F	220 Btu/hr ft^2 °F
Materials of Construction:		
Absorber	Carbon Steel	Carbon Steel
Stripper	Carbon Steel	Lined Carbon Steel
Reboiler	Stainless Steel	Stainless Steel
Reclaimer	Stainless Steel	N.A.
Pumps	Carbon Steel	Stainless Steel
Piping	Carbon Steel	Stainless Steel
Condenser	Carbon Steel	Carbon Steel
Heat Exchangers	Carbon Steel	Stainless & Carbon
Steam Requirements:		
No sulfur in gas	132 lb steam/ mole CO_2	91 lb steam/ mole CO_2
Low sulfur in gas.	132 lb steam/ mole CO_2	100 lb steam/ mole CO_2
High sulfur in gas	174 lb steam/ mole CO_2	134 lb steam/ mole CO_2

Exhibit 5-6 , continued

OPTIMISTIC DESIGN		
	Parameter Values	
Parameter	MEA Solution	K_2CO_3 Solution
Concentration	30 wt% MEA	30 wt% K_2CO_3
Lean Loading	0.10 mole CO_2/ mole MEA	0.10 mole CO_2/ mole K_2CO_3
Rich Loading	0.43 mole CO_2/ mole MEA	0.50 mole CO_2/ mole K_2CO_3
Absorber Temperature	130°F	125°F
Stripper-Reboiler Temperature . .	225°F	130°F
Reclaimer Temperature	240°F	N.A.
Gas Conditioning	Filter Water Wash	Filter
Heat Transfer Coefficients:		
Solution-Solution.	110 Btu/hr ft^2 °F	145 Btu/hr ft^2 °F
Condenser-Water.	110 Btu/hr ft^2 °F	175 Btu/hr ft^2 °F
Cooler, Solution-Water . . .	130 Btu/hr ft^2 °F	140 Btu/hr ft^2 °F
Reboiler	120 Btu/hr ft^2 °F	220 Btu/hr ft^2 °F
Materials of Construction:		
Absorber	Lined Steel	Lined Steel
Stripper	Stainless Steel	Lined Steel
Reboiler	Stainless Steel	Stainless Steel
Reclaimer	Stainless Steel	N.A.
Pumps	Stainless Impellers	Stainless Steel
Piping	Stainless Steel	Stainless Steel
Condenser	Carbon Steel	Carbon Steel
Steam Requirements:		
No sulfur in gas	106 lb steam/ mole CO_2	71.4 lb steam/ mole CO_2
Low sulfur in gas	--	78 lb steam/ mole CO_2
High sulfur in gas	--	104 lb steam/ mole CO_2

of the MEA system absorbs CO_2 more readily than that of the K_2CO_3 system, but utilizes more steam to recover CO_2. A comparison of steam efficiencies for recovering CO_2 using K_2CO_3 and MEA systems is presented in Exhibit 5-7. Both systems require corrosion-resistant metals in key pieces of equipment.

A listing of conditions and construction materials are given for an optimistic design, where the concentration of MEA and K_2CO_3 and regeneration conditions are pushed to the limit. Careful control of the system would be required, and R&D preliminary work might well be appropriate.

5.5 DETAILED DESIGN CONCEPTS FOR THE MEA PROCESS

5.5.1 Introduction

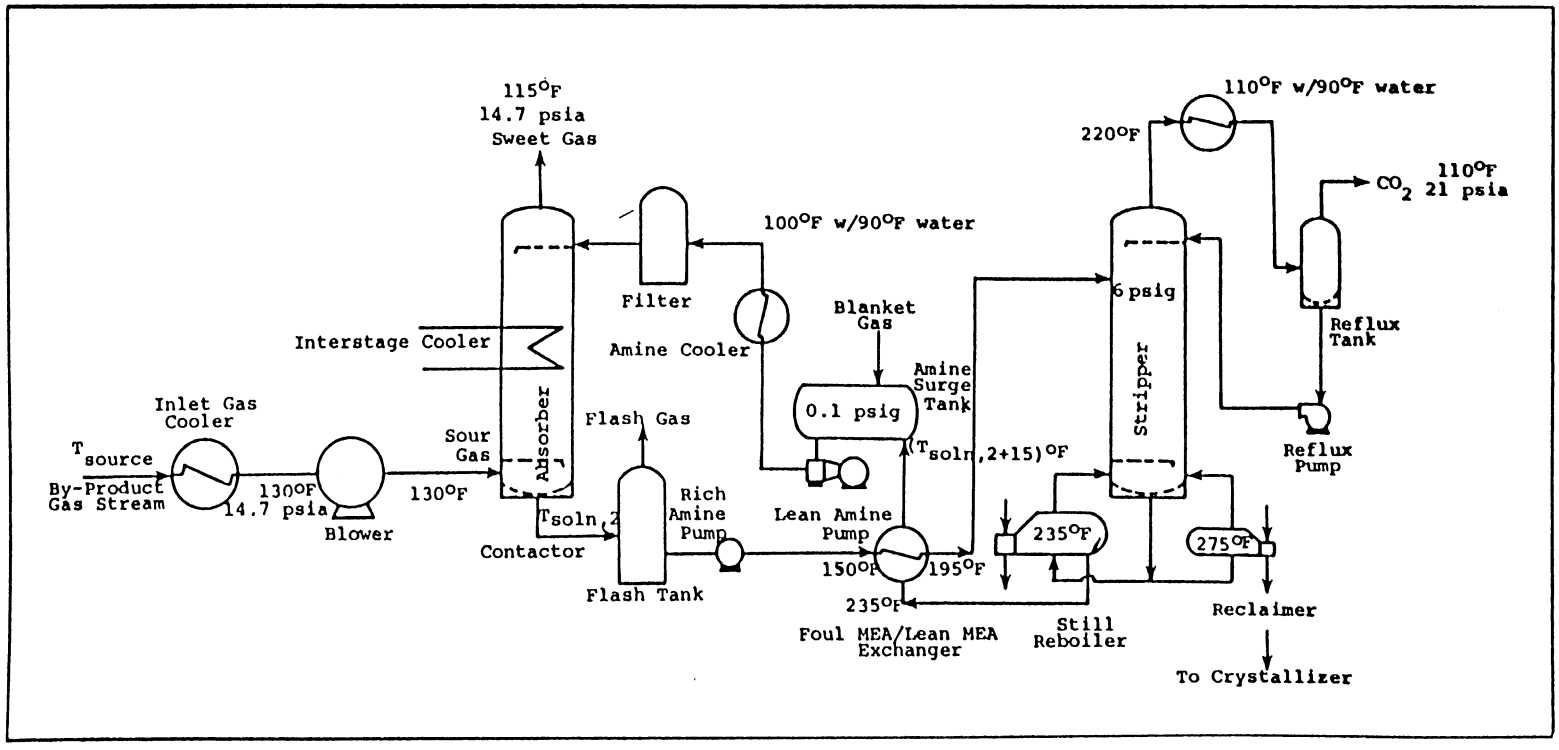
Exhibit 5-8 is a detailed version of the MEA design shown in Exhibit 5-4. The by-product gas bearing the CO_2 enters a preliminary gas cooler prior to receiving a boost by the blower to enable it to overcome the absorber column pressure drop. A 20-tray column has been specified for economic calculations, although a packed tower may be a better design. The conditions of the by-product gas depend on the source being considered (typical conditions are listed in Exhibit 5-2). The gas is then depleted of most of its CO_2 by counter-current contact with MEA solution in the absorber. Interstage cooling may be necessary in the absorber column in order to prevent overheating of the amine solution. The rich amine from the bottom of the column first passes to a flash tank to remove any traces of hydrocarbons. Then the solution is pumped through the amine-amine heat exchanger to the top of the stripper. CO_2 is stripped from the solution by the MEA's downward flow against the rising steam (the steam being produced by heating the lean MEA solution in the reboiler at the bottom of the stripper). A small side stream is taken off at the bottom of the column and is sent to the reclaimer. Almost pure CO_2 is recovered from the top of the stripper by first condensing the steam and recovering the CO_2 from the top of the reflux tank, and then sending the CO_2 to the dryer-compressor train.

The lean MEA solution is drawn off from the reboiler, through the amine-amine heat exchanger and is returned to the top of the absorber column via a surge tank, amine cooler, and a filter. The temperatures and pressures indicated at different parts of the flow diagram are fairly typical. Two

SYSTEM	EFFICIENCY
PRESENT DESIGNS	SCF CO_2/LB STEAM
20 Wt% K_2CO_3, (No Sulfur)	4.17
30 Wt% K_2CO_3, (No Sulfur) - Vacuum	5.26
20 Wt% MEA, (No Sulfur)	2.86
30 Wt% MEA, (No Sulfur)	3.58
20 Wt% MEA, (High Sulfur)	2.18
OTHER RESULTS	
30 Wt% MEA - Best Possible	5.2
Commercial Pressurized K_2CO_3	4.7 - 6.8
Pilot MEA System on Flue Gas (With Sulfur)	1.3

Exhibit 5-7: Comparison of Steam Efficiencies for CO_2 Recovery

Exhibit 5-8: A Detailed Flow Diagram of the MEA Process



Source: Modified from Ref. 26, p. 56, Figure 3.4, Courtesy Oil and Gas Journal.

temperatures that cannot be generalized are the by-product source gas temperature (T_{source}) in Exhibit 5-2 and the solution outlet temperature at the bottom of the absorber ($T_{soln,2}$) which must be calculated. The detailed design procedure for the MEA process is given as a step-by-step process in Appendix N.

Basic MEA systems for 15 cases at 90, 60, and 30 percent recovery have been designed in order to estimate the cost of recovering CO_2 from various sized units within different types of plant. Note that most plants are made up of a number of production units, and since each unit is normally a fairly independent entity, CO_2 was considered to be recovered separately from each unit rather than from the plant as a whole. For example, a 500 MW power plant may well consist of two 200 MW units and one-100 MW unit. The cost of recovering CO_2 from each of these smaller units will be shown to be higher than the cost of recovering CO_2 from one single larger unit due to economies of scale. The number of units for a given plant can normally only be determined by direct contact with plant personnel. MEA systems have been designed to recover CO_2 from the following units:

Gas-Fired Power Plants: 582 MW Unit, 248 MW Unit, 113 MW Unit
Coal-Fired Power Plants: 480 MW Unit, 213 MW Unit, 75 MW Unit
Fluid Cat-Cracking Unit Regenerators: 185,000 Bbls/D Unit, 60,000 Bbls/D Unit, 32,500 Bbls/D Unit
Gas-Fired Dry Cement Plants: 900 Ton/D Unit, 480 Ton/D Unit, 170 Ton/D Unit
Coal-Fired Wet Cement Plants: 1000 Ton/D Unit, 710 Ton/D Unit, 430 Ton/D Unit
Optimistic MEA Design: 480 MW Coal-Fired Power Plant with FGD System

The detailed design of a given MEA CO_2 recovery system concentrates on three main areas; the absorber, the stripper, and ancillary equipment such as heat exchangers and pumps. A detailed outline of the design procedure for each of the three areas is provided in Appendix N and is summarized in the following Sections.

5.5.2 Absorber Design

Absorber design is strongly affected by the amount of CO_2 that is to be recovered from the by-product gas streams.[24,26] It was assumed that 90% of the CO_2 was considered redeemable, although high sulfur content in flue gases may necessitate restrictions on the design which prohibit ready removal of 90% CO_2.

From a knowledge of the mass transfer coefficients for CO_2 recovery under different circumstances,[46] the diameter of a packed absorber column and the height of packing required to recover the desired amount of CO_2 can be determined. Mechanical considerations generally restrict the packed beds used for absorption to a diameter no greater than 20 feet and a height of packing no greater than approximately 50 feet. The column height was permitted to be up to approximately 60 feet to allow for a water wash at the top of the column and gas distributors at various heights. In many cases more than one absorber was required to effect the desired CO_2 removal while remaining within the mechanical limitations set. Using mass transfer coefficient data from Ref. 46, short heights of five to ten feet were generally all that were required. It should be noted that the data in Kohl and Risenfeld[24] rely on inaccurate absorption coefficient data (from a small column experiment) and overestimates of column height.

Calculations were made for packed towers and plate towers. While the packed bed is technically better, a plate tower design was used in the final absorber design and economic analysis because this is normal industrial practice and because the computer program (see Appendix N) made this calculation simpler. The number of trays was 20 for sulfur-free gases and 30 for sulfur-present gases, to be consistent with the data of Sears.[46] An interstage MEA solution cooler was also required near the center of the column under certain circumstances to prevent overheating of the MEA. This procedure probably overestimates absorber and blower requirements; thus, providing a conservative design. The primary factor in column diameter (or number of absorbers at 20-feet diameter) is the superficial gas velocity to restrict liquid entrainment.

5.5.3 Stripper Design (Plate Tower)

Stripper design is much more of an art than the design of the absorber.[24,26] The key in designing the stripper was to size it so the superficial velocity of the rising steam was approximately five to ten feet per second. This dictated the diameter of the column, but again because of mechanical considerations, this diameter was not permitted to exceed 20 feet. The height of the stripper was dictated by the number of trays required to effect the desired CO_2 removal from the rich MEA solution. Normally 20 trays were required for this stripping; a further three trays were required at the top of the column for a water wash. Thus, the column height was 46 feet assuming a typical value of two feet for inter-tray spacings. In many cases more than one stripper was required in order to effect the desired CO_2 removal from the rich MEA solution.

5.5.4 Ancillary Equipment

Heat exchangers are the primary items under the heading ancillary equipment. Included in this broad category are: the by-product gas cooler, the amine-amine heat exchanger, the lean amine cooler, the stripper condenser, the stripper reboiler, and the stripper reclaimers. The required heat transfer area for each of these exchangers was designed once the individual heat duties and operating temperatures had been determined. A typical overall heat transfer coefficient (Exhibit 5-6) for the given piece of equipment was obtained from Reference 26.

Under other miscellaneous equipment, the horsepower of amine pumps was determined from a knowledge of pressure drop through equipment and the amount of amine solution circulating in gallons-per-minute.[26] The horsepower of the by-product gas blower was calculated from the volumetric flowrate of the by-product gas stream and the pressure drop incurred by the gas stream passing through the absorber. Finally, the diameter of the reflux tank was determined by restricting the superficial velocity of the entering water to five to six feet per second, and the height of the tank was assumed to be approximately three times its diameter. Note that the amine filter, flash tank, and surge tank were not specifically designed. Their cost was assumed to be included in the contingency factor applied during the economic analysis.

Due to there being more than one absorber and/or more than one stripper in a particular design, in many cases multiples of a given piece of ancillary equipment were required. For example, each stripper was considered to always have an associated reclaimer, reboiler, condenser, reflux tank, and reflux pump. The system design tended to become slightly more complex when the number of absorbers required was different from the number of strippers. The specifications for the equipment are depicted in the Exhibits of Appendix N.

5.6 DETAILED DESIGN CONCEPTS FOR THE K_2CO_3 PROCESS

5.6.1 Introduction

A simplified schematic flow diagram for the basic K_2CO_3 process is shown in Exhibit 5-5. The by-product gas containing CO_2 enters into the absorber column after going through a primary gas cooler and a booster compressor, if necessary. Whether a primary gas cooler or booster is required or not depends on the condition of the by-product gas (see Exhibit 5-2) and the design for absorber temperature and pressure. The procedure and example calculations for K_2CO_3 systems design is shown in Appendix O. Requirements for ancillary equipment such as a reclaimer, crystallizer, and/or a K_2SO_4 regenerator will depend on the condition of the by-product gas. For example, the CO_2 recovery system for flue gases from coal-fired power plants will contain SO_2; this system will require K_2SO_4 crystallizer and regenerator units. A description of the K_2CO_3 process and the functions of the major equipment are described in Section 5.3.

Basic K_2CO_3 systems at 90%, 60%, and 30% CO_2 recovery were designed in order to estimate the cost of recovering CO_2 from various sizes and types of plants, as shown below.

Gas-Fired Power Plants: 582 MW Unit, 248 MW Unit, 113 MW Unit
Coal-Fired Power Plants: 480 MW Unit, 213 MW Unit, 75 MW Unit
Fluid Cat-Cracking Unit Regenerators: 185,000 Bbls/D Unit, 60,000 Bbls/D Unit, 32,500 Bbls/D Unit
Gas-Fired Dry Cement Plants: 900 Ton/D Unit, 480 Ton/D Unit, 170 Ton/D Unit
Coal-Fired Wet Cement Plants: 1000 Ton/D Unit, 410 Ton/D unit, 430 Ton/D Unit
Optimistic K_2CO_3 Design: 480 MW Coal-Fired Power Plant with FGD System

The detailed design of given K_2CO_3 system for CO_2 recovery concentrates on three main areas: the absorber, the stripper, and the ancillary equipment. A detailed outline of the design procedures for each of the three areas is provided in Appendix O and is summarized in the following Sections.

5.6.2 Absorber Design

The absorber design is strongly affected by the amount of CO_2 that is to be recovered and by the concentration of CO_2 in the gas stream, temperature of the gas stream, and the pressure of the gas stream from which the CO_2 is to be recovered. Based on the results of the CO_2 recovery systems designed for 500 MW coal-fired power plants using 30%, 60%, and 90% CO_2 recovery, the absorber was designed for 90% recovery although it is not clear whether 90% recovery is environmentally feasible. For CO_2 from other sources such as gas-fired power plants and FCCU regenerators, 90% of the CO_2 was considered to be redeemable due to the much lower or nonexistent SO_2 levels in the flue gas streams. The designs are considered somewhat conservative in the sense that the amount of CO_2 absorbed for a given temperature and pressure was assumed to be approaching 60% of the equilibrium solution capacity level at the bottom of the absorber.

Two types of absorber were designed, spray towers/packed bed and a tray tower. Using mass transfer coefficients[46] for CO_2 recovery under different circumstances, the diameter and height of the absorber were calculated for the packed tower. The mechanical restrictions for packed beds were assumed to be identical to those discussed in Section 5.5.2 on the absorber design for MEA Systems.

For tray-tower absorbers, the number of trays in sulfur-free gases was set at 30, and the number was set at 20 in sulfur-present gases. The difference is due to a slight increase in mass transfer absorption with the presence of K_2CO_3/K_2SO_4 in the system.[46] Either design should be adequate for absorption of the given percent recovery. The tray-tower absorber was the system used in the final design and the economic analysis. A packed bed system (or preferably a spray tower) if developed, would offer the best operational system.

5.6.3 Stripper Design

The stripper diameter design was based on a vapor-velocity limitation and was established from a general correlation.[24]

$$U = K_v \sqrt{\frac{\rho_L - \rho_g}{\rho_g}}$$

where:

U = allowable superficial vapor velocity, ft/sec
In our design, allowable superficial velocity was kept in the range of 5 to 10 ft/sec

ρ_L = liquid density lb/cu ft

ρ_g = gas density lb/cu ft

K_v = empirical constant

The coefficient K_v was determined from a tabulated correlation of K_v and F_v.[24] F_v was calculated using the equation:

$$F_v = \frac{L}{G} \sqrt{\frac{\rho_g}{\rho_L}}$$

where:

L = liquid flow rate lb/sec

G = gas flow rate lb/sec

ρ_g = gas density lb/ft^3

ρ_L = liquid density lb/ft^3

The allowable superficial vapor velocity calculated using the above equations dictated the diameter of the column, with the restriction for mechanical considerations that this diameter was not permitted to exceed 20 feet. Additional stripper columns were required in that instance. The height of the stripper was dictated by the number of trays required to strip the CO_2 from the rich K_2CO_3 solution. It was decided to use 20 trays for stripping and three trays for water wash with a typical value of two feet per tray for inter-tray spacing giving an overall column height of 46 feet. In a preliminary design such as this, a stripper design requiring 14 trays or 20 trays would not make much difference in the final cost of the SO_2 recovery system. Therefore, it was decided to assume that 20 trays are required for stripping.

5.6.4 Ancillary Equipment

Ancillary equipment includes: heat exchangers, pumps, stripper condensers, stripper reboilers, stripper reclaimers, a K_2SO_4 crystallizer, and a regenerator. The required heat transfer area for each of the heat exchangers was calculated once the individual heat duties and operating temperatures had been determined from process conditions. Typical values for overall heat transfer coefficients (Exhibit 5-6) were taken from Reference 26. Needed horsepower for lean and rich K_2CO_3 pumps was calculated based on the gallons-per-minute of circulating K_2CO_3. Finally, the diameter of the reflux tank was determined by restricting the superficial velocity of the vapor, the height of the tank was assumed to be three times its diameter. Note that other associated equipment such as the K_2CO_3 filter, the surge tank, and the storage tanks were not specifically designed. Their cost was assumed to be covered by the contingency factor applied during the economic analysis.

In many cases due to there being more than one absorber and/or stripper in a particular design, multiples of a given piece of ancillary equipment were required as stated in Section 5.5.4.

5.6.5 Optimistic Design

An optimistic design based on the vacuum carbonate approach is shown in Exhibit 5-9. This approach eliminates the lean/rich heat exchanger, and also

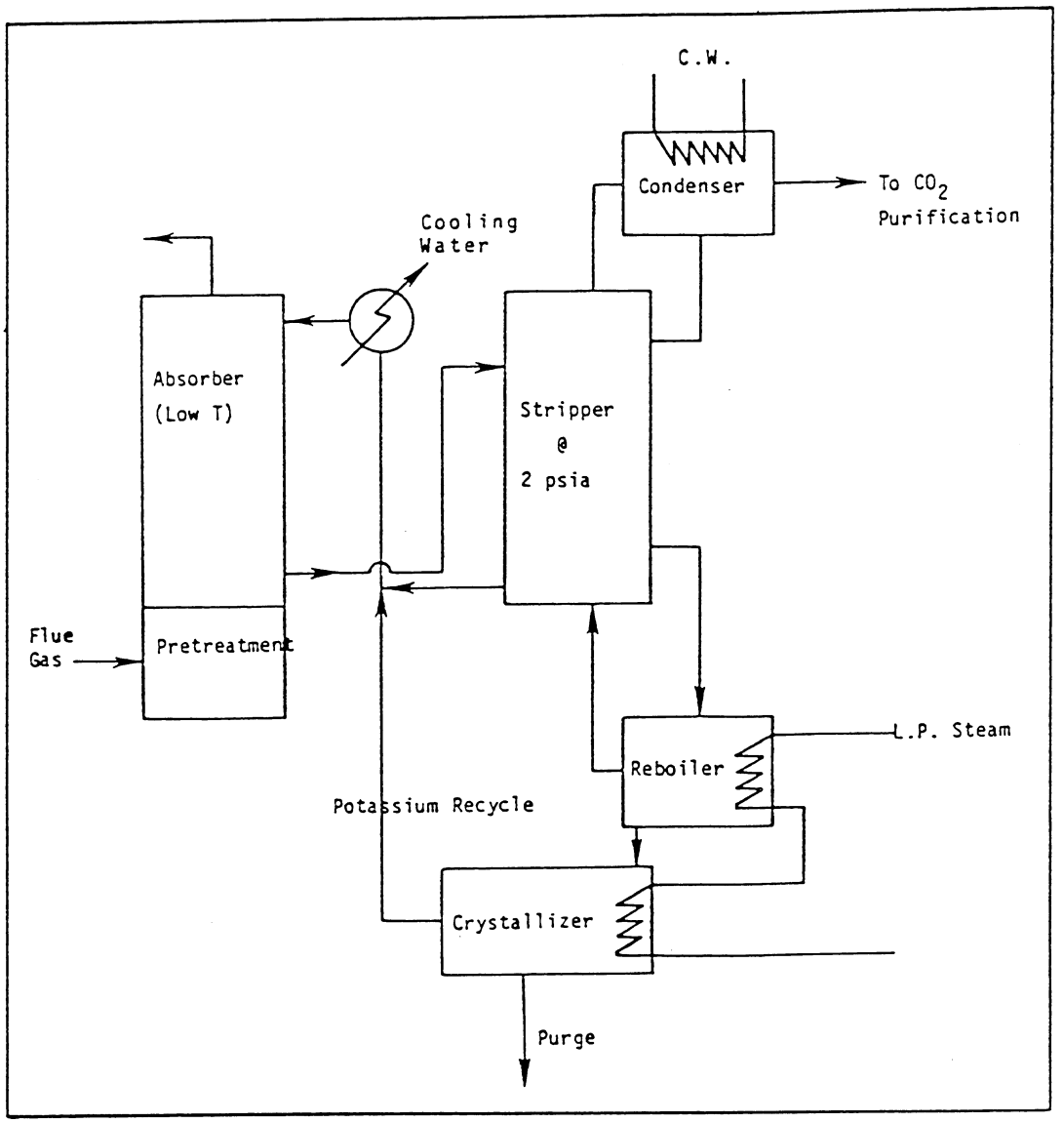


Exhibit 5-9: Possible Vacuum Potassium Carbonate Process

decreases steam use in the stripper from flashing and less solution heating. A major question remains as to whether salt deposition might occur through the system, resulting in fouling problems. Thus, R&D might be required, especially with respect to the handling of sulfur-present gases. A spray-tower absorber design, after the TVA venturi-spray or direct-spray designs for SO_2 recovery, might help alleviate potential deposition problems and might reduce absorber pressure drop.

5.7 ECONOMIC ANALYSIS

5.7.1 Recovery Cost

In order to compare the total costs of various CO_2 by-product recovery systems, the required selling price (in constant dollars) to achieve a specified rate of return has been calculated for each system, using discounted cash flows. The assumptions common to all systems and the basic methodology, are described in Appendix P.

The information needed for each recovery system in order to perform the analysis includes:

- Total capital investment
- Depreciable investment
- Working capital
- Yearly operating cost
- Yearly production volume
- Tax rates and return-on-investment rates

This information is obtained from the detailed equipment and operating costs in Appendices N and O. The resulting costs for each size and type of plant are given in Exhibits 5-9 and 5-10. This information is also shown graphically (for the 90% recovery case) in Exhibits 5-12 through 5-23.

These results indicate that MEA is the cheaper recovery process for low-sulfur coal-fired power plants and coal-fired wet cement plants, while the K_2CO_3 process is cheaper for all the other cases considered.

Exhibit 5-10: Recovery Cost Summary for Power Plants

Type of Plant	Plant Capacity (Input CO_2 Rate)		Percent Recovery					
			30		60		90	
			MEA	K_2CO_3	MEA	K_2CO_3	MEA	K_2CO_3
Gas-Fired Power Plant	80 MMSCFD	Total Capital ($MM)	41.9	45.4	55.9	64.9	75.1	92.1
		Operating Cost ($MM)	18.8	16.1	32.0	26.8	45.8	38.5
		CO_2 Volume (MMSCFD)	24.5	24.5	49.0	49.0	72.7	72.7
		Price 1 ($/MSCF)	2.95	2.72	2.35	2.16	2.24	2.08
		Price 2 ($/MSCF)	2.66	2.41	2.16	1.93	2.07	1.87
	35 MMSCFD	Total Capital ($MM)	19.1	21.2	24.9	29.3	34.6	42.9
		Operating Cost ($MM)	9.9	8.8	15.6	13.4	21.6	18.6
		CO_2 Volume (MMSCFD)	10.5	10.5	20.7	20.7	31.5	31.5
		Price 1 ($/MSCF)	3.50	3.32	2.66	2.48	2.43	2.29
		Price 2 ($/MSCF)	3.20	2.98	2.46	2.25	2.25	2.07
	16 MMSCFD	Total Capital ($MM)	10.0	10.9	12.6	14.7	16.4	20.0
		Operating Cost ($MM)	6.4	5.9	9.0	7.9	11.6	10.2
		CO_2 Volume (MMSCFD)	4.8	4.8	9.6	9.6	14.4	14.4
		Price 1 ($/MSCF)	4.72	4.52	3.24	3.04	2.79	2.64
		Price 2 ($/MSCF)	4.36	4.14	3.01	2.78	2.59	2.40
Coal-Fired Power Plant (High Sulfur)	96 MMSCFD	Total Capital ($MM)	43.5	53.2	64.7	82.6	91.8	116.1
		Operating Cost ($MM)	14.6	12.6	23.3	19.2	32.5	26.2
		CO_2 Volume (MMSCFD)	28.8	28.8	57.7	57.7	86.5	86.5
		Price 1 ($/MSCF)	2.14	2.11	1.66	1.62	1.55	1.49
		Price 2 ($/MSCF)	1.88	1.80	1.47	1.38	1.38	1.27
	43 MMSCFD	Total Capital ($MM)	20.9	25.1	29.7	37.8	43.5	53.7
		Operating Cost ($MM)	8.8	7.9	12.7	10.8	16.8	14.0
		CO_2 Volume (MMSCFD)	12.9	12.9	25.8	25.8	38.7	38.7
		Price 1 ($/MSCF)	2.70	2.66	1.91	1.88	1.75	1.68
		Price 2 ($/MSCF)	2.42	2.33	1.72	1.63	1.56	1.45
	25 MMSCFD	Total Capital ($MM)	14.1	16.4	20.1	24.4	29.2	34.0
		Operating Cost ($MM)	6.5	5.9	8.7	7.6	11.3	9.5
		CO_2 Volume (MMSCFD)	7.6	7.6	15.2	15.2	22.8	22.9
		Price 1 ($/MSCF)	3.28	3.23	2.38	2.17	2.00	1.88
		Price 2 ($/MSCF)	2.96	2.86	2.01	1.90	1.78	1.63
Coal-Fired Power Plant (Low Sulfur)	96 MMSCFD	Total Capital ($MM)	31.1	43.6	48.6	73.3	72.0	107.0
		Operating Cost ($MM)	11.0	11.1	17.7	17.8	24.9	24.8
		CO_2 Volume (MMSCFD)	28.8	28.8	57.7	57.7	86.5	86.5
		Price 1 ($/MSCF)	1.58	1.80	1.26	1.47	1.20	1.40
		Price 2 ($/MSCF)	1.40	1.55	1.12	1.26	1.06	1.19
	43 MMSCFD	Total Capital ($MM)	15.1	20.7	24.0	33.6	34.4	49.8
		Operating Cost ($MM)	6.8	6.8	9.8	9.8	13.1	13.0
		CO_2 Volume (MMSCFD)	12.9	12.9	25.8	25.8	38.7	38.7
		Price 1 ($/MSCF)	2.04	2.25	1.51	1.69	1.37	1.56
		Price 2 ($/MSCF)	1.84	1.98	1.36	1.47	1.22	1.34
	25 MMSCFD	Total Capital ($MM)	10.4	13.6	15.5	21.7	23.9	31.3
		Operating Cost ($MM)	5.5	5.5	7.2	7.2	9.3	9.1
		CO_2 Volume (MMSCFD)	7.6	7.6	15.2	15.2	22.9	22.9
		Price 1 ($/MSCF)	2.68	2.88	1.81	2.01	1.64	1.77
		Price 2 ($/MSCF)	2.45	2.58	1.63	1.76	1.46	1.54
	96 MMSCFD Optimistic Design	Total Capital ($MM)	31.7	21.3	49.3	30.3	72.8	43.3
		Operating Cost ($MM)	10.3	8.1	17.2	11.9	24.1	16.1
		CO_2 Volume (MMSCFD)	28.8	28.8	57.7	57.7	86.5	86.5
		Price 1 ($/MSCF)	1.57	1.14	1.24	.83	1.18	.76
		Price 2 ($/MSCF)	1.39	1.01	1.10	.74	1.04	.67

NOTE a) CO_2 volumes are calendar day.
b) Price 1 is for 10-year life, 50% debt.
c) Price 2 is for 15-year life, 75% debt.

Exhibit 5-11: Recovery Cost Summary for FCCU and Cement Plants

Type of Plant	Plant Capacity (Input CO_2 Rate)		Percent Recovery					
			30		60		90	
			MEA	K_2CO_3	MEA	K_2CO_3	MEA	K_2CO_3
Refinery FCCU	185,000 BBL (37 MMSCFD)	Total Capital ($MM)	19.1	21.1	24.4	28.3	32.0	39.2
		Operating Cost ($MM)	11.0	9.7	17.7	15.0	24.7	20.8
		CO_2 Volume (MMSCFD)	11.1	11.1	22.2	22.2	33.4	33.4
		Price 1 ($/MSCF)	3.58	3.34	2.74	2.48	2.51	2.29
		Price 2 ($/MSCF)	3.29	3.01	2.55	2.27	2.35	2.10
	60,000 BBL (12 MMSCFD)	Total Capital ($MM)	6.6	7.3	8.4	9.9	11.3	13.8
		Operating Cost ($MM)	5.8	5.3	7.9	7.1	10.2	8.9
		CO_2 Volume (MMSCFD)	3.6	3.6	7.2	7.2	10.8	10.8
		Price 1 ($/MSCF)	5.35	5.12	3.64	3.41	3.12	2.92
		Price 2 ($/MSCF)	5.03	4.77	3.43	3.18	2.95	2.70
	35,000 BBL 6.4 MMSCFD)	Total Capital ($MM)	4.4	4.8	5.5	6.4	7.3	9.0
		Operating Cost ($MM)	4.6	4.4	5.8	5.3	7.1	6.4
		CO_2 Volume (MMSCFD)	1.9	1.9	3.9	3.9	5.8	5.8
		Price 1 ($/MSCF)	7.73	7.51	4.84	4.63	3.99	3.80
		Price 2 ($/MSCF)	7.32	7.07	4.60	4.35	3.78	3.53
Gas-Fired Cement Plant	900 TPD (9.8 MMSCFD)	Total Capital ($MM)	4.7	5.2	6.3	7.5	8.5	10.5
		Operating Cost ($MM)	5.0	4.6	6.5	5.9	8.2	7.3
		CO_2 Volume (MMSCFD)	3.0	3.0	5.9	5.9	8.9	8.9
		Price 1 ($/MSCF)	5.45	5.25	3.60	3.41	3.03	2.87
		Price 2 ($/MSCF)	5.17	4.94	3.41	3.19	2.86	2.67
	479 TPD (5.2 MMSCFD)	Total Capital ($MM)	3.3	3.5	4.2	4.9	5.6	6.8
		Operating Cost ($MM)	4.2	4.0	5.0	4.7	5.9	5.5
		CO_2 Volume (MMSCFD)	1.6	1.6	3.2	3.2	4.7	4.7
		Price 1 ($/MSCF)	8.39	8.20	5.09	4.91	4.06	3.92
		Price 2 ($/MSCF)	8.02	7.79	4.85	4.64	3.85	3.67
	168 TPD (1.8 MMSCFD)	Total Capital ($MM)	2.2	2.3	2.7	2.9	3.4	3.9
		Operating Cost ($MM)	3.6	3.5	3.9	3.8	4.2	4.0
		CO_2 Volume (MMSCFD)	.5	.5	1.1	1.1	1.6	1.6
		Price 1 ($/MSCF)	21.20	21.01	11.19	11.04	8.24	8.16
		Price 2 ($/MSCF)	20.38	20.16	10.73	10.54	7.86	7.72
Coal-Fired Wet Cement Plant	1,000 TPD (13 MMSCFD)	Total Capital ($MM)	6.8	8.2	9.1	12.3	12.5	16.9
		Operating Cost ($MM)	4.5	4.5	5.4	5.4	6.4	6.4
		CO_2 Volume (MMSCFD)	3.9	3.9	7.8	7.8	11.8	11.8
		Price 1 ($/MSCF)	3.83	4.21	2.49	2.68	2.04	2.21
		Price 2 ($/MSCF)	3.75	3.85	2.29	2.41	1.86	1.97
	710 TPD (9.3 MMSCFD)	Total Capital ($MM)	5.4	6.4	7.2	9.4	9.9	12.9
		Operating Cost ($MM)	4.1	4.1	4.8	4.8	5.6	5.5
		CO_2 Volume (MMSCFD)	2.8	2.8	5.6	5.6	8.4	8.4
		Price 1 ($/MSCF)	5.12	5.27	3.03	3122	2.43	2.59
		Price 2 ($/MSCF)	4.78	4.87	2.81	2.93	2.23	2.33
	430 TPD (5.5 MMSCFD)	Total Capital ($MM)	4.0	4.6	5.2	6.5	7.1	8.8
		Operating Cost ($MM)	3.8	3.8	4.2	4.2	4.7	4.6
		CO_2 Volume (MMSCFD)	1.7	1.7	3.4	3.4	5.0	5.0
		Price 1 ($/MSCF)	7.52	7.66	4.26	4.44	3.30	3.44
		Price 2 ($/MSCF)	7.09	7.17	3.99	4.10	3.05	3.13

NOTE a) CO_2 volumes are calendar day.
b) Price 1 is for 10-year life, 50% debt.
c) Price 2 is for 15-year life, 75% debt.

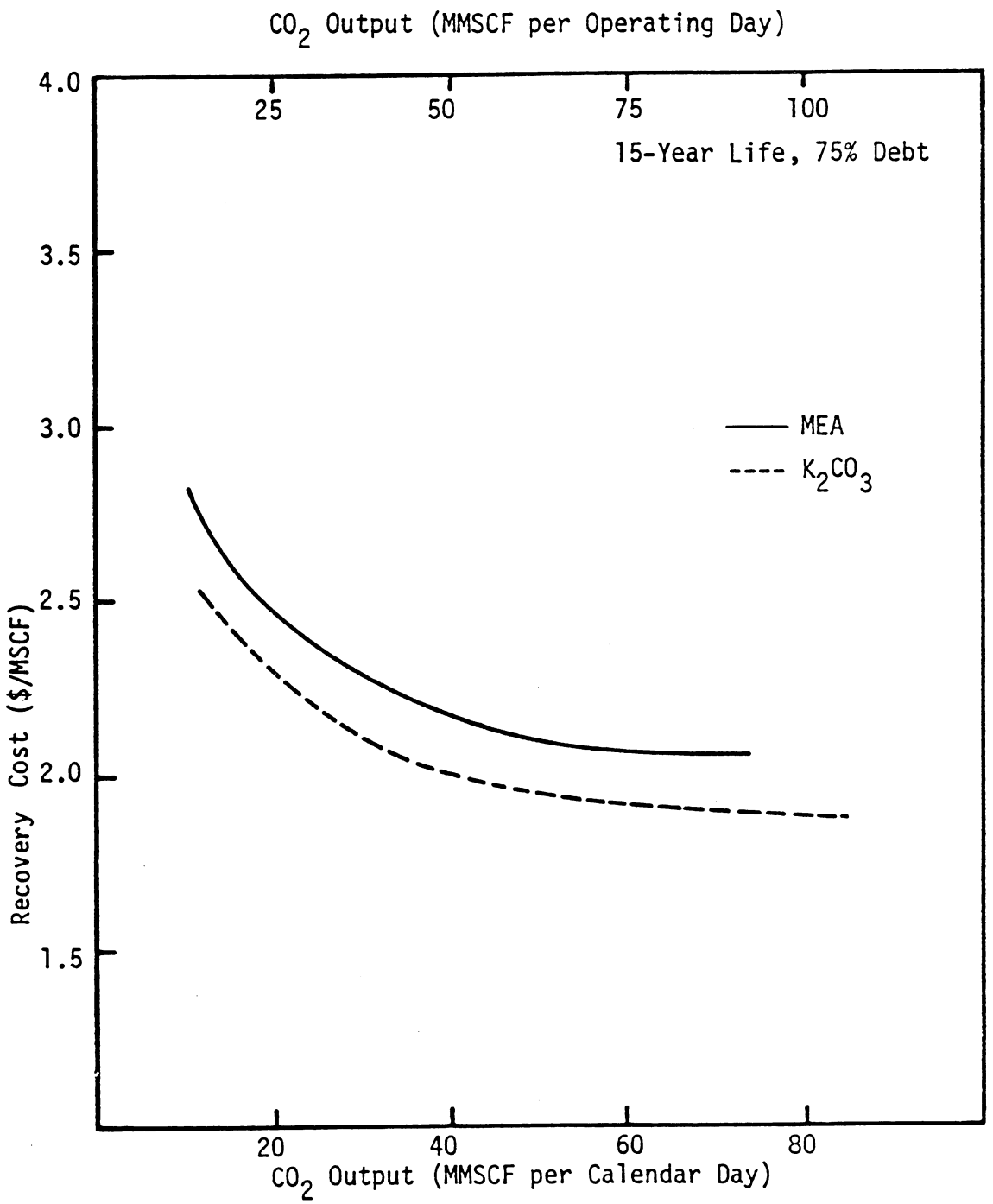


Exhibit 5-12: Recovery Cost for Gas-Fired Power Plants

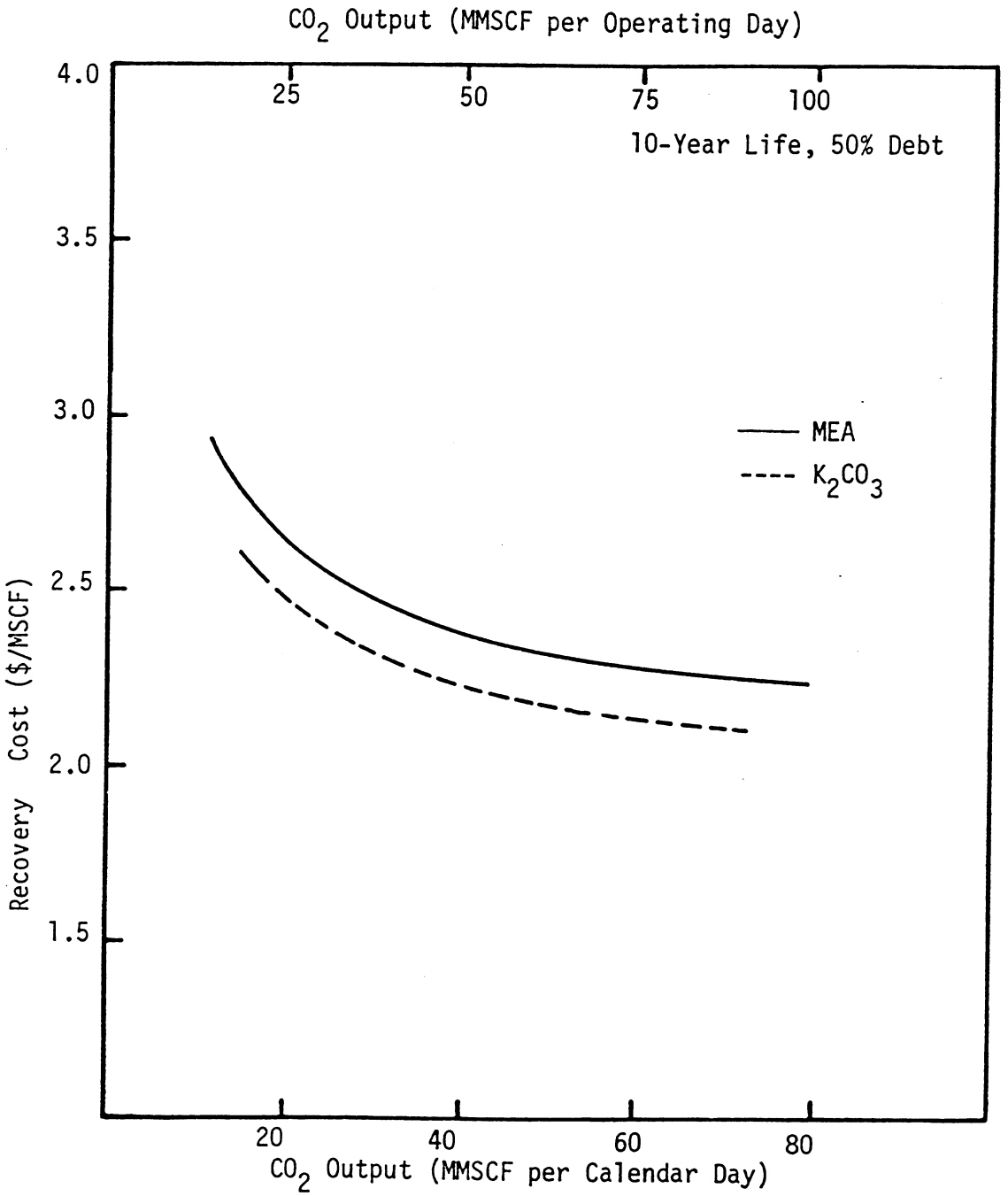


Exhibit 5-13: Recovery Cost for Gas-Fired Power Plants

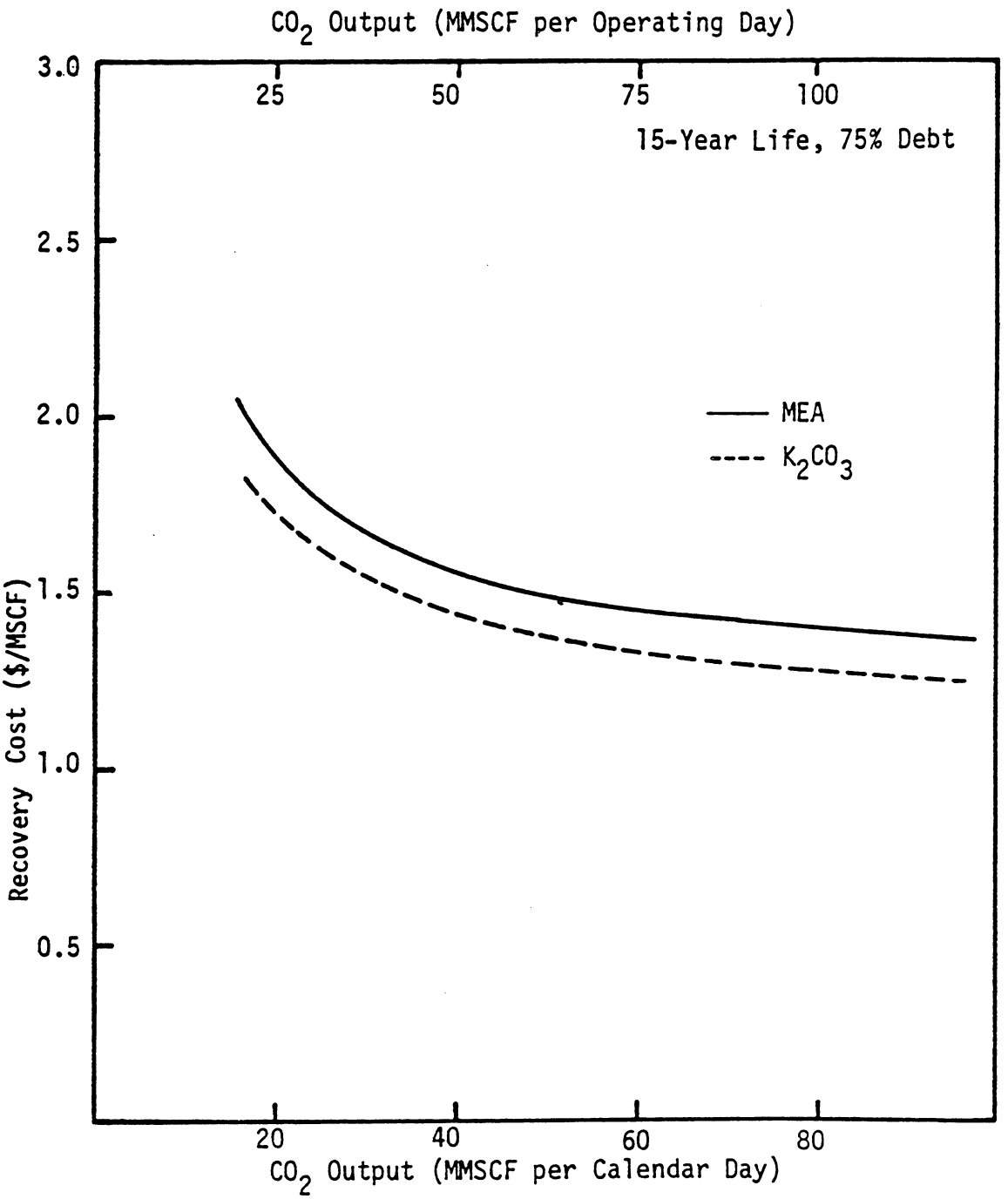


Exhibit 5-14: Recovery Cost for Coal-Fired Power Plants (High Sulfur)

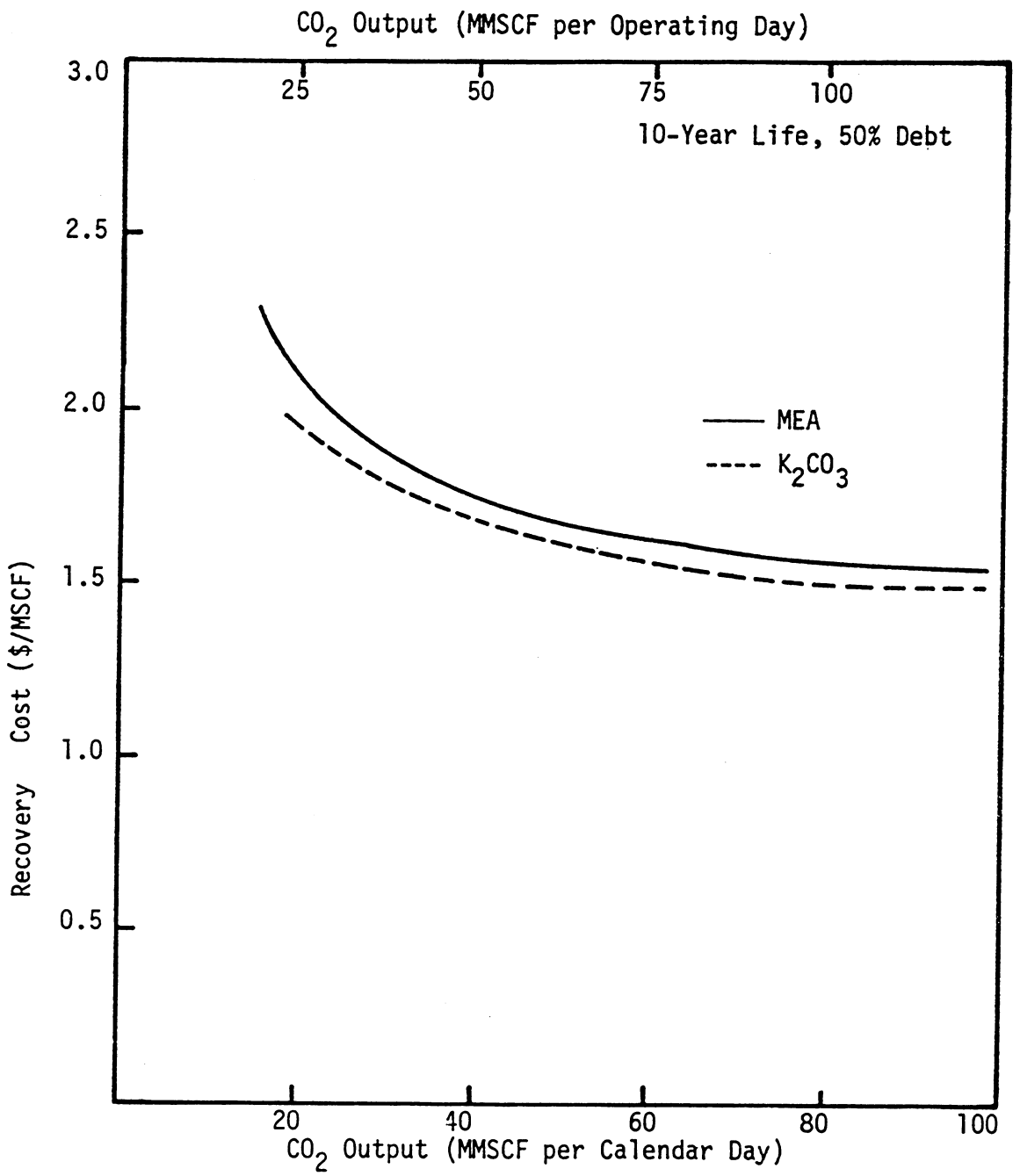


Exhibit 5-15: Recovery Cost for Coal-Fired Power Plants (High Sulfur)

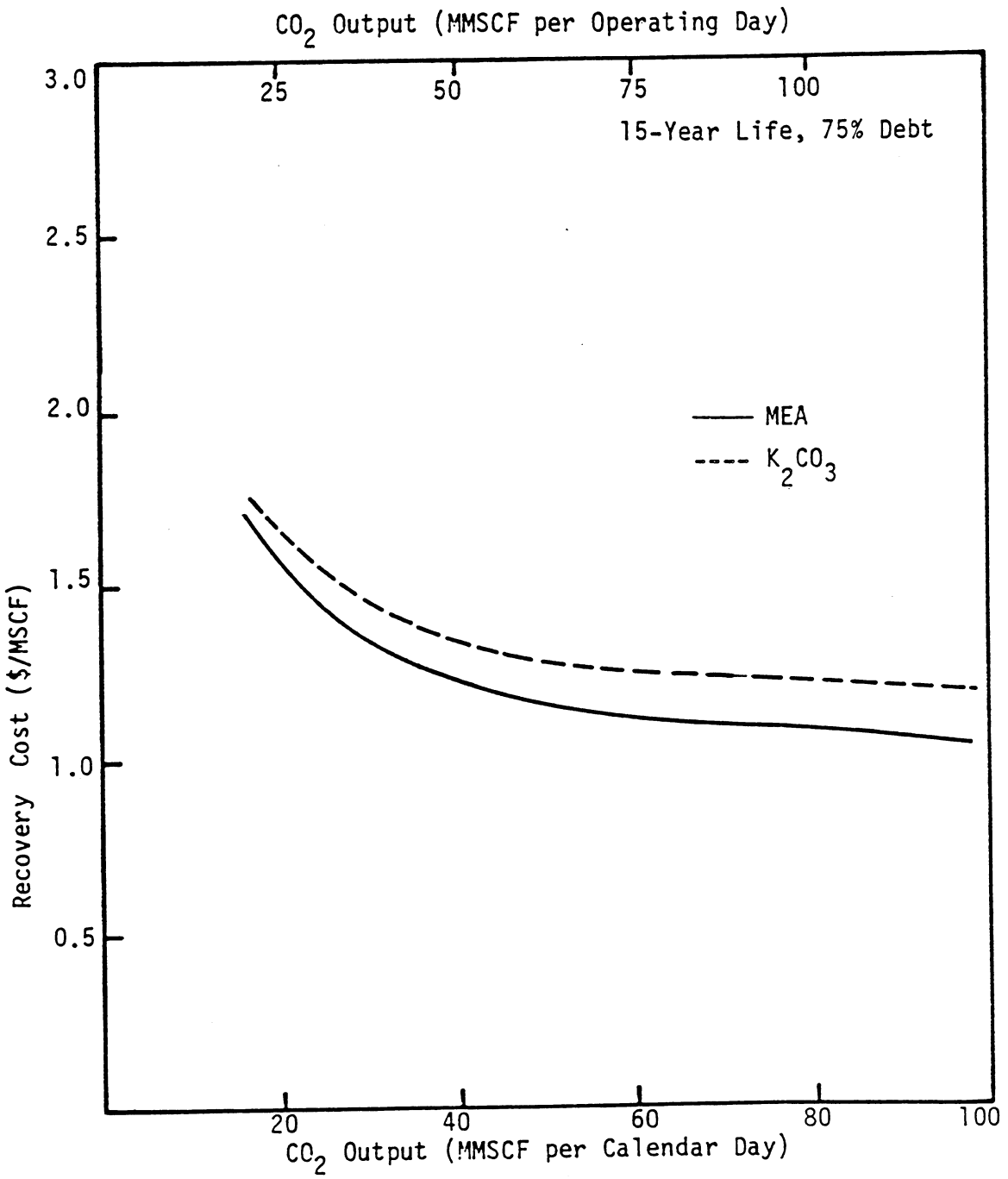


Exhibit 5-16: Recovery Cost for Coal-Fired Power Plants (Low Sulfur)

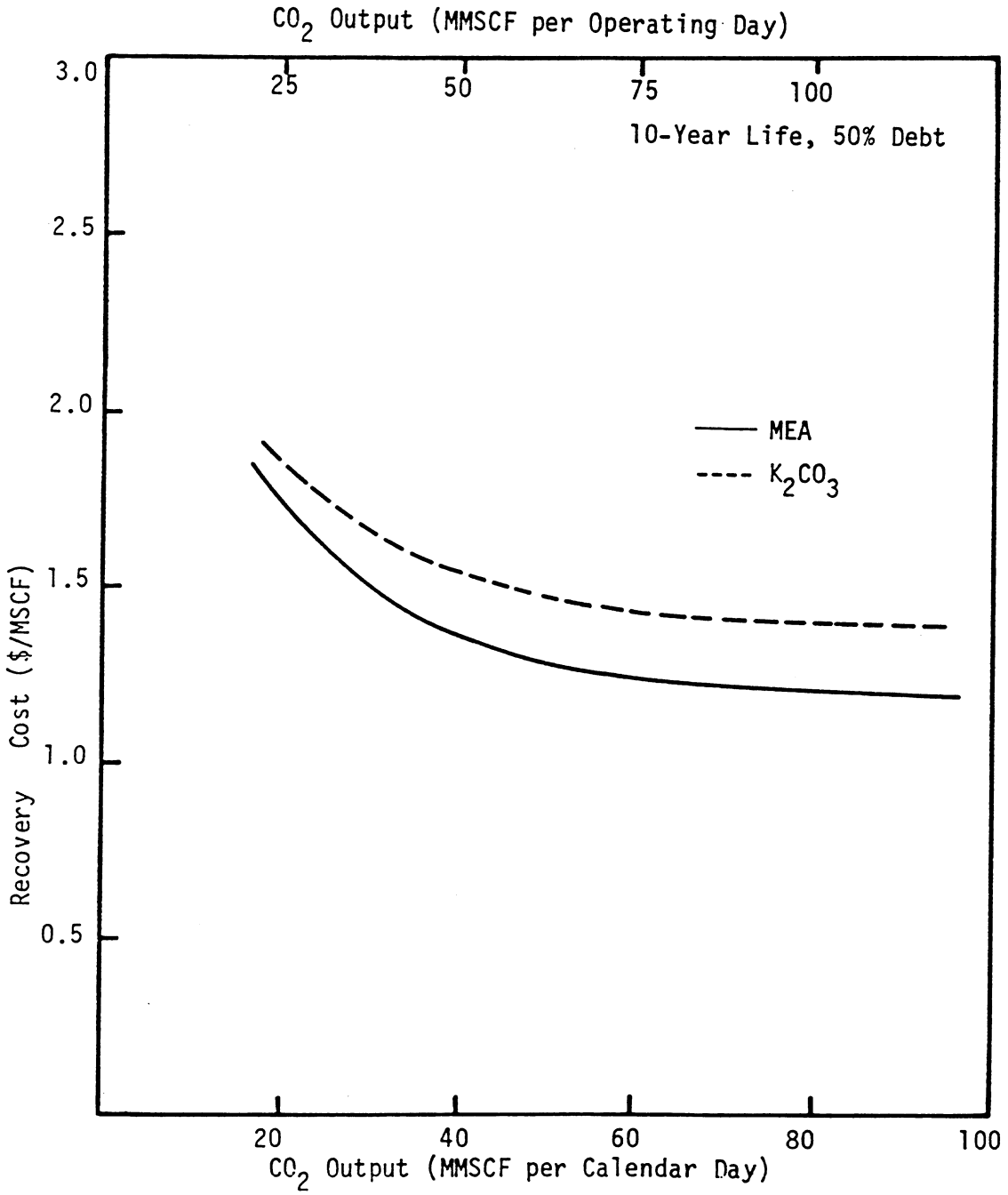


Exhibit 5-17: Recovery Cost for Coal-Fired Power Plants (Low Sulfur)

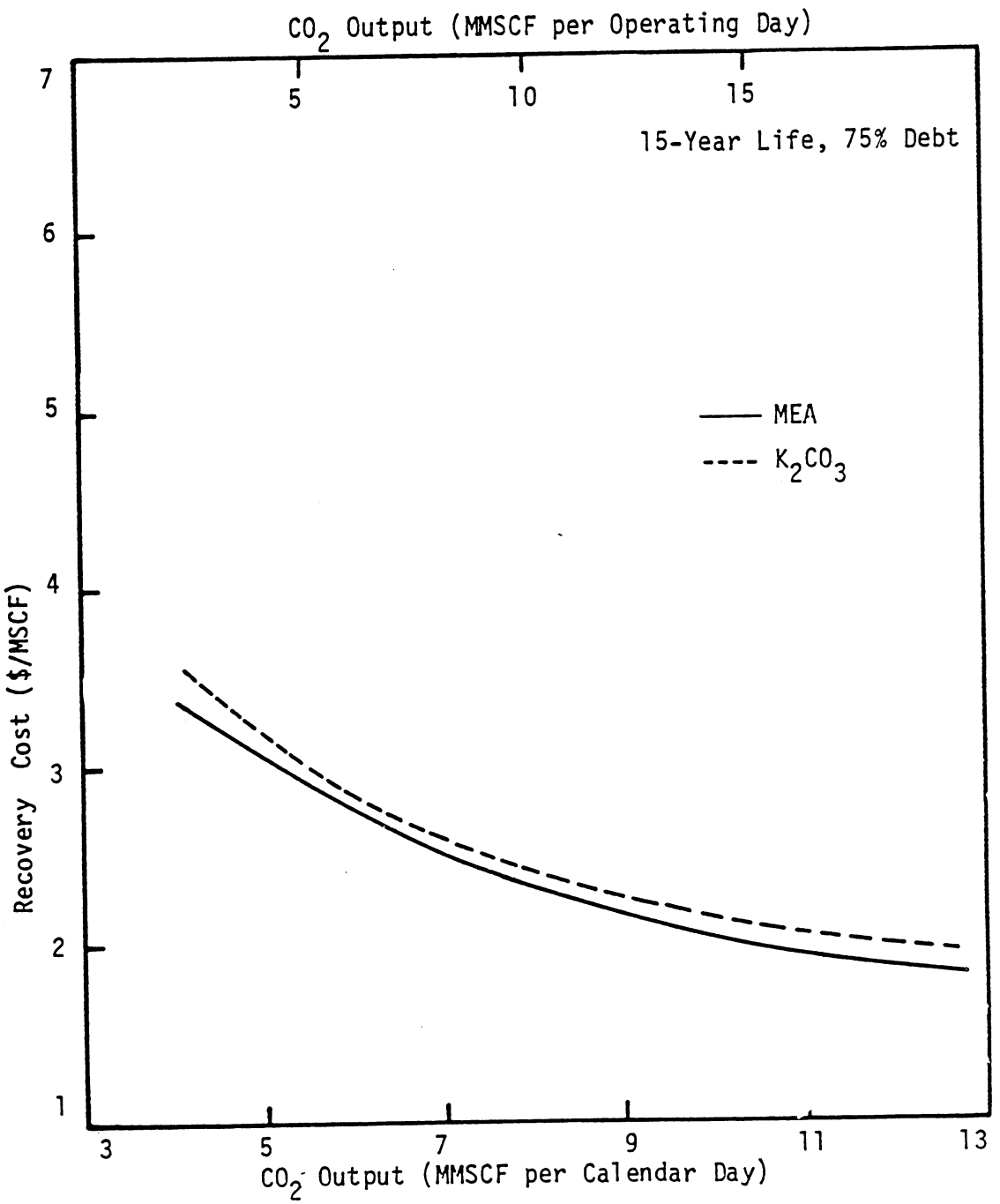


Exhibit 5-18: Recovery Cost for Coal-Fired Wet Cement Plants

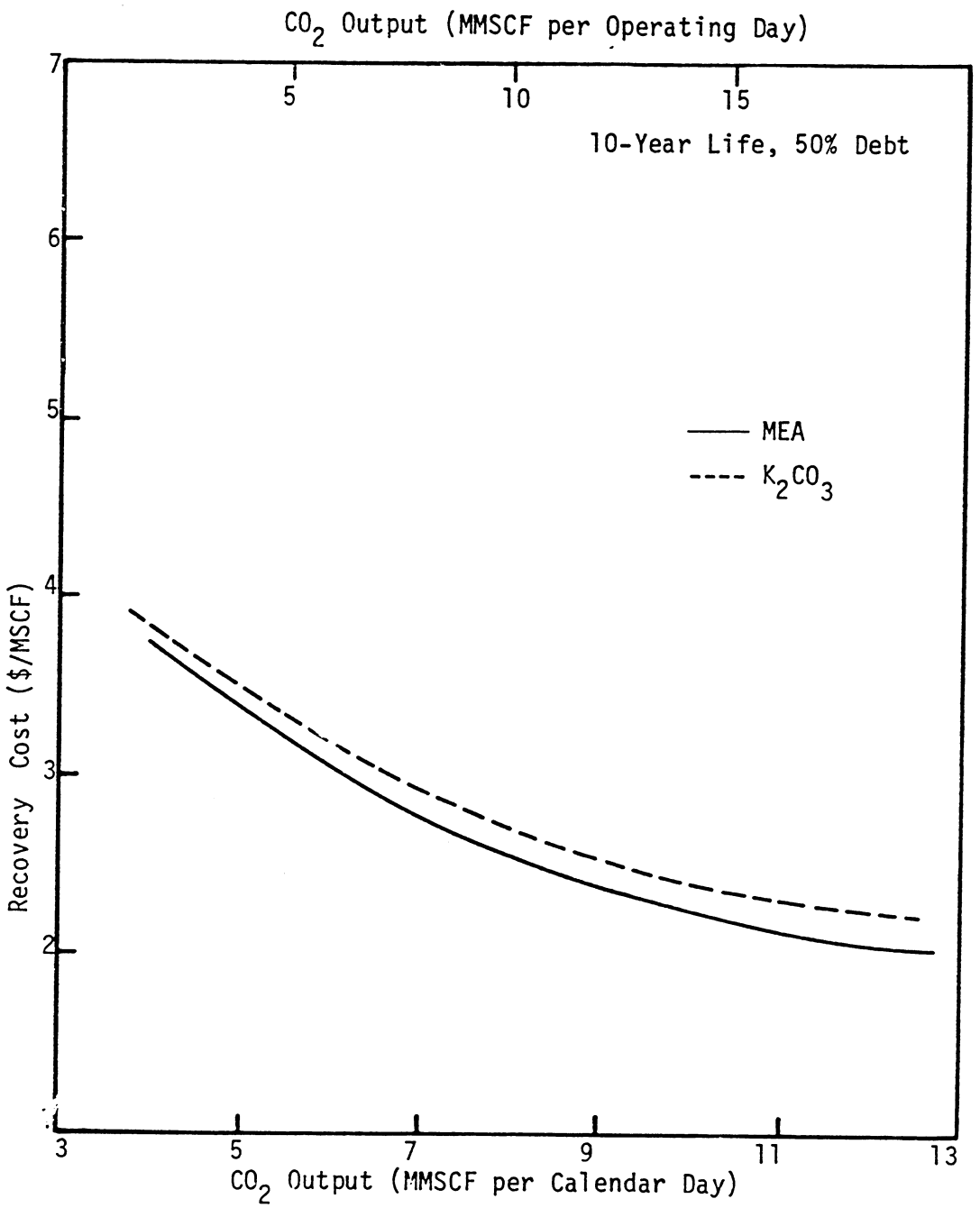


Exhibit 5-19: Recovery Cost for Coal-Fired Wet Cement Plants

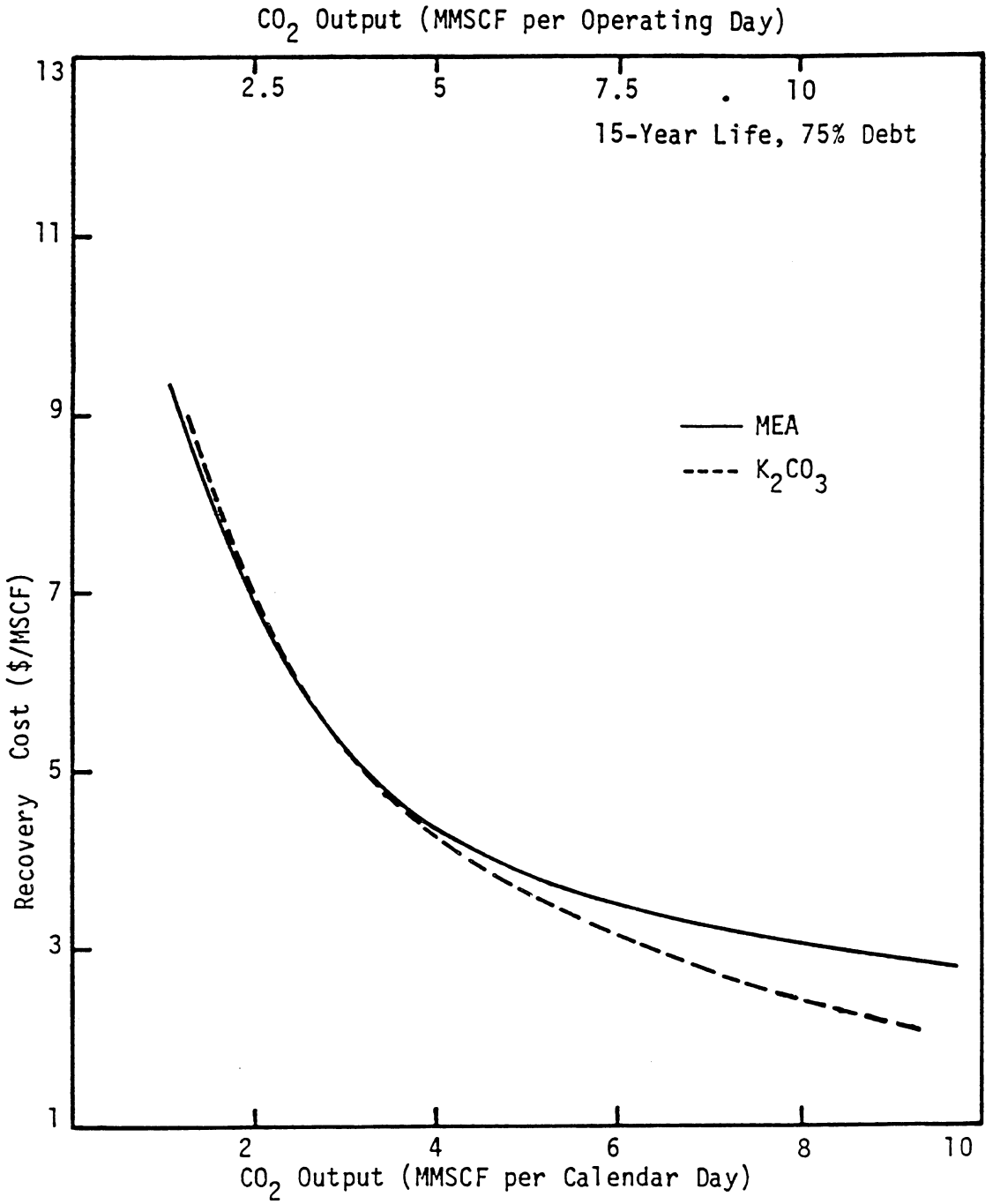


Exhibit 5-20: Recovery Cost for Gas-Fired Cement Plants

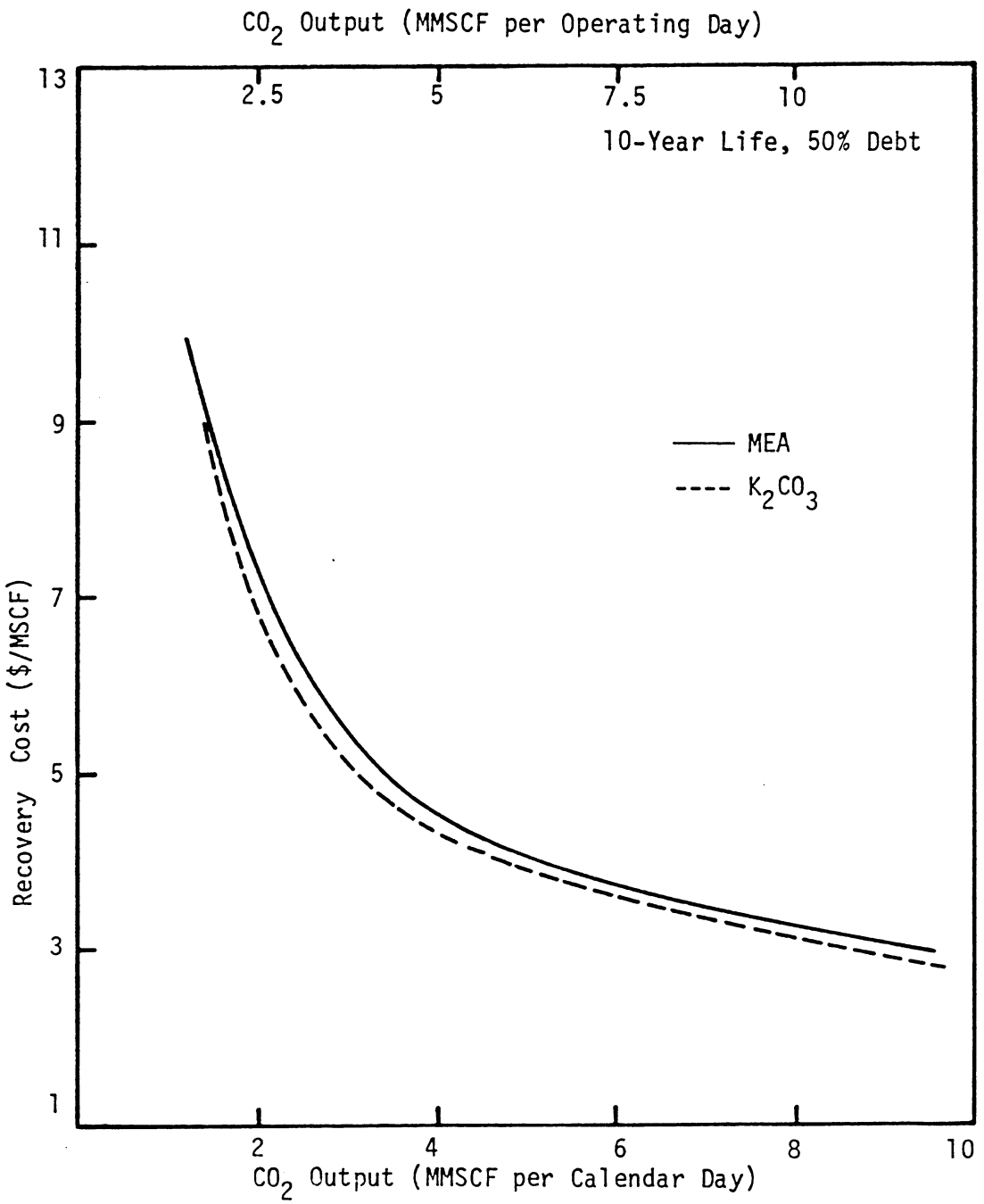


Exhibit 5-21: Recovery Cost for Gas-Fired Cement Plants

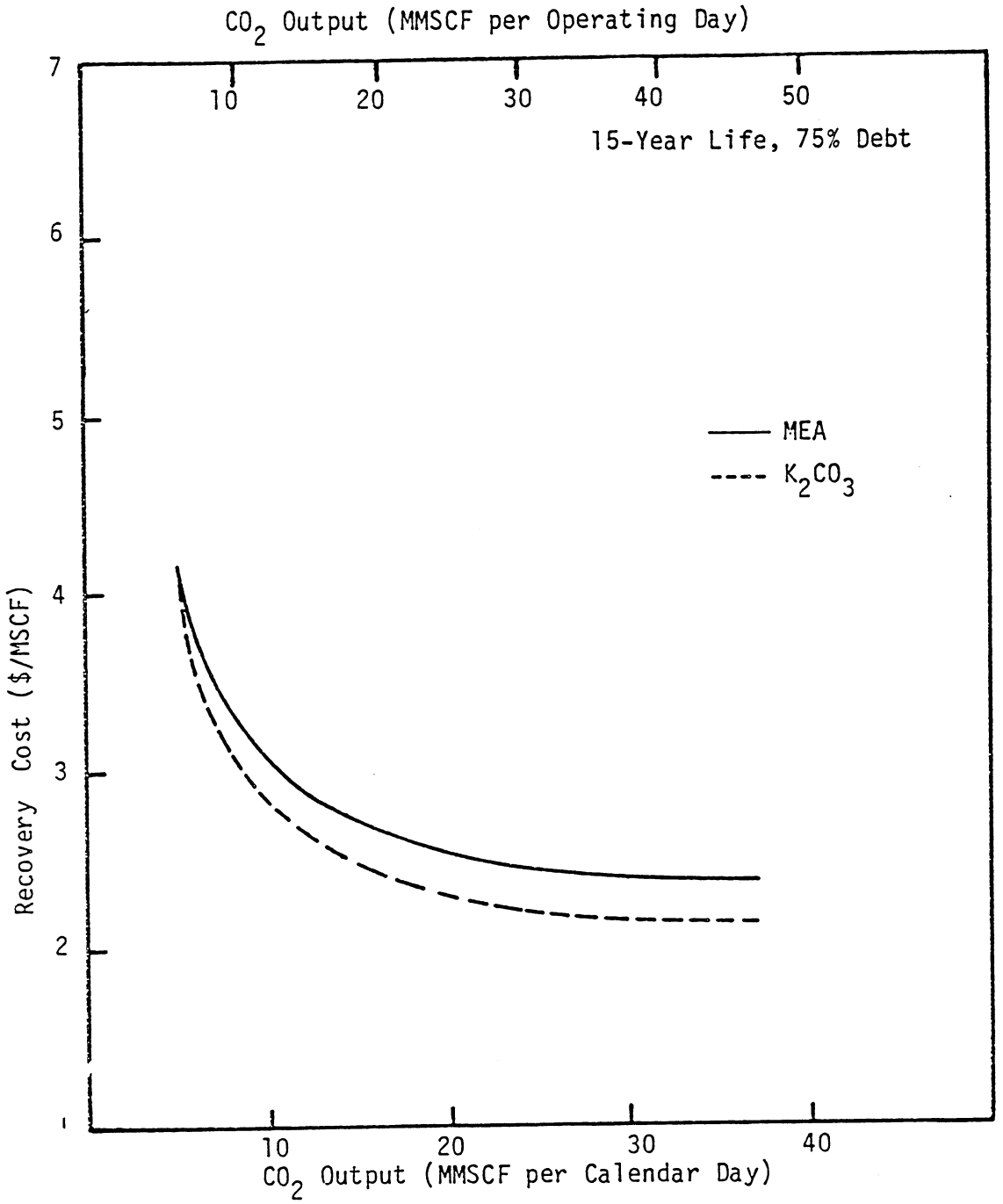


Exhibit 5-22: Recovery Cost for Refinery FCCU

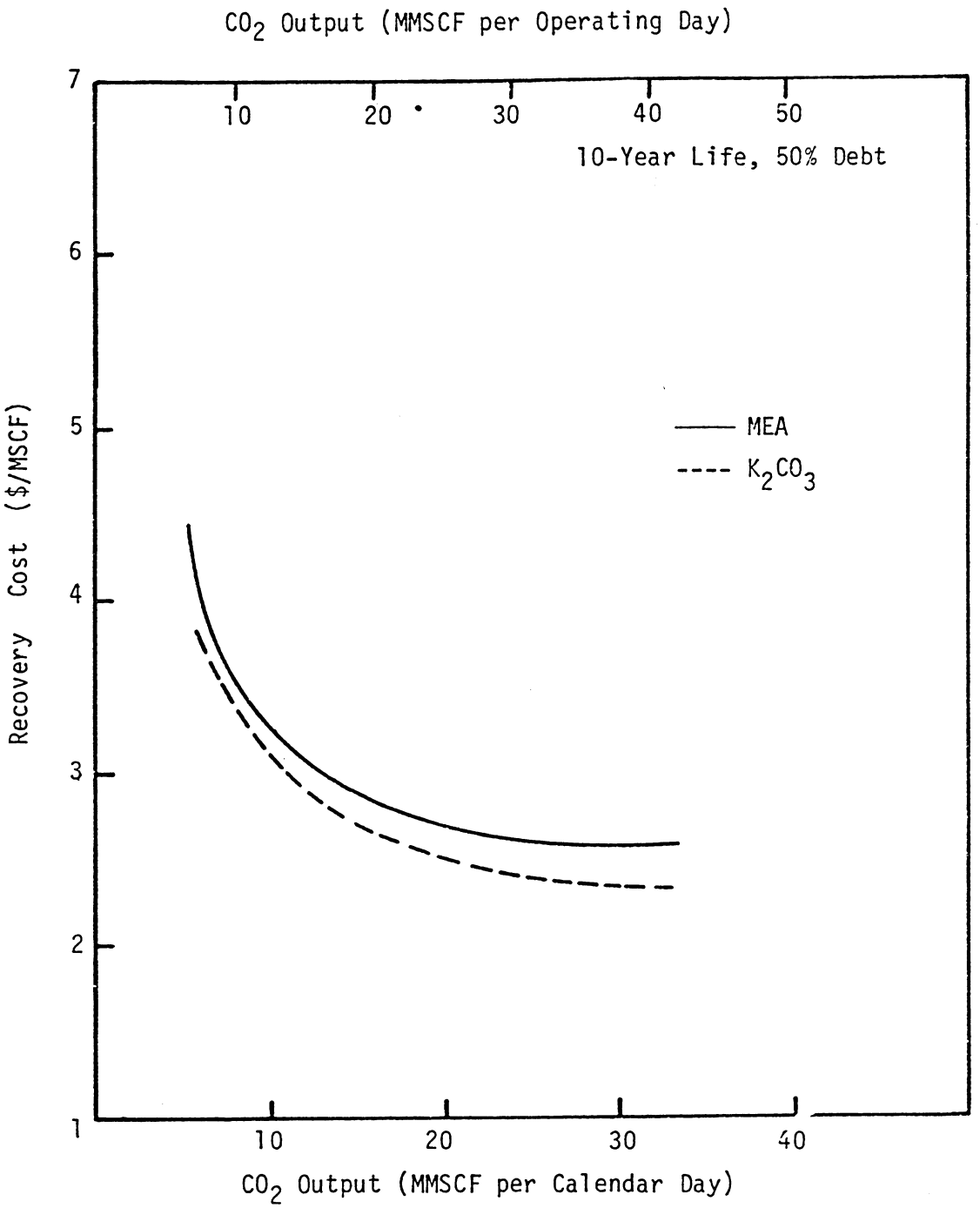


Exhibit 5-23: Recovery Cost for Refinery FCCU

5.7.2 Sensitivity Analysis

In order to estimate the effect the financial assumptions have on the CO_2 recovery cost, the recovery cost was calculated for various values of the financial parameters, changing only one parameter at a time. The base case used for this analysis was a gas-fired power plant with a K_2CO_3 system and 90% CO_2 recovery, with an output of 39.4 MMSCF per operating day. The results are presented below. The base case recovery cost is $2.29.

Parameter	Base Value	Alternate Values	CO_2 Recovery Cost ($/MSCF)	% Change From Base Case
Project Life	10 Years	15 Years 20 Years	2.17 2.11	-5 -8
Return on Equity	15%	10% 20%	2.19 2.41	-4 +5
Debt/Equity Ratio	.5	.25 .75	2.41 2.19	+5 -4
Loan Rate	.10	.05	2.24	-2
Capital Cost	$42.9MM	+20% -20%	2.43 2.15	+6 -6
Operating Cost	$18.6MM	+20% -20%	2.62 1.97	+14 -14

5.8 DISCUSSION ON CO_2 RECOVERY SYSTEM DESIGNS AND COSTS

Exhibits 5-10 and 5-11 show that as the amount of CO_2 recovered from a given source increases, the cost of the CO_2 in $/MSCF decreases. Cost is not a strong function of percent recovery, but appears to be nearing a limit as the percent recovery approaches 100.

Two important points need to be discussed. (1) The cost of recovered CO_2 is not a strong function of percent recovery. This means that if the by-product CO_2 source is large, it is not necessary to recover all the CO_2, but only enough to meet the expected demand. (2) Present development towards by-product CO_2 recovery is an extension of commercial CO_2 recovery from such sources as natural gas or coke ovens. High CO_2 recovery is required in these

commercial installations. It is not required in by-product flue-gas recovery. Present development generally uses plate tower absorption for high percent recovery. This increases operating costs by increasing tower pressure drop and most importantly by requiring purer solutions and hence, more stripping steam. However, point (1) shows that these parameters are not automatically necessary, and variations in absorption tower design should be investigated.

Exhibits 5-12 through 5-23 indicate that the cost of recovery at 30 to 90% CO_2 recovery is roughly the same for absorption by MEA or K_2CO_3 solutions. The capital costs are generally less with MEA, but stripping steam requirements and operating costs are less in the K_2CO_3 solution. Note that the accuracy of these estimates ($\pm$ 30%) are such that the costs are not significantly different. The costs for 99% recovery would undoubtedly favor the MEA over K_2CO_3 solution because of the high absorption coefficient for MEA. However, for 80% recovery where outlet $P_{CO_2} \geq 0.4$ psia, even present commercial practice indicates K_2CO_3 absorption is viable, as (P_{CO_2}) out ≥ 0.4 psia is specified as the commercial limit. Thus, the choice of absorbent for CO_2 recovery for EOR will probably depend on future development, using the factors of operability, low stripping costs, and simple process design.

It should also be pointed out that a large source is required to hold costs to a reasonable level. For example, if \$2.00/MCF CO_2 is a reasonable figure for economic recovery costs for EOR, then Exhibits 5-10 and 5-11 indicate only very large sources are potential CO_2 sources.

Exhibit 5-10 also indicates that the optimistic designs dramatically decrease costs, assuming they can be made commercially operable. The increase in concentration of active species, reductions in heat requirements (such as in the vacuum carbonate alternative), and the use of cheap fuel (such as lignite coal) are the important parameters in cost reduction. Capital cost reductions are also possible if a spray tower absorber design is used instead of a plate tower. This is especially reasonable in lieu of the non-necessity for high percent recovery. If \$1.50/MSCF CO_2 is the reasonable figure for economic recovery for CO_2, then development of the new design seems required for by-product CO_2 use in EOR.

In summary, it seems that further careful analysis and development work are needed for ultimate, economical recovery of by-product CO_2 for EOR. The extension of technologies developed for high-recovery situations in reducing gases must not be cursory.

5.9 DESCRIPTION OF COMPRESSION AND MOISTURE REMOVAL PROCESSES

The carbon dioxide recovered from the many sources indicated previously is basically pure and is saturated with water vapor. In order to produce pipeline quality CO_2, the wet CO_2 gas has to be dried to a maximum water vapor content of 50 ppm by volume(at 14.7 psia and 60°F) and must be compressed to 2000 psig for pipeline transportation. The drying process was designed for CO_2 with one of the two following conditions:

Ammonia Plants, Ethylene Oxide Plants, etc.

- Stream temperature = 250°F
- Stream pressure = 19 psia
- Initial water content = 7% by volume

Power Plants and Cement Plants

- Stream temperature = 110°F
- Stream pressure = 14.7 psia
- Initial water content = 7% by volume

5.9.1 Wet CO_2 Gas Drying Process

Given the above inlet and outlet conditions, many gas dehydration processes were considered. These processes included a liquid dehydration technique such as the glycol absorption system, and a solid adsorption system using silica gel or a molecular sieve as the adsorbent. A liquid dehydration system uses absorption in a liquid to remove water vapor from the gas stream, while a solid drying technique retains the water in a solid by adsorption.

In a typical liquid dehydration system, a glycol solution is used as the absorbent. A glycol solution is usually introduced to an absorber counter-current to the wet gas stream. Upon contact with the glycol solution, the gas leaving the absorber column will be virtually dry. The spent glycol solution will then be regenerated by boiling off the water absorbed in the solution.

A solid drying system is based on the concept that water can be removed from the gas phase if a highly active surface area exists on which water molecules can be selectively adsorbed. Any of a number of adsorbents (e.g., silica gel or activated alumina), which are selective for water rather than CO_2 adsorption, can be used . Regeneration of the moisture-laden adsorbent is

generally accomplished by desorbing the water vapor at a high temperature with a dry gas.

A thorough study of both drying techniques indicated that solid adsorption dehydration systems are best suited for drying CO_2 gas. This recommendation is based on the following factors:

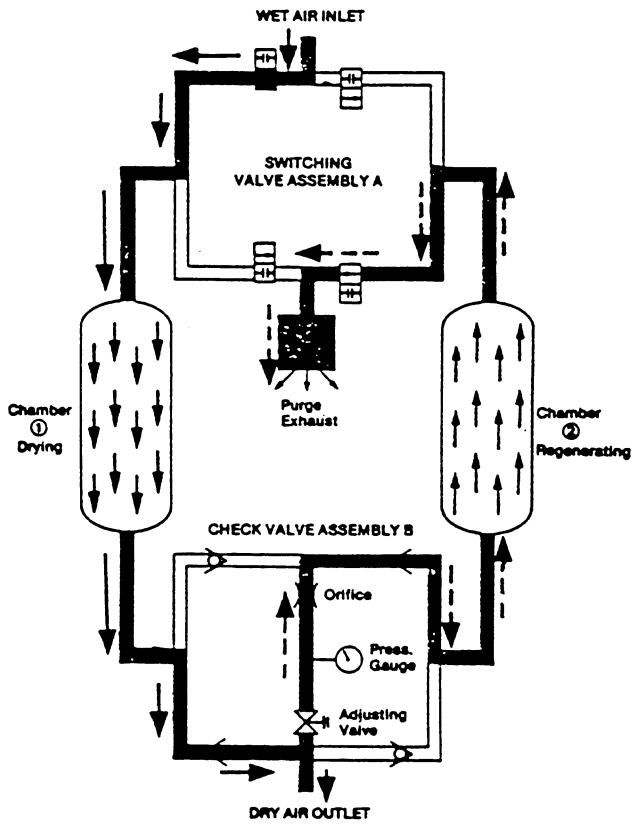
- Many problems have been encountered with liquid absorption in drying gases (e.g., degradation of the absorbent, spillage of liquid glycol, and inadequate mist extraction).
- According to a glycol dehydrator vendor (C.E. Natco[6]), technical information on drying CO_2 gas using a glycol system is not readily available and therefore, it is difficult to design such a system and estimate its cost.
- Contact with many industrial sources revealed that the current technology for drying CO_2 gas streams employs the solid adsorption system, using a wide variety of adsorbents.

For most adsorption drying systems, the required operating temperature ranges from 80 to 120°F and the operating pressure varies from 100 to 120 psia. The typical pressure drop across such a system is usually 20 psia. An adsorption dryer generally consists of two columns of dessicants. At any given time one column is in the operating mode, while the other is being regenerated. The spent dessicant bed is regenerated by heating up the adsorption bed with electric heater coils, and the evaporated water vapor is purged with a slipstream of the dry CO_2 gas produced. After the regeneration cycle is completed, the drying operation is then switched to the newly regenerated bed, while the other dessicant column is ready for regeneration. The drying-regeneration cycle usually lasts about eight hours. Exhibit 5-24 shows a typical two-tower dryer unit.

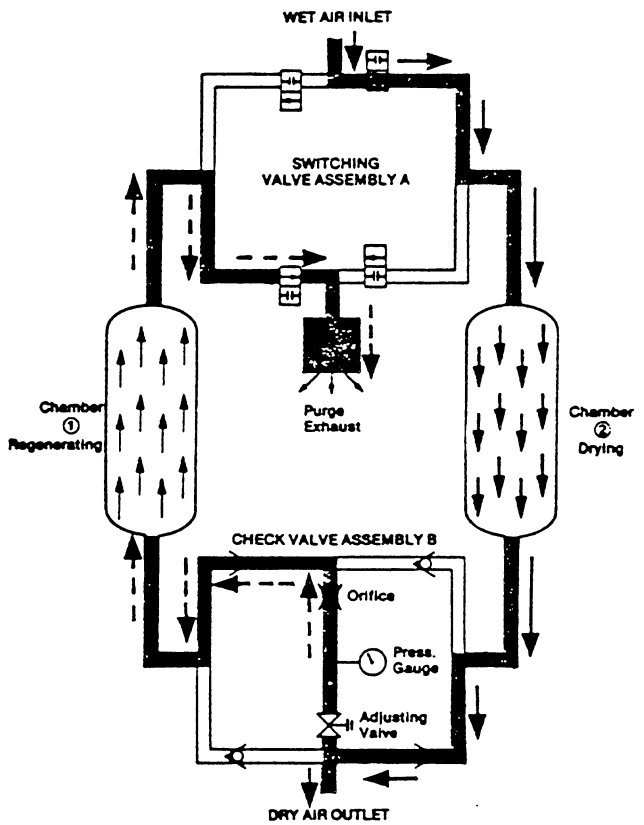
The dry CO_2 gas introduced into the chamber during the regeneration cycle is taken from a sidestream of the dry CO_2 gas produced from the dryer. This purging stream (about 2% of the dry CO_2 produced) can then be vented directly to the atmosphere or can be recycled to the wet inlet CO_2 gas stream, with the water vapor being condensed from the purge gas which is cooled and removed from the system. A dryer manufacturer has indicated that his firm offers both types of dryer purging units. The cost of a recycled-purge-gas unit is higher than a vented-purge-gas unit. The selection of the appropriate dryer unit depends on the economics of the CO_2 production process. The cost for a 10,000-SCFM CO_2 dryer is about $200,000.[34]

PURGE STREAM

DRY STREAM



5-24a



5-24b

Source: Ref. 33, Brochure.

Exhibit 5-24: Typical Two-Tower Dryer Operations

5.9.2 Overall Flow Diagram

The wet CO_2 gas stream received from the recovery process must be cooled and compressed. A schematic diagram for producing pipeline-quality CO_2 gas is illustrated in Exhibit 5-25.

The wet CO_2 gas stream received from a high purity source is at 250°F. By lowering the temperature of this stream to 100°F, the volumetric flow rate can be reduced significantly, and thus, the compressor designed for handling the gas stream can be smaller. The heat exchanger will be a shell-and-tube type. Process water will be used as the cooling medium and is assumed to be available at 70°F. Since the CO_2 gas stream is saturated with water, condensed water may react with CO_2 to form corrosive carbonic acid which will damage the process equipment. To avoid corrosion problems, stainless steel is recommended as the construction material for the heat exchanger.

It has been recommended that the wet CO_2 gas stream pass through the tube side, while process water is passed through the shell side. In such a design, the only components of the cooler to be made of stainless steel are the tubes, while the shell can be made of regular carbon steel. This design will therefore, minimize the equipment cost.

The cost for such a water cooler with surface area of 1500 ft^2 is quoted at an average price of $28,000.[3,10] For a cooler of a different size, the cost will vary according to the design's surface area. Cost estimation of different sizes of heat exchangers will be discussed in a later Section.

The design and selection of different types of compressors (i.e., centrifugal, axial, and reciprocating compressors) for this process are governed by the following design constraints:

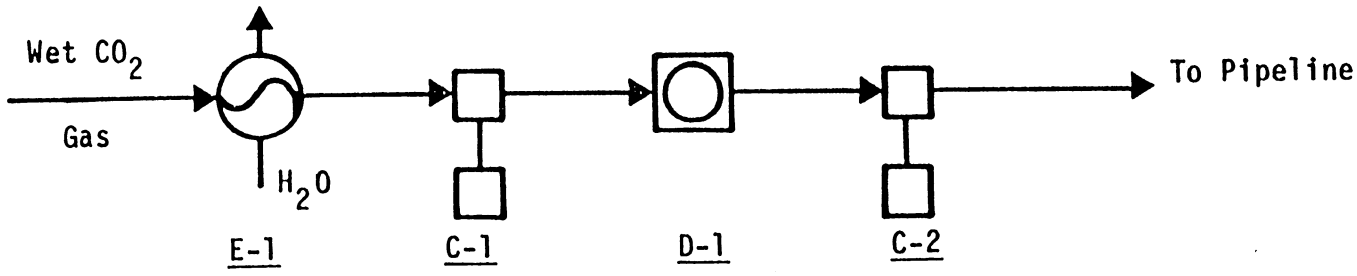
1. Reciprocating compressors can handle gas volumetric flow rate of 100 SCFM to 10,000 SCFM.

2. A reciprocating compressor is more efficient than a centrifugal compressor in compressing the gas to a high pressure (e.g., P>1500 psig).

3. Centrifugal compressors are best suited for handling a large volumetric flow rate of gas (from 20,000 SCFM to 150,000SCFM).

4. After each compression stage, the temperature of the compressed gas stream is increased, but due to mechanical limitations, the gas temperature should be kept below 400°F. If the gas temperature exceeds this limit, interstage cooling is required.

Exhibit 5-25: Diagram of the CO_2 Gas Drying Process



E-1 = heat exchanger (water cooler)

C-1 = compressor 1 (from 17 psia to 135 psia)

D-1 = dryer

C-2 = compressor 2 (from 115 psia to 2000 psia)

5. The adiabatic efficiency of the compressor is assumed to be 75%.

6. Where high-pressure steam is available and is required for a CO_2 removal system (such as in the case of CO_2 recovered from powerplant flue gas), noncondensing steam turbines are used as drivers for the compressors. Otherwise, electric motors will be used as drivers (sources of pure CO_2) without the need for additional steam. The required steam is assumed to be available in the form of superheated steam at 750 psig and 1000°F, and the exit steam from the turbine will be at 65 psig and 502°F.

With these design constraints the compressors for a number of plants have been developed. For small CO_2 gas streams ranging from 1 to 50 MMSCFD, the drying process for wet CO_2 is basically the same as that of Exhibit 5-25. It consists of a heat exchanger, a compressor to boost the stream pressure from 17 to 135 psia, a dryer, and another compressor to compress the gas from 115 to 2000 psia. For a large flow rate of CO_2 gas (e.g., flow rate $\geq$100 MMSCFD), it has been recommended that the stream be split into smaller streams operating in parallel and having equal flow rates. Such a design will ensure a continuous production of CO_2 gas with a minimum production capacity of 50%

5.10 ECONOMIC EVALUATION OF COMPRESSION AND MOISTURE REMOVAL

5.10.1 Capital Cost

The basic process train for drying and compressing a stream of pure, wet carbon dioxide consists of four major pieces of equipment which were described in Section 5.9. Costs were estimated for these pieces of equipment using two basic methods -- extrapolating recent quotes obtained from vendors and using Guthrie's book on cost estimation.[22] Once the basic equipment costs were estimated, then the total installed cost of the plant was obtained through the use of factors that account for direct installation costs (materials and labor), indirect installation costs, and contingency and fees, as shown in Appendix P. The plant was designed to operate at 80% nominal capacity.

Heat Exchanger: Quotes were obtained from two different vendors for a heat exchanger of the recommended design. The two quotes were very similar. For extrapolating this cost to smaller exchangers, a capacity exponent (on the area of 0.62) was used, taken from Perry's handbook,[37] and for larger exchangers, 0.95 was used, per the vendor's recommendation.

Molecular Sieve Dryer: Quotes were obtained from two different vendors for complete molecular sieve dryer units. The quotes were very similar. Costs were obtained both for dryers (relatively small--less than 5000 SCFM) in which the gas used for purging the sieve (part of the CO_2) is vented and for dryers (so-called split flow) in which the CO_2 used for purging is cooled to condense the water, and is recovered. These quotes were extrapolated with the use of recommended capacity exponents.

Compressor: Quotes were obtained from vendors for two- and three-stage reciprocating compressors with motor drives. These quotes were extrapolated with recommended capacity exponents (on the flow rate). For centrifugal compressors and reciprocating compressors with turbine drivers, quotes were not provided by the vendors. Costs were estimated for these types of compressor systems from the information in Guthrie's manual.[22]

As the information in Guthrie's book dates from 1970, an escalation index had to be applied to bring these costs up-to-date. For this purpose, the equipment index for pumps and compressors from Chemical Engineering[7] was used to bring 1970 costs up to first quarter 1981 costs. It should be noted that this index increased much faster than either the index for equipment as a whole or the plant cost index. Guthrie's costs indicated that motor drivers cost more than turbine drivers.

Although the costs estimated from Guthrie compared fairly well with the vendor's quotes at the prescribed capacity, the two types of estimates extrapolated rather differently. The vendor recommended a capacity exponent of 0.75 compared with an exponent of less than 0.6 for Guthrie's correlation.[22] The result was that for large compressor systems, the extrapolation of the vendor's quote is larger than the estimation from Guthrie, creating some inconsistency between the estimates for flue gas systems (which utilize turbine-driven compressors--cost estimations from Guthrie) and systems for smaller CO_2 sources (which use motor-driven compressors--extrapolated vendor's quotes).

Total Installed Costs: Equipment costs are not all that is involved in building a plant. Direct installation costs, consisting of materials and labor for such items as piping, concrete, steel, instruments, electricity,

insulation, and paint must be added; and these costs are frequently estimated on the basis of the type of equipment to be installed. Factors for these costs were obtained from Guthrie.[22]

An example calculation of the determination of size and cost of heat exchangers, compressors, and dryers is given in appendix Q.

The cost basis for developing the capital equipment costs by scaling factors is shown in Exhibit 5-26. A summary of the capital equipment costs is given in Exhibit 5-27.

5.10.2 Operating Costs

The yearly operating costs are determined by applying the assumptions given in Appendix P to the yearly electricity, water, and steam requirements, and manpower. A summary of the utility requirements and operating costs is given in Exhibit 5-28.

The cost of steam (for power plants and cement plants) was obtained by determining the cost of coal required to produce the steam in the existing power plant boilers (the extra coal represents only 5% of the boiler output so no extra boiler cost was included).

5.10.3 Revenue Requirements

The required selling price to achieve a 15% rate of return on equity, given the capital and operating costs of Sections 5.10.1 and 5.10.2 and the basic financial assumptions of appendix P, is shown in Exhibit 5-29 for power and cement plants, and in Exhibit 5-30 for ammonia plants, hydrogen plants, and other high purity sources. The prices are shown both for an operating factor of 80% (equivalent to 7000 hours per year for a former plant) and also on a calendar-day basis, since the CO_2 demand figures are given on a calendar-day basis.

The main reason for the lower cost for power plants and cement plants is the use of steam to drive the compressors.

1. Heat Exchanger		
Area < 2000 ft^2	Cost = $\$28,000 \left(\frac{A}{1466}\right)^{0.62}$	
Area > 2000 ft^2	Cost = $\$28,000 \left(\frac{A}{1466}\right)^{0.95}$	
2. Compressors		
3-stage reciprocating compressor operating between 115 and 2000 psia (includes motor, intercoolers, etc.)	Cost = $\$385,000 \left(\frac{SCFM}{3500}\right)^{0.75}$	
2-stage reciprocating compressor motor driver	Cost = $\$320,000 \left(\frac{SCFM}{3500}\right)^{0.75}$	
Ref. 30, p.165-171		
3. Dryer		
non-split flow:		
flow rate < 7.5 MMscfd 5200 SCFM	Cost = $\$34,500 \left(\frac{SCFM}{743}\right)^{0.5}$	
split flow:		
flow rate < 10,000 SCFM	Cost = $\$200,000 \left(\frac{SCFM}{10,000}\right)^{0.75}$	
flow rate > 10,000 SCFM	Cost = $\$200,000 \left(\frac{SCFM}{10,000}\right)^{0.85}$	

Exhibit 5-26: Cost Basis for Determining Scaling Factors for Compression and Drying Costs

CO_2 Nominal Flow Rate (MMSCFD) :	High Purity Sources					Flue Gas			
	1	5	10	20	50	20	50	100	200
Heat Exchanger									
Area (sq ft)	105	530	1050	2118	5270	--	--	--	--
Cost ($K)	5.5	15	23	39.7	95				
Installed Cost	12.6	34.5	52.9	91.3	218.5				
Compressor 1									
Type	Reciprocating	-------		Centrifugal	--	-------	-------	-------	-------
Number of Stages	2	2	2	6	6	6	6	6	6
Power (Hp)	172	857	1715	3487	8960	3487	8960	8960	8960
Driver Type	Motor	-------	-------	-------	-------	Turbine	-------	-------	-------
Number of Units	1	1	1	1	1	1	1	2	4
Cost ($K)	100	335	563	949	1762	864	1369	2738	5476
Installed Cost	156.7	524.3	880.8	1485	2758	1352	2142	4284	
Dryer									
Type	Non-split Flow		Split Flow	-------	-------	-------	-------	-------	-------
Number of Units	1	1	1	1	1	1	1	2	4
Cost ($K)	34.5	77.2	160	280	610	280	610	1220	2440
Installed Cost	54.0	120.8	250.4	438.2	954.6	438.2	954.6	1909.2	
Compressor 2									
Type	Reciprocating	-------	-------	-------	-------	-------	-------	-------	-------
Number of Stages	3	3	3	3	3	3	3	3	3
Power (Hp)	196	980	1960	3942	10024	3942	10024	10024	10024
Driver Type	Motor	-------	-------	-------	-------	Turbine	-------	-------	-------
Number of Units	1	1	1	1	1	1	1	2	4
Cost	131.3	439.3	738	1177	2465	892.7	1394	2788	5576
Installed Cost	205.6	687.5	1154.9	1842.3	3857	1397	2182	4364	8728
Direct Installed Equipment Cost ($K)	428.9	1367	2339	3856.8	7788.1	3187	5279	10558	21116
Working Capital (6% of above)	25.7	82.0	140.3	231.4	467.3	191.2	316.7	633.5	1267
Other Indirect Costs (Interest, Engineering Fee, Contractor's Fee, Process Contingency --65% in Total)	278.8	888.6	1520	2507	5062	2071.6	3431.4	6862.7	13725.4
TOTAL CAPITAL ($K)	733.4	2337.6	3999.3	6595.4	13317.3	5449.8	9027.1	18054.2	36108.4

Exhibit 5-27: Capital Equipment Cost Summary for Compression and Drying of Carbon Dioxide

CO_2 Nominal Flow Rate (MMSCFD) :	High Purity Sources					Flue Gas			
	1	5	10	20	50	20	50	100	200
Steam Requirement (10^9 lbs/yr)	-	-	-	-	-	.48	1.2	2.4	4.8
Coal (Tons/year)	-	-	-	-	-	14,093	34,450	68,900	137,800
Coal Cost ($K/yr)	-	-	-	-	-	132.3	331	661	1323
Electricity Consumption (10^6 KWH/yr)	2.1	10.3	20.6	41.7	106	1.4	3.4	6.9	13.8
Electricity Cost ($K/yr)	74.2	359.9	719.7	1458	3710	41.3	103.2	206.4	412.8
Water Consumption (Million gal/yr)	56	280	560	1540	3900	1230	3120	6240	12480
Water Cost ($K/year)	5.6	28.0	56.0	154.0	390.0	123.2	310	620	1240
Direct Operating Manpower	1	1	1	1	1	.4	.43	.5	1
Labor Cost (Incl. Supv. & Admin.) ($K/yr)	285	285	285	285	285	118.5	122.2	142.4	285
Local Taxes & Insurance	19.5	62.0	106.1	175.0	353.4	149.9	239.6	479.1	958.2
Maintenance & Supplies ($K/yr)	17.0	54.1	92.6	152.7	308.4	126.2	209.1	418.1	836.2
Total Operating Cost ($K/yr)	401.3	789	1259	2225	5047	691	1315	2527	5055

Exhibit 5-28: Operating Cost Summary for Compression and Drying of Carbon Dioxide

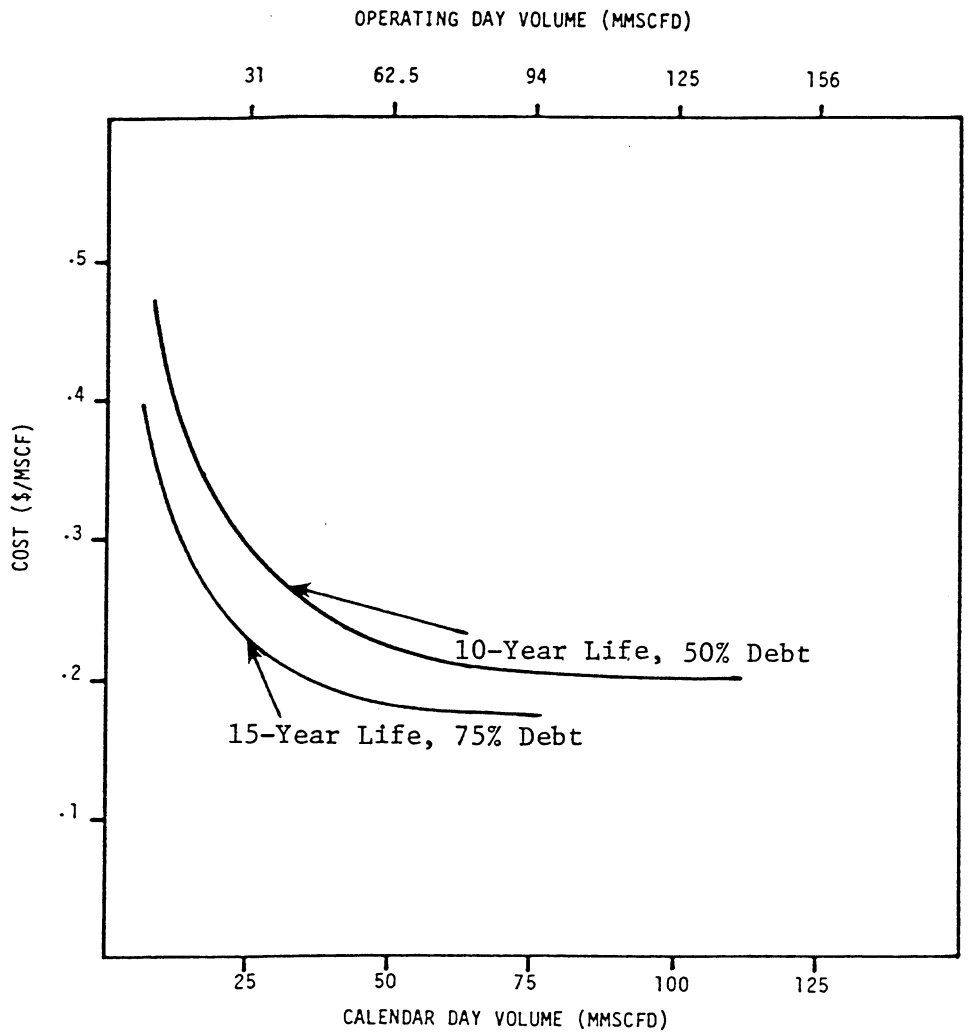


Exhibit 5-29: Compression and Drying Cost (Using Steam for Compression)

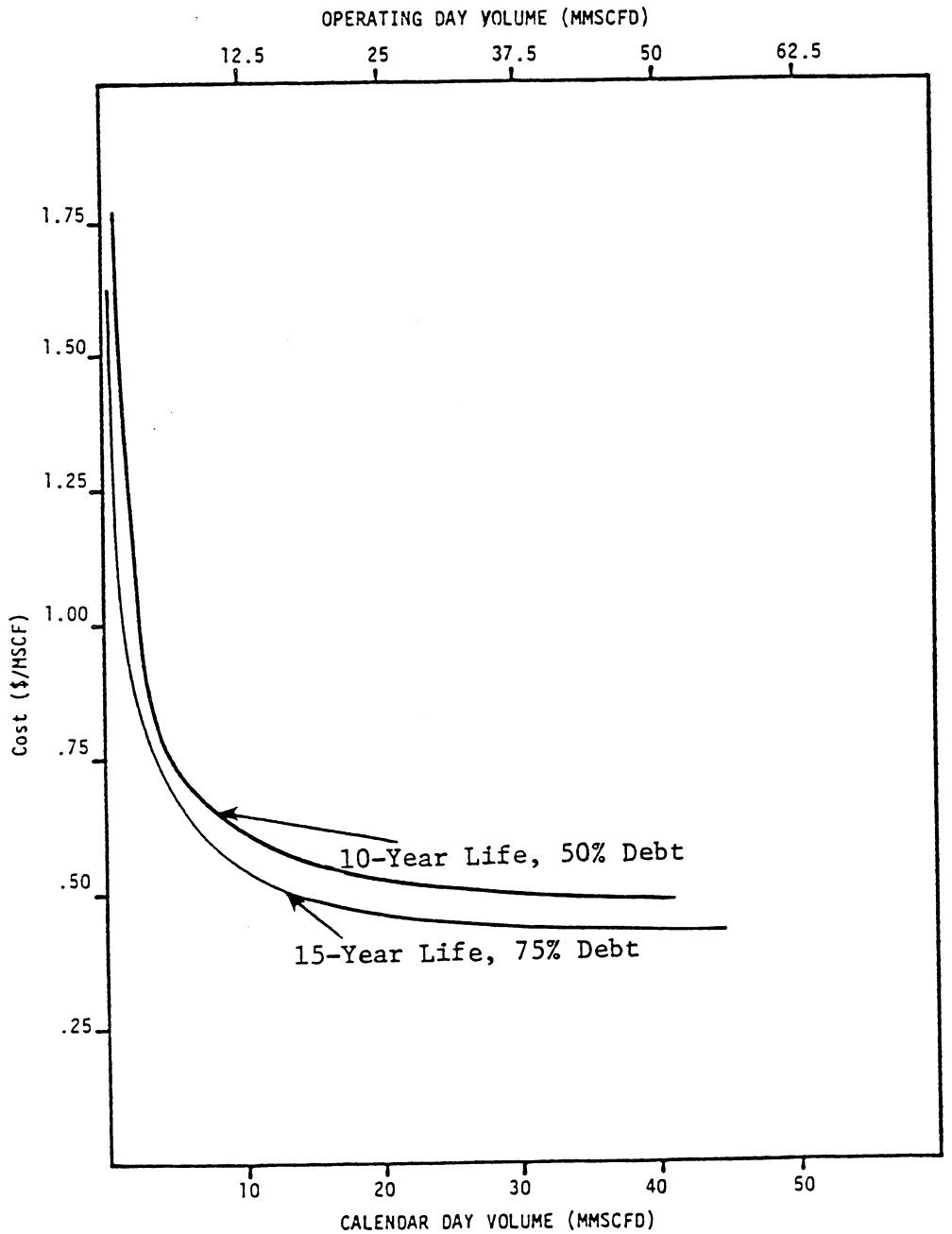


Exhibit 5-30: Cost for Compression and Drying (for 15% Rate of Return, Using Electrically Driven Compressors)

6. CARBON DIOXIDE TRANSPORTATION, STORAGE AND INJECTION COSTS

6.1 TRANSPORTATION COST

The transportation modes considered in this study are pipeline, truck, rail, and barge. The analysis was based on results of previous studies where possible, and provides only a preliminary estimate.

In order to evaluate a specific CO_2 flooding prospect, a more detailed analysis, including site specific factors such as terrain and accessibility, needs to be considered.

6.1.1 Pipeline

Based on previous studies by Pullman-Kellogg[41] and Science Applications, Inc.,[45] a super-critical pipeline carrying CO_2 in vapor form was assumed, with pressures ranging from 1400 to 2000 psi. The line size was determined from the SAI report,[45] which is based on very low average velocities with attendant low pressure losses and minimal compression requirements.

Flow Rate (MMSCFD)	Pipeline Nominal Diameter (in)
500	30
250	22
125	16
50	10
20	8
10	5
5	4
2	3
1	2

The following assumptions were made in determing the cost of transportation:

- Flat terrain.
- The line would have a 20-year life (the costs for a ten-year life are also shown).
- The construction time is two years.
- The line would operate at full capacity. Since the CO_2 requirements for an individual field decrease with time, this assumption implies that several neighboring fields will be developed in such a way as to maintain a steady CO_2 requirement.

- Zero salvage value.
- Total investment cost of $23,800/inch nominal pipeline diameter per mile length for the entire pipeline system (in first quarter-1981 dollars). NOTE: This figure was obtained by escalating the value of $20,000/inch nominal pipeline diameter per mile of Ref. 45 by 19%, in order to convert from mid-1979 dollars to first quarter-1981 dollars (using the Oil and Gas Journal Pipeline Cost Index[38] and the CPI[2]).
- Depreciable capital is 86.8% of total investment. (Based on data from the Oil and Gas Journal[38]).
- Yearly operating cost is 1% of the total investment cost.
- Operating factor of 80%.

The basis of the financial analysis is given in Appendix P. The costs are summarized in Exhibit 6-1.

Because of the assumptions made, the transportation cost is a linear function of distance for a fixed flow rate. Exhibits 6-2 and 6-3 show the cost for a 100-mile pipeline at any given flow rate. The cost for any other distance can be obtained by:

$$\text{cost (x miles)} = \frac{X}{100} \text{ (cost for 100 miles)}$$

6.1.2 Truck Transport

Tractor-trailer distribution of CO_2 was investigated, using existing insulated steel containers at 300 psi. The lowest transportation cost is achieved by transporting the CO_2 in liquid form at 0^oF (density 63.8 lb/cu ft).

Distribution of CO_2 in vapor form by a high pressure (1000 psi) trailer at 67° was also considered (52 lb/cu ft density). Such a trailer could be constructed using current technology, although it is not presently available.

The methodology used is based on Ref. 45, but all costs have been updated to first quarter-1981 dollars, and different financial assumptions are used. The details are discussed below.

Flow Rate (MMSCFD)		Distance (Miles)	Diameter (Inches)	Capital Cost ($MM) Including Interest	Transportation Cost ($/MCF)	
Operating Day	Calendar Day				20-Year Life	10-Year Life
500	400	100	30	78.5	.11	.12
250	200	100	22	57.6	.16	.19
125	100	100	16	41.9	.23	.26
50	40	100	10	26.2	.36	.43
20	16	100	8	21.9	.72	.84
10	8	100	6	15.7	1.08	1.26
5	4	100	4	10.5	1.42	1.66

Exhibit 6-1: Pipeline Transportation Costs

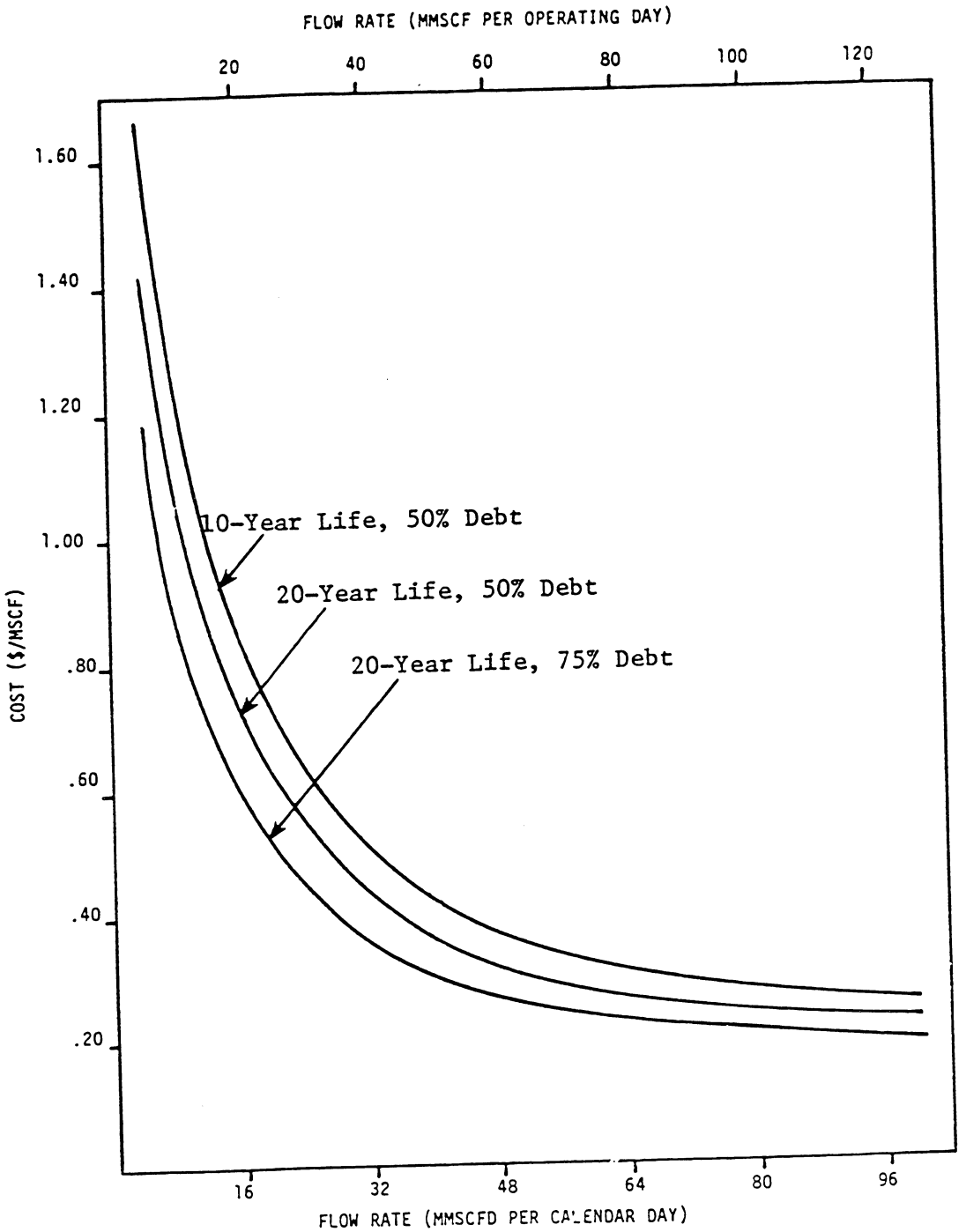


Exhibit 6-2: Transportation Cost for 100-Mile Pipeline at Low Flow Rates

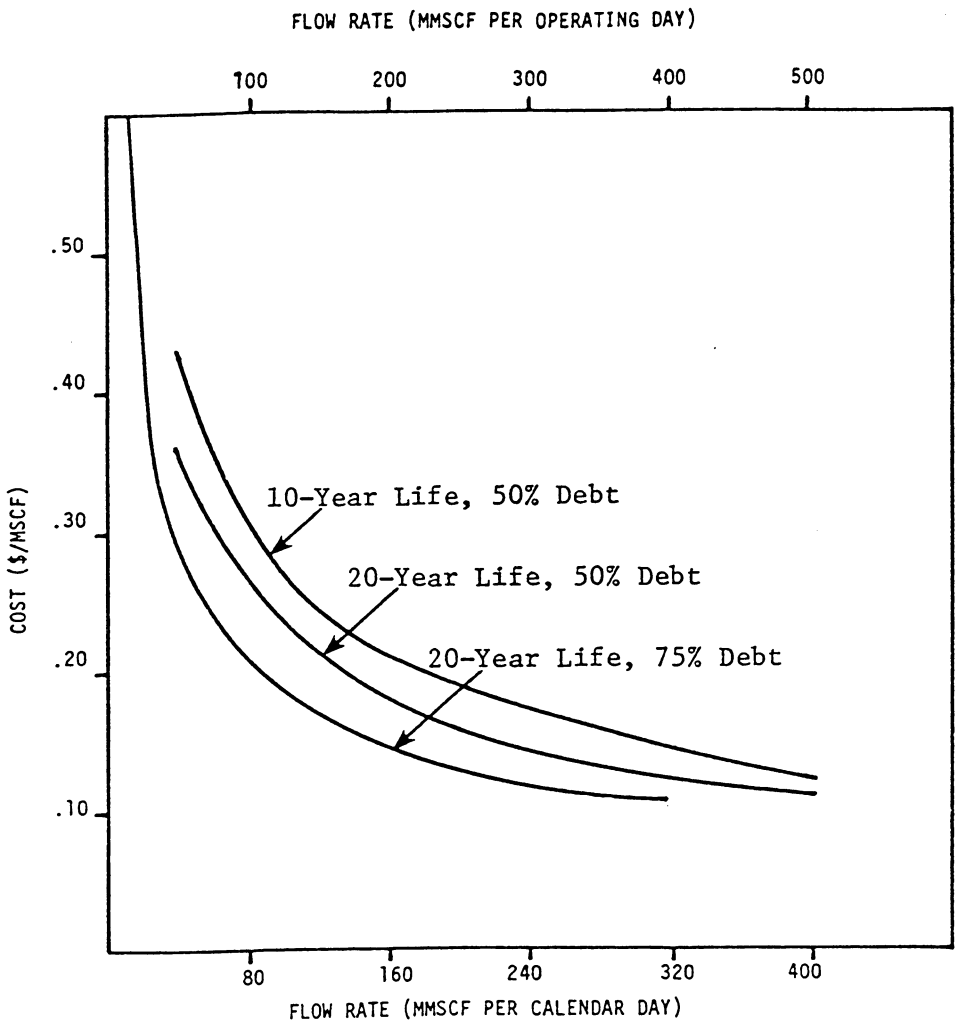


Exhibit 6-3: Transportation Cost for 100-Mile Pipeline at High Flow Rates

Trailer size: 5900 gallons

Trailer weight limit: 44,000 lbs.

Trailer capacity: .38MMSCF @ 300 psi and $0^{o}F$ liquid

.35MMSCF @ 1000 psi and $67^{o}F$ vapor

(The first case above is limited by weight)

Trailer fill time: 0.75 hour

Trailer hitch and turn around time: 0.25 hour

Trailer drain time: assumed to be a function of CO_2 demand rate

Average travel time (D=one way haul,miles): 2 X D/(30 mph)hr

Trailer availability: 95%

Tractor availability: 64%

Under these conditions, the number of tractors (T) and trailers (TL) are given by:

$$T = (0.5Q + QD/15)/(15.36C)$$

$$TL = 1.0526 + QD/(342C) + .0439\ Q/C$$

where Q is demand rate (MMSCFD)

C is trailer capacity (MMSCF)

D is one-way haul distance

It is also assumed that tractor and trailer usage can be prorated over similar EOR projects; i.e., "fractional" tractors and trailers are charged to each project.

The costs (in mid-1979 dollars[45]) are:

Tractor: $50,000

Trailer: $45,000 ($90,000 for 1000 psi trailer)

Driver Labor: $30,000 per year X 4 drivers/tractor

Tractor Operation: $0.35/mile (fuel, tire, maintenance)

Trailer Operation: $0.10/mile

Tractor Fixed Cost: $6,000/year

Trailer Fixed Cost: $1,000/year

The transportation costs were calculated using the financial assumptions of Appendix P, with a seven year vehicle life and straight line depreciation.

These costs were then escalated 23% to first quarter-1981 dollars, based on the following:

Driver Labor: 50% of total cost	=	8.0%
Escalated by 16%		
(Based on average weekly earnings)		
Vehicle Cost: 10% of total cost	=	3.3%
Escalated by 33%		
(Based on manufacturer's quote)		
Operating Costs: 40% of total cost	=	11.6%
Escalated by 29%		
(Based on CPI for Transportation)		
		22.9%

The results are given in Exhibits 6-4, 6-5, and 6-6. The 300 psi truck carrying liquid CO_2 has the cheapest transportation cost. However, if the cost of liquefaction is included (approximately \$0.43/MSCF at 300 psia and 0^oF), then the 1000 psia truck has a cheaper delivered CO_2 cost.

Comparison of pipeline and truck transportation costs for low CO_2 demand rates indicates that the pipeline is the cheapest method at low distances (0-30 miles), and also at large distances (beyond the range of single shift driving; i.e., approximately 100 to 150 miles). At CO_2 demand rates greater than 20 MMSCFD, the pipeline is the cheapest form of transport for all distances.

6.1.3 Rail

There are three considerations in transporting carbon dioxide by rail: cost, transit time, and availability.

Cost

Carbon dioxide transported by rail is normally in liquid form, in special tank cars such as Department of Transportation Class 105A500W, which have an

Demand (MMSCFD)	300 psia, 0°F, saturated liquid One-Way Distance (miles)					
	5	10	20	40	80	100
0.5	.23	.28	.37	.56	.93	1.12
1.0	.17	.21	.31	.49	.87	1.05
2.0	.13	.18	.27	.46	.83	1.02
5.0	.11	.16	.25	.44	.81	1.00
10.0	.11	.15	.25	.43	.81	0.99

Demand (MMSCFD)	1000 psia, 67°F, saturated vapor One-Way Distance (miles)					
	5	10	20	40	80	100
0.5	.31	.38	.53	.77	1.21	1.41
1.0	.21	.27	.38	.62	1.03	1.24
2.0	.16	.21	.32	.53	.95	1.16
5.0	.12	.17	.27	.48	.90	1.11
10.0	.11	.16	.26	.47	.87	1.08

Exhibit 6-4: Summary of Transport Costs for Truck-Delivered CO_2 ($/MSCF)

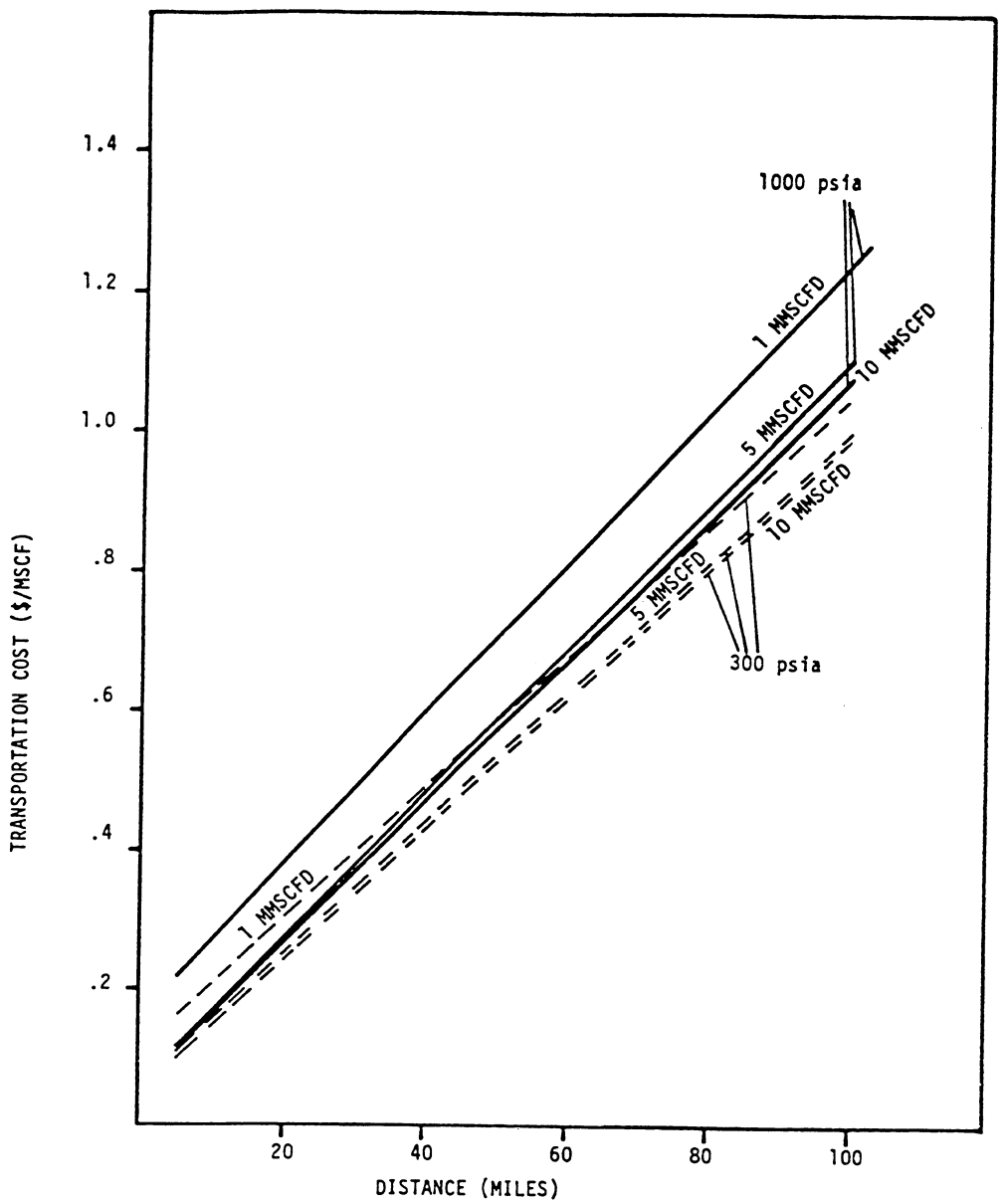


Exhibit 6-5: CO_2 Transportation Cost as a Function of Distance

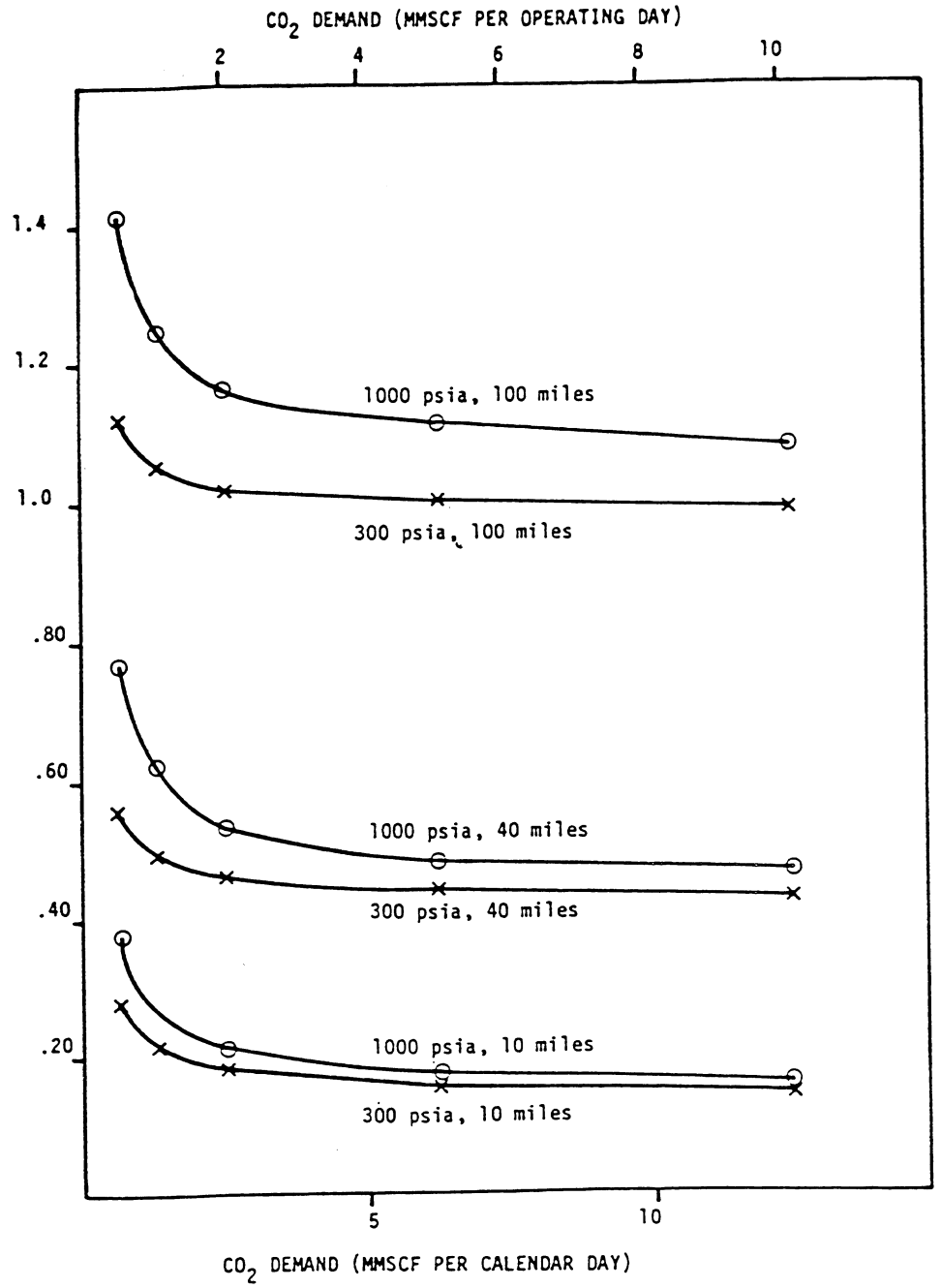


Exhibit 6-6: CO_2 Transportation Cost as a Function of Demand Rate

83.25 ton maximum product weight, and a 375 psi working pressure. Assuming liquid CO_2 at 300 psi and 0^oF, this corresponds to a volume of 1.4 MMSCF.

The cost of leasing such a car was quoted by GATX[17] as $650/car/month (however, the cars may have to be built specially for each customer, since the number of available cars is limited). This cost is partially offset by a credit of $75/100 loaded miles against the railroad freight rate. This corresponds to 5.36 cents/MSCF per 100 loaded miles.

Freight rates were obtained directly from the rate department of two railroads: Burlington Northern; and Atchison, Topeka and Santa Fe.

Rates were obtained between several sources and destinations. For the Williston Basin, the average cost from a large power plant at Stanton, ND, was $1.74/MSCF ($1.56/MSCF with lease car credit), over a distance of 341 rail miles (generally much longer than the straight line or road distance). This cost was based on a commodity rate. The average straight line distance between the same points is 115 miles; i.e., the rail miles are three times the straight line miles. For this distance, the truck transport cost would be $1.13 (for 10 MMSCFD), while the pipeline cost would be $0.83/MSCF (16 MMSCFD) to $0.26/MSCF (100 MMSCFD).

From Colstrip, MT, to the Williston Basin (400 rail miles average), a class 30 rate was quoted, averaging $4.27/MCF (4.06 with lease car credit). The straight line distance here averages 286 miles, giving a pipeline cost of $2.06/MCF for 20 MMSCFD.

For the Permian Basin, the following average rates were calculated based on the quotes reviewed.

Rail Miles	Cost ($/MSCF)	Cost/100 miles
150	.87	.58
300	1.30	.44
500	1.75	.35

The average rail miles are 1.23 times the straight line miles. For a stright line distance of 122 miles, corresponding to 150 rail miles, the pipeline cost would vary from $.87/MSCF at 12 MMSCFD, to $.24/MSCF for 100 MMSCFD.

Because of the complexity of rail freight rates, and the possibility of cheaper rates for large, steady volumes of traffic, no general cost for rail

transport as a function of distance and volume can be given. However, rail transport does appear to be more expensive than pipeline or road transport.

Transit Time

The average daily freight car mileage in 1979 was 59.2 miles[2]. This would correspond to six days for a 340-mile rail haul. However, on medium length hauls entirely on one railroad, the average would probably be higher.

If each car makes three round trips per month, then the leasing cost amounts to 15.5 cents/MSCF, which must be added to the freight charge above.

Availability

While the majority of the CO_2 by-product sources are adjacent to rail-lines, many of the target reservoirs for CO_2 flooding are 20 miles or more from a rail-line, necessitating truck or pipelines for the final distribution, at an additional cost.

The identification of fields suitable for rail transport will have to be done on an individual project basis, and is beyond the scope of this report.

The chief advantage of rail over other forms of transport is the fact that no initial capital investment is necessary. This makes it especially attractive for pilot projects, where the main production phase, if the project is successful, could then use a pipeline for transport.

6.1.4 Barge

Barge transport is not feasible for the CO_2 target reservoirs identified in this study, since there are no commercially navigable waterways in the vicinity of the oil fields. (Barge transport could be feasible in Louisiana and Mississippi, but no details on reservoirs amenable to CO_2 flooding in those areas were available for this study.) A map of commercial navigable waterways of the United States published by The American Waterways Operators Inc., Arlington, VA, is shown as Exhibit 6-7.

6.2 CO_2 STORAGE AND INJECTION COSTS

Except for mini- or pilot-tests, the CO_2 for EOR projects will be supplied in gaseous form and there will be no need for onsite CO_2 storage since CO_2 can be stored in the pipeline by increasing the pressure.

INSERT
EXHIBIT G-3 MAP

PG 171

If the CO_2 is supplied in liquid form, which is generally the case with experimental field tests such as mini- and pilot-tests, the CO_2 would be stored in storage tanks. A typical schematic diagram for CO_2 storage and injection facilities for Gulf Oil Company's mini-test at the Little Knife Mini-Test in North Dakota is presented in Exhibit 6-8.

For larger size field tests, it would be more economical to supply CO_2 in gaseous form through pipelines. Depending on the depth and pressure requirements at the field, pipeline pressures can be adjusted.

Once CO_2 has been delivered to the target oil field, the remaining costs are associated with the injection, separation, and compression of the CO_2 recovered from the associated gas. These costs do not depend on the original source of the CO_2, and so do not need to be considered in comparing the cost of alternative sources. However, these costs will affect the final oil selling price required to recover costs. Accordingly, only a brief summary of these costs is given.

The costs of recycled CO_2 in mid-1980 dollars have been estimated by Lewin and Associates[25] as follows:

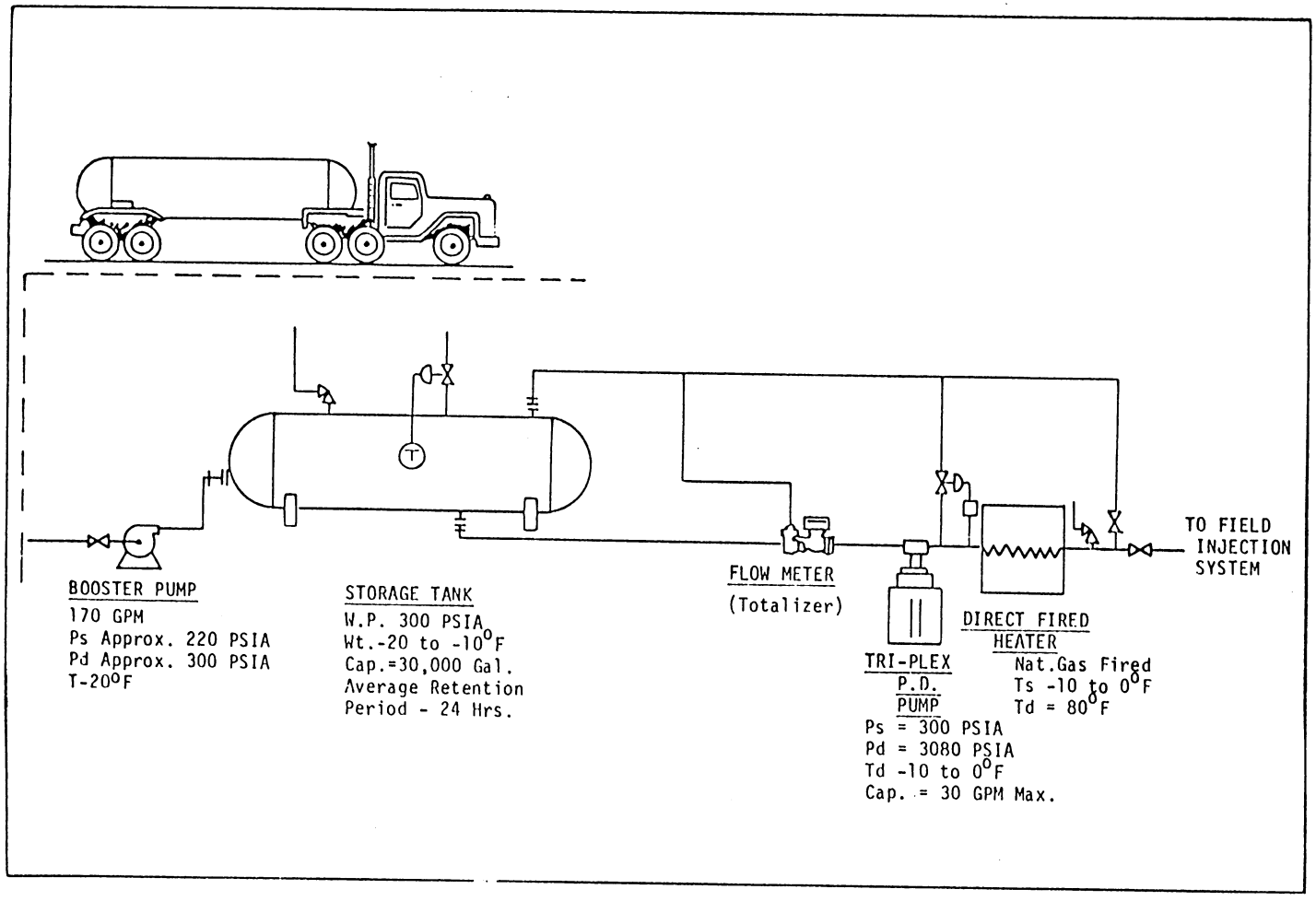
$0.26/MCF for separation of CO_2 from hydrocarbons and H_2S

$0.28/MCF for repressurizing

$10,000 capital investment for separation and compression equipment sufficient for 1 MMSCF of CO_2 per year

$85,000 + (1.85 Depth) per well to convert new or existing injection wells to CO_2 injection (cost also varies with location)

Exhibit 6-8: Schematic of CO_2 Storage and Injection Facilities



Source: Gulf Oil Exploration and Production Company, 1979; in Science Applications, Inc., Environmental Assessment of Proposed CO_2 Flood EOR Minitest at Little Knife Field, Billings County, North Dakota: DOE Contract DE-AT21-78MC08333, Task 14, p. 3-12, Exhibit 3-8, May 25, 1979.

7. THE FEASIBILITY AND ECONOMICS OF CO_2 GENERATION AT EOR SITES

7.1 INTRODUCTION

On site CO_2 generators are not yet available commercially for enhanced oil recovery operations. Consequently, processes must first be identified that appear to be strong candidates. The prime candidate for CO_2 generation would appear to be the onsite combustion of various fossil fuels followed by CO_2 recovery from the generated flue gas. Commercial CO_2 was actually produced this way before the second world war. However, the advent of large scale chemical plants such as ammonia plants producing large quantities of cheap, pure CO_2 rendered the old CO_2 processes obsolete.

Onsite CO_2 generation by burning oil was considered first. Section 3 of this report indicated that one barrel of fuel oil when burned produces approximately 8900 SCF of CO_2 with flue gas concentrations of 12.3% by volume. Section 2 showed that approximately 6800 SCF of almost pure CO_2 would be required to recover one additional barrel of crude. Thus, some 0.8 barrels of oil must be burned in order to recover one barrel of additional crude. This is obviously uneconomic, especially when the cost of recovering CO_2 from the flue gas is added to the fuel cost.

The combustion of associated gas (impure natural gas produced at the well head) would at first glance seem more attractive than using oil. Section 3 indicated that the combustion of 1000 SCF of natural gas produces approximately 1100 SCF of CO_2 at concentrations in the flue gas of 9.1% by volume. Thus, at least 7000+ SCF of associated gas would be required - if 90% of the generated CO_2 is recovered from the flue gas - at a cost of about $21 to produce enough CO_2 for the ultimate recovery of one additional barrel of crude. In addition, Section 5.9 inferred that the recovery of 6800 SCF of pure CO_2 from the flue gas would cost at least another $14 to $28 depending on the total volume of flue gas to be treated. Therefore, fuel costs and CO_2 recovery costs alone are between $35 and $49 to recover one barrel of oil worth approximately $35. The use of associated gas purely to produce CO_2 is again uneconomic. Oil and gas combustion processes could be made more attractive by using the heat released during combustion to raise steam for use in the CO_2 recovery system, or for driving compressors and other onsite equipment. However, in practice, only a small credit could be taken for the

steam, since excessive amounts would be produced which would be of no use except in unusual circumstances when CO_2 injection sites were in city centers or close to industrial complexes.

If coal were to be used, the amount required would depend strongly on the type of coal burned. If 60 percent of the CO_2 were recovered from the flue gas, it would require the combustion of 0.48 tons of North Dakota lignite or 0.44 tons of North-Central Texas bituminous coal to recover enough CO_2 for the production of one additional barrel of crude. This would be at fuel costs of about $14 and $21, respectively, assuming a delivered fuel cost of $2 per MMBtu. Thus, the approximate total cost of generating and recovering the CO_2 would be between $28 to $42 for North Dakota lignite and $35 to $49 for North-Central Texas bituminous coal, just to recover one additional barrel of oil. Thus, burning any fossil fuel purely with the intent of recovering CO_2 from the flue gas, without taking any energy credit, would be uneconomic, although the combustion of lignite appears to offer the best possible case.

In order to investigate the feasibility and economics of CO_2 manufacture at EOR sites, two processes will be considered. (1) Coal "combustion" via the wet air oxidation (WAO) process where the coal is oxidized in a high pressure steam and oxygen environment rather than burned. This novel process has the advantage of directly producing high pressure, pure CO_2 rather than low grade flue gas, although the process is much more capital-intensive than conventional combustion equipment. (2) The combustion of lignite (and, for comparison, bituminous coal) in a fluidized bed boiler and the subsequent recovery of CO_2 from the flue gas by an activated potassium carbonate recovery system. A fluidized bed combustion (FBC) boiler was chosen since it has a much higher carbon combustion efficiency than normal boilers as well as the capacity to severely restrict sulfur dioxide emissions. Each process will be considered separately.

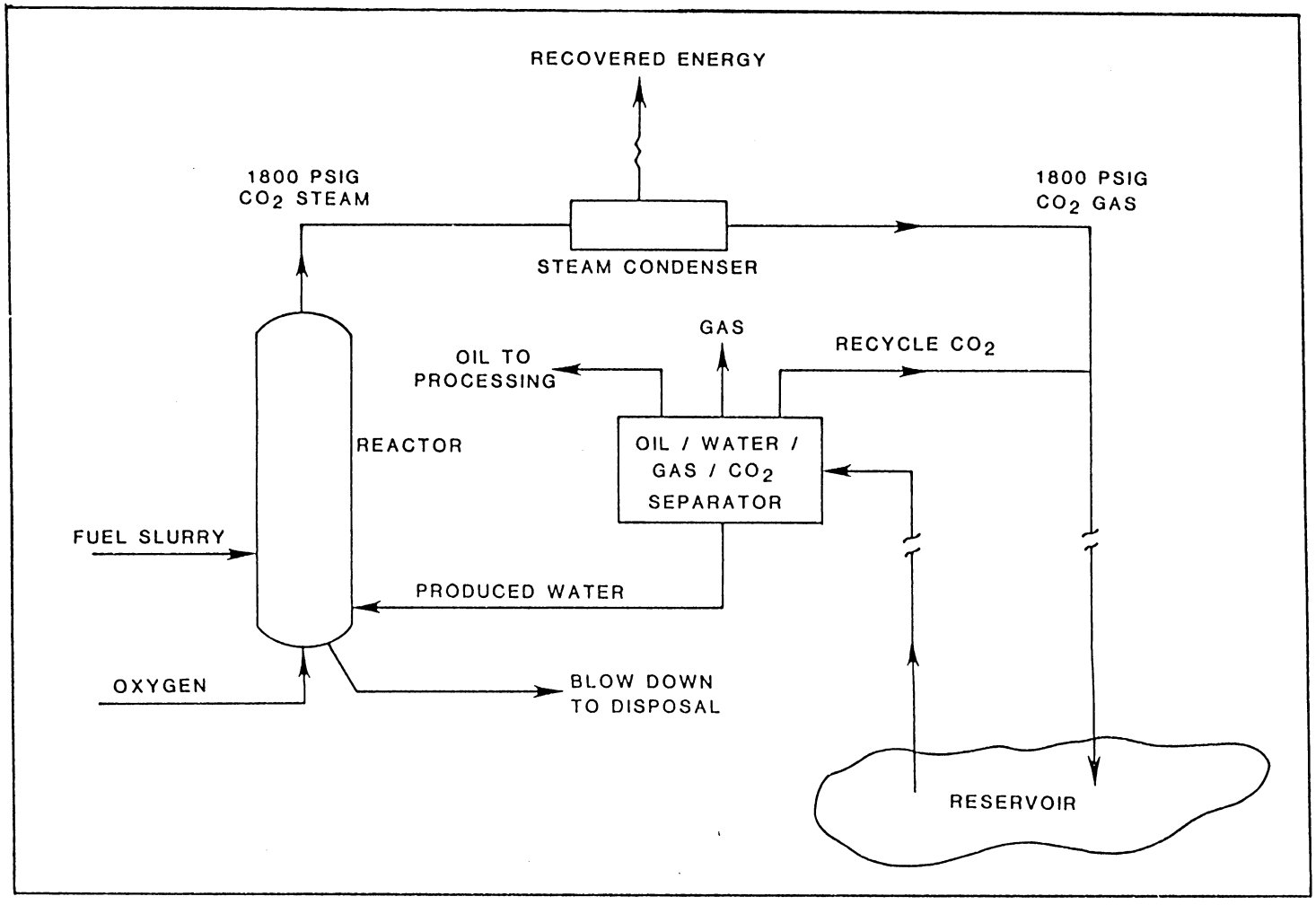
7.2 WET AIR OXIDATION (WAO) PROCESS

The WAO process is currently being used in a number of countries for the treatment of aqueous wastes; and recently a modification of the process has been developed as a steam generator for thermal enhanced oil recovery operations. WAO reactors typically operate at pressures of 300 to 3000 psig and temperatures of 350 to 650°F in order to provide a suitable environment

for the number of aqueous phase oxidation and hydrolysis reactions that occur.[58] Exhibit 7-1 is a schematic provided by the manufacturers of WAO equipment which indicates how the process may be employed for generating CO_2 for use in EOR operations. With reference to Exhibit 7-1, the coal is crushed and slurried with water, compressed, and injected into the reactor. The recycled water stream from the oil/water/gas/CO_2 separation equipment is also pressurized and fed to the reactor along with a separate compressed oxygen supply from a cryogenic air separation plant. In the reactor, oxygen combines with the organic material in the coal, releasing the heat of combustion and vaporizing the water in the reactor. The remaining water, together with dissolved and suspended inorganic material, is withdrawn from the reactor. By adding a mixture of limestone or dolomite to the reactor with the fuel, the sulfur originally present in the coal can be withdrawn with this waste stream in the form of sulfates. The resulting offgases from the reactor are composed of only steam and CO_2, since the chemistry of the WAO reaction is such that no SO_2 or NO_x is generated. Particulates in the offgas are also at negligible levels. One particular advantage of this process is that the CO_2/steam mixture leaves the reactor at about 1800 psig and, once steam has been removed in a condenser, the CO_2 is ready for injection into the reservoir without further compression. Some of the heat recovered by steam condensation could be of use onsite.

In terms of the economics of the process, some difficulty is encountered since the process is unproven for CO_2 EOR even though WAO is well established in other fields. Two plant sizes were considered for economic analysis, a small plant generating 2.2 MMSCFD of CO_2 and a much larger plant generating 22 MMSCFD of CO_2. Basic assumptions made were that the project would have a ten-year life with a 15% annual rate of return, and the delivered fuel was estimated to cost $2 per MMBtu. Furthermore, since much of the economics data were supplied by Zimpro-AEC Ltd[57] - the manufacturers (see Exhibit 7-2) - a 25% contingency was added to their figures to account for a probably over-enthusiastic sales pitch as well as extra items too small to be considered separately. The capital investment in first quarter-1981 dollars was estimated to be approximately $23 MM for the small facility and $90 MM for the large facility including both the WAO plant and the cryogenic separation plant supplying the oxygen. The calculated costs of CO_2 in dollars per MSCF are given in Exhibit 7-3 for North Dakota lignite and North Central Texas

Exhibit 7-1: The Wet Air Oxidation Process



Source: Ref. 58, p. 3.

Exhibit 7-2: Cost of Producing CO_2 by WAO

OPERATING RATE - 330 Days/Year

PRODUCT GAS - 1800 psig

PLANT SIZE	2.2 MMSCFD, 126 TPD		22 MMSCFD, 1260 TPD	
Operating Cost Elements				
Power, Operating KW	2400		21375	
Fuel-Lignite, TPD, 35% Moisture	89		890	
$CaCO_3$ TPD	1.5		15	
Operating Labor, Manhours/Day	46		124	
Solids for Disposal, Dry TPD	9.9		99	
bbl/day, 50% Moisture	65		650	
Clean Water, 1000 Gallons/Day	80		800	
Maintenance Labor, Manhours/Day	20		50	
"Waste Heat" Recovered As Thermal Energy, MMBtu/Hr	45		470	
As Electric Power, KW	3034		32975	
ANNUAL COSTS	MOST FAVORABLE	LEAST FAVORABLE	MOST FAVORABLE	LEAST FAVORABLE
Fuel $1.00-$2.00/MM Btu	$ 426,000	$ 852,000	$ 4,260,000	$ 8,520,000
$CaCO_3$ @ $20/Ton	10,000	10,000	100,000	100,000
Operating Labor, $15/Hour	228,000	228,000	614,000	614,000
Solids Disposal, $1.75/bbl	38,000	38,000	380,000	380,000
Water $.20/1000 Gallons	5,000	5,000	50,000	50,000
Maintenance Labor $20/Hour	132,000	132,000	330,000	330,000
Repair Parts and Materials	130,000	130,000	700,000	700,000
Net Energy Credit	(1,000,000)	(150,000)	(10,000,000)	(1,000,000)
Annual Capital Charge	1,400,000	4,000,000	7,000,000	20,000,000
Annual Net Cost	1,369,000	5,245,000	3,434,000	29,694,000
Per MSCF	$2.07	$7.22	$0.47	$4.09
Per Ton	$36.	$126.	$8.	$72.

Source: Ref. 57, p. 12, Table 2.

Fuel	CO_2 Generated (MMSCFD)	CO_2 Recovered for EOR (MMSCFD)	CO_2 Cost ($/MSCF)	Size of Energy Credit Taken
North Dakota Lignite ($2/MMBtu)	22	22	3.05	Zero
	22	22	2.36	Medium
	22	22	1.67	Maximum
	2.2	2.2	4.71	Zero
	2.2	2.2	4.02	Medium
	2.2	2.2	3.33	Maximum
North Central Texas Bituminous Coal ($2/MMBtu)	22	22	3.84	Zero
	22	22	3.15	Medium
	22	22	2.46	Maximum
	2.2	2.2	5.50	Zero
	2.2	2.2	4.81	Medium
	2.2	2.2	4.12	Maximum

Exhibit 7-3: The Economics of Onsite CO_2 Generation Using the WAO Process

bituminous coal. The difference between the manufacturer's figure of $0.47 for the 22 MMSCFD plant and our price of $1.67 is due to the use of a higher coal cost ($.59/MSCF extra), and the 25% contingency factor ($.61/MSCF). The extent of the energy credit depends on how much of the waste heat recovered from steam condensation can be sold. At worst for the zero energy credit case, it was assumed that each facility was energy self-sufficient and excess heat was merely disposed of. Exhibit 7-3 indicates that producing 22 MMSCFD of CO_2 using North Dakota lignite as fuel, pure CO_2 can be produced for $3.05 per MSCF with zero energy credit; with North Central Texas bituminous coal, CO_2 would be more expensive at $3.84 per MSCF. These costs are considerably greater than the cost of recovering CO_2 from say a power plant (see Section 5), but bearing in mind that for an onsite WAO CO_2 generator there would be no CO_2 transportation and no compression costs, the process appears to be very competitive with the by-product CO_2 sources considered. For the smaller 2.2 MMSCFD WAO CO_2 generators, the costs climb to $4.71 per MSCF and $5.50 per MSCF with zero energy credit for North Dakota lignite and North Central Texas bituminous coal, respectively.

The zero energy credit case was considered as the most widely applicable, since credit can only be taken for the steam if there is a demand for it in the vicinity of the WAO plant. The amount of steam produced is 470 MMBtu/hr for a 22 MMSCFD plant, and 45 MMBtu/hr for the 2.2 MMSCFD plant.

If full credit is taken for the steam produced, then the cost of the CO_2 is drastically reduced: to $1.67 at 22 MMSCFD, and $3.33 at 2.2 MMSCFD using lignite. One possible use for the steam is in the air separation plant used to generate the oxygen for the process.

Additionally, the WAO process generates large amounts of nitrogen which is also being considered for use in EOR. A plant producing 22 MMSCFD of CO_2 from lignite would produce approximately 120 MMSCFD of nitrogen, which at $.25/MSCF would be worth as much again as the energy credit ($10,000,000), or $1.35/MSCF.

In conclusion, the WAO process would seem to be capable of providing onsite CO_2 at a cost competitive with the other offsite by-product sources considered, especially when the WAO process is generating over 20 MMSCFD of CO_2 and is using low grade lignite. It is difficult to be more positive at this stage about the WAO process since it represents unproven technology for

CO_2 EOR applications. However, the process certainly warrants serious consideration by oil companies planning future CO_2 enhanced recovery operations.

7.3 FLUIDIZED BED COMBUSTION

A fluidized bed combustion (FBC) boiler is merely a very efficient and very clean way to burn coal in air. An Ahlstrom fluidized bed system is shown in Exhibit 7-4.[42] Fuel and limestone are introduced into the combustion chamber and high air velocities in the Ahlstrom system are used to circulate the fuel and limestone through the combustion chamber and into a cyclone collector that separates the hot gases from the solid material. The hot gases from the cyclone are ultimately passed to a waste heat boiler. Most of the heat is generated in the combustion chamber and the remainder in the waste heat boiler (this heat is used in both parts of the system to raise steam). The cooled flue gas is then normally vented after dust collection.

From calculations similar to those performed in Section 3, it has been determined that when one ton of North Dakota lignite is combusted in the presence of limestone in an FBC boiler, 24,000 SCF of CO_2 are liberated including the CO_2 from limestone calcination. Assuming that the lignite is combusted with 20% excess air the composition of the stack gas is:

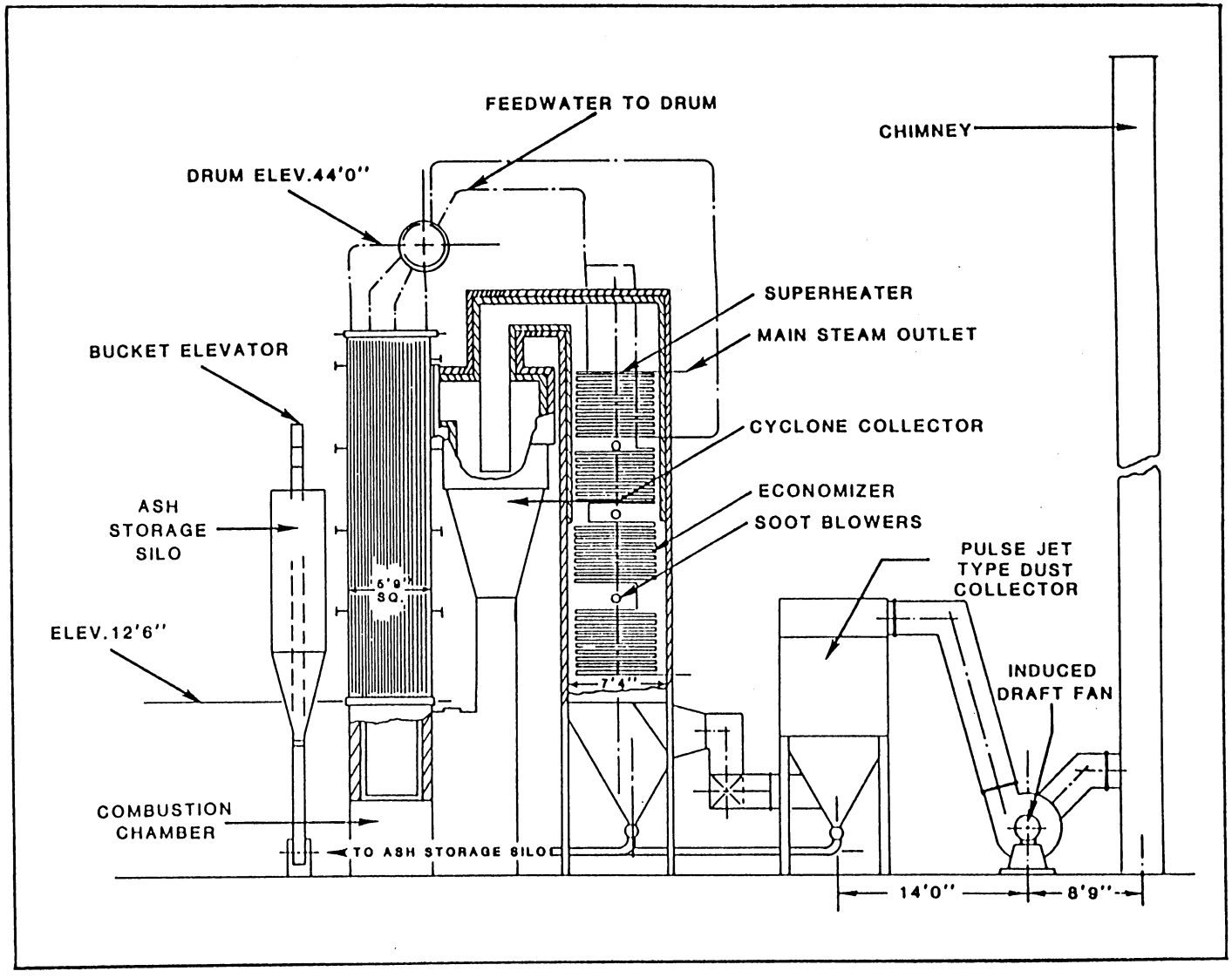
	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	13.4	1.7	67.8	0.19	0.03	16.9

When one ton of North Central Texas bituminous coal is combusted in a fluidized bed combustor, it has been estimated that 27,700 SCF of CO_2 are released with the following stack gas composition calculated assuming 20% excess air:

	CO_2	O_2	N_2	NO_x	SO_2	$H_2O(v)$
percent volume	14.9	3.1	75.2	0.13	0.11	6.9

Two sizes of fluidized bed boilers were considered: generation of 3.6 MMSCFD of CO_2, and generation of 36 MMSCFD of CO_2. Thus, by recovering 60% of the liberated CO_2 through mean of an activated hot potassium carbonate system,

Exhibit 7-4: Typical Layout of FBC Boiler Unit



Source: Ref. 42, p. 13, DWG. No. 5260001A.

2.2 MMSCFD and 22 MMSCFD of recovered pure CO_2 can be made available, respectively, from the flue gases of the two boilers.

An economic analysis was performed on each of the two systems. The capital investment required in order to recover 2.2 MMSCFD of CO_2 by this method is approximately $4.5 MM for the FBC boiler and approximately $5.6 MM for the appropriate CO_2 recovery system (Section 5). For the onsite generation and recovery of 22 MMSCFD by this scheme, some $28.3 MM is the required investment for the boiler and $28.7 MM for the activated hot potassium carbonate system. The capital costs for FBC boilers using North Dakota lignite were supplied by Pyropower Corporation.[43] For higher sulfur coals the capital costs would increase slightly. The results of the economic analysis are given in Exhibit 7-5. A 25% contingency factor was used, and it was assumed that the project should provide an annual return on investment of 15% over a ten-year and fifteen-year project life. Lignite and coal were assumed to cost $2 per MMBtu delivered. The steam credits refer to the amount of money that can be recovered by the sale of excess steam generated as a by-product in the FBC boiler (steam was assumed to be worth $4 per 1000 lb). In many cases one may not be able to take any energy credit (zero credit case) since it is unlikely that the quantities of steam generated will be of use in the immediate vicinity of most CO_2 EOR injection sites, except in the few cases where these sites are within city limits or close to industrial complexes. It can be seen from Exhibit 7-5 that CO_2 for a fifteen-year project will cost $4.49 per MSCF from the 22 MMSCFD plant and $5.93 per MSCF from the 2.2 MMSCFD CO_2 generation scheme when North Dakota lignite is combusted and zero energy credit is taken. CO_2 is shown to be even more expensive when a higher grade fuel such as North Central Texas bituminous coal is used.

If the full steam credit is taken (at $4/1000 lb.), then the price for the large plant is reduced to $1.94/MSCF, and that for the small plant to $2.11/MSCF using lignite. The prices with bituminous coal are considerably higher.

The WAO process is more economic than the fluidized bed, although the initial capital investment required is much higher. Even if no energy credits are taken, the WAO process is competitive with other CO_2 sources for EOR, especially those far from a source of by-product or natural CO_2. If energy credits for steam can be utilized, then either of these two onsite generation methods are well worth considering, especially WAO.

Fuel	CO_2 Generated (MMSCFD)	CO_2 Recovered (MMSCFD)	CO_2 Cost ($/MSCF)		Size of Steam Credit Taken
			10-Year Project Life	15-Year Project Life	
North Dakota Lignite ($2/MMBtu)	36	22	4.73	4.49	Zero
	36	22	3.46	3.22	Medium
	36	22	2.18	1.94	Maximum
	3.6	2.2	6.52	5.93	Zero
	3.6	2.2	2.25	4.66	Medium
	3.6	2.2	2.70	2.11	Maximum
North Central Texas Bituminous Coal ($2/MMBtu)	36	22	6.84	6.60	Zero
	36	22	5.57	5.33	Medium
	36	22	4.29	4.05	Maximum
	3.6	2.2	8.62	8.04	Zero
	3.6	2.2	7.35	6.77	Medium
	3.6	2.2	6.07	5.49	Maximum

Exhibit 7-5: The Economics of Onsite CO_2 Generation Using an FBC Boiler Linked to an Activated Hot Potassium Carbonate CO_2 Recovery System

7.4 LOCATION OF SNG PLANTS NEAR EOR SITES

The main factors involved in locating SNG plants close to EOR sites are:

a) Extra transport cost for coal to the site

b) Extra transport cost for the SNG to market

c) Reduced cost of transporting CO_2 to EOR site

d) Suitability of site for SNG plant, including environmental and other permits, and water availability.

A plant producing 250 MMSCFD of SNG, with a by-product CO_2 production of 312.5 MMSCF was considered. Based on design of the Great Plains Gasification Associates Plant, this plant would require lignite in the amount of 28,000 tons per day. Using a unit train coal cost of $1.33/ton/100 miles, the increased cost due to coal transportation for various distances is:

100 miles	$12.3 MM/year	= $.12/MSCF of CO_2
200 miles	$24.6 MM/year	= $.24/MSCF of CO_2
300 miles	$36.9 MM/year	= $.36/MSCF of CO_2

The CO_2 transportation cost (at a 15% rate of return) is $0.12/MSCF/100 miles (from Exhibit 6-1). Finally, the cost of transporting SNG is approximately 15% less than the cost for CO_2 giving an extra cost of $.10/MSCF/100 miles of SNG.

As an example, an SNG plant with two alternative sites was considered: (1) Coal minemouth plant, 50 miles from a population center; (2) Near an oil field suitable for CO_2 flooding, 200 miles away from the coal field or 150 miles further from the market for the gas.

Costs Increase:	$.24 for coal transportation
(per MSCF of CO_2)	$.12 for extra SNG transport
	$0.36
Cost Saving:	$0.24

In this case, there would be no benefit from locating the SNG plant near the oil field.

No general statement can be given as to when relocation closer to an oil field would be economic, since the total costs also depend on location of the coal source and on the market for the SNG. In addition, the number of suitable sites for large SNG plants is limited, due to other factors such as environment, water availability, and socio-economic impacts on small communities.

Most proposed SNG plants are located close to a coal source, since the cost of transporting the raw coal is generally higher per Btu than that for the product gas. The Williston and Appalachian Basins where the coal and oil are found in the same general area are thus, the most likely candidates for SNG plant relocation. The bituminous coal-fields of north central Texas are 150 miles or more from the main Permian oil fields, while the lignite deposits of east Texas are a similar distance from the Gulf Coast oil fields. There are no significant coal fields in California. Thus, the Los Angeles and Permian Basins do not appear to be promising areas for location of SNG plants near a CO_2 demand point for use in EOR.

8. TOTAL CO_2 COST ANALYSIS

In this Section the methodology for determining the total delivered cost for CO_2 is developed and illustrated by some specific examples. Following this, the supply/demand balance for a whole region is studied in detail in order to determine the average cost of providing all the CO_2 required for EOR. This analysis is conducted by modeling the situation as a classical transportation problem, and then using the "out-of-kilter" network algorithm to determine the minimum cost of supplying the specified demand under the existing constraints.

Before the total CO_2 cost can be determined, the cost of purchasing flue gas (from power plants, cement plants, FCCU) and high purity CO_2 (from ammonia plants, hydrogen plants, etc) is required. A survey of reported cost data is given below. These costs are only a rough guide, since any large increase in demand would probably lead to an increase in the CO_2 cost.

8.1 CO_2 INITIAL PURCHASE COST

Natural CO_2:

The following costs for purchased CO_2 have been reported in Enhanced Recovery Weekly.[13]

2/2/81:	$1.40/MSCF by Shell, from McElmo Dome to Jordan Field, others (Crane & Ector counties)
9/2/81:	$1.50/MSCF by Arco, from Sheep Mountain to Wasson Field, Texas
3/23/81:	$1/MSCF by Mobil, from McElmo Dome to Kent and Gaines counties, Texas

These figures all apply to a distance of approximately 500 miles. Assuming a cost of $1.40/MSCF, a flow rate of 300 MMSCFD, and a transportation cost of $0.12/MSCF/100 miles (from Exhibit 6-1), the cost of natural CO_2 appears to be approximately $0.80/MSCF after compression.

Flue Gas

The only reported cost is a figure of \$0.067/MCF CO_2 recovered (0.36 cents/MSCF flue gas) by Wiggins to a Lubbock public utility, for approximately 20 MMSCFD.[11] A cost of \$0.1/MSCF CO_2 recovered is assumed for this report.

High Purity By-Product Sources

Enhanced Recovery Weekly[11] reported the following numbers for CO_2.

2/9/81: Arco paying \$1.15/MSCF to a Tosco refinery in Los Angeles, for 2.6 MMSCFD.

2/12/81: Phillips paying \$1.20/MSCF to an ammonia plant in Sterlington, Louisiana

3/2/81: Long Beach Oil paying \$2/MSCF (delivered 3.5 miles by pipeline) to a hydrogen plant in Los Angeles, for 12MMSCFD.

Based on these figures, \$1.50/MSCF will be assumed as the purchase cost for high purity CO_2. In order to allow for decreases in price with increased competition, CO_2 delivered costs based on a purchase price of \$1/MSCF are also calculated.

8.2 TOTAL DELIVERED COST

8.2.1 Methodology

The general procedure for determining the total delivered cost from a specified source to a particular reservoir using the results of Sections 5 and 6 is:

1. Determine the CO_2 injection rate, on a calendar-day basis, or on any desired operating factor. To use the graphs in this report, either a calendar-day basis or an 80% operating-day basis can be used.

   If the flow rate is known at some operating factor X, say 300 days per year (80%), the flow rate at any other operating factor y% is given by:

   $$\text{Flow rate at } y\% = \left(\frac{(\text{Flow Rate at } x\%)}{(y\%)}\right)(x\%)$$

If we want to find flow rate for a 100% operating factor (say 365 calendar-days) and flow rate for 82% operating factor (300 days) is known, then:

$$\text{Calendar-day flow rate} = \frac{(\text{Flow rate at } 82\%)}{(100)} \; (82)$$

$$= .82 \; (\text{Flow rate at } 82\%)$$

2. Using the maps and appendices on CO_2 sources, determine possible sources with sufficient volume within some cutoff distance to fulfill the expected demand (see Section 8.3 for guidelines).

3. Determine the initial CO_2 cost for the types of sources available, from Section 8.1.

4. Determine the purification cost from Section 5.7 if the source is a power plant, cement plant, or refinery FCCU.

5. Determine the compression cost from Section 5.10. If a source of steam is available, use the graph based on steam-driven compressors, otherwise, use the graph based on electrically-driven compressors.

6. Determine the distance between source and demand points, and transportation cost. Use Exhibits 6-1 through 6-3 for pipelines, and Exhibits 6-4 through 6-6 for truck transport. If rail is being considered, quotes for a given volume can be obtained from the railroad(s) serving the area. The transportation cost can be based on the demand volume (if no other projects in the vicinity are planned) or on the source volume if all the supply from this source is transported to the vicinity of the planned project.

7. Add all the preceding costs, and rank the sources in order of increasing price.

8. Consider other non-cost factors, such as leadtime for full operation, stability of supply, capital investment requirements.

8.2.2 Specific Examples

Consider a reservoir with a projected calendar-day demand of 10 MMSCFD, with two possible sources:

a. A high sulfur coal-fired power plant with a CO_2 volume of 30 MMSCFD on a 300 day-per-year basis.

b. An ammonia plant, with a CO_2 volume of 12.5 MMSCFD on a 300 day-per-year basis.

Case a

First, all volumes will be converted to a calendar-day basis. Thus, for the supply,

30 MMSCFD at on a 300-day basis = 24 MMSCFD on a 365-day basis

Assuming 90% recovery of CO_2, the volume is 24 x .9 = 21.6 MMSCFD. The cost components can now be calculated as follows:

Purchase Cost: $0.10/MSCF

Purification Cost: $1.67/MSCF, based on a potassium carbonate system with a 15-year life (Exhibit 5-14), and assuming all the CO_2 supply can be sold.

Compression and Drying Cost: $0.25/MSCF based on steam-powered compression (Exhibit 5-29) and assuming all the CO_2 supply can be sold.

Transportation Cost: (1) $0.48/MSCF/100 miles, based on a 20-year pipeline life (Exhibit 6-1) and a volume of 21.6 MMSCFD; (2) $0.78/MSCF/100 miles, based on a volume of 10 MMSCFD.

Total:	(1)	100 miles: 0.1 + 1.67 + .25 + .48	= $2.50/MSCF
		200 miles: 0.1 + 1.67 + .25 + 2(.48)	= $2.98/MSCF
		500 miles: 0.1 + 1.67 + .25 + 5(.48)	= $4.42/MSCF
	(2)	100 miles	$2.80/MSCF
		200 miles	$3.58/MSCF
		500 miles	$5.92/MSCF

Case b

Converting to a calendar-day basis gives a flow rate of 12.5 x .8 = 10 MMSCFD.

We then have the following costs:

Purchase price: $1.50/MSCF
Purification Cost: $0
Compression and Drying: $0.55/MCF, based on electrically-driven compressors (Exhibit 5-30).

Transportation Cost:

100 miles: 2.05 + .78 = $2.83/MCF
200 miles: 2.05 + 2(.78) = $3.61/MCF
500 miles: 2.05 + 5(.78) = $5.90/MCF

8.2.3 Total Delivered CO_2 Cost

In the rest of this Section, the most economic recovery method (MEA or K_2CO_3) will be used, with 90% recovery and a 15-year project life.

Using the methodology described above, the total CO_2 cost was determined for each type of source, at distances of 50, 200, and 500 miles. These results are presented in tabular form in Exhibit 8-1 and 8-2, and graphically in Exhibits 8-3 through 8-9.

The only by-produce sources that have delivered CO_2 costs of less than $2/MSCF at 50 miles are coal-fired power plants recovering above 25 MMSCF CO_2 per calendar-day, and high-purity sources such as ammonia plants recovering above 9 MMSCFD CO_2.

8.2.4 Maximum Economic Transportation Distance

Since the purification, compression, and transportation costs for CO_2 vary with the daily flow rate, by-product CO_2 sources of differing sizes will have different delivered costs at equal distances. The approximate maximum distance for transporting CO_2 by pipeline from sources of different sizes is shown in Exhibits 8-10 to 8-13 based on economic limits of $2, $2.50, $3, and $4/MSCF, respectively.

Exhibit 8-1: Delivered CO_2 Cost (10-Year Life)

Type of Plant	Calendar Day CO_2 Output (MMSCFD)	MEA 50 Miles	MEA 200 Miles	MEA 500 Miles	K_2CO_3 50 Miles	K_2CO_3 200 Miles	K_2CO_3 500 Miles
Gas-Fired Power Plant	75	2.67	3.04	3.79	2.52	2.89	3.64
	30	3.07	3.79	5.23	2.92	3.64	5.08
	15	3.57	4.62	6.72	3.46	4.51	6.61
Coal-Fired Power Plant (High Sulfur)	75	1.90	2.37	3.12	1.94	2.31	3.06
	30	2.38	3.20	4.64	2.40	3.12	4.56
	15	3.06	4.11	6.21	2.86	3.91	6.01
Coal-Fired Power Plant (Low Sulfur)	75	1.64	2.01	2.76	1.84	2.21	2.96
	30	2.10	2.82	4.26	2.27	2.99	4.43
	15	2.75	3.80	5.90	2.81	3.86	5.96
Refinery FCCU	30	3.34	4.06	5.50	3.11	3.83	5.27
	15	3.85	4.90	7.00	3.67	4.72	6.72
	5	5.91	7.92	11.94	5.61	7.62	11.64
Gas-Fired Cement Plant	10	4.00	5.41	8.23	3.90	5.31	8.13
	5	5.49	7.50	11.52	5.32	7.33	11.35
	3	7.09	9.37	13.93	6.74	9.02	13.58
Coal-Fired Wet Cement Plant	13	2.86	4.12	6.84	3.06	4.32	7.04
	10	3.19	4.60	7.42	3.36	4.77	7.59
	5	4.67	6.68	10.70	4.82	6.83	10.85
		Purchased at $1/MCF			Purchased at $1.50/MCF		
Ammonia Plant and other High-Purity Sources	30	1.72	2.44	3.88	2.22	2.94	4.38
	15	1.92	2.97	5.07	2.42	3.47	5.57
	5	2.41	4.42	8.44	2.91	4.92	8.94

Based on: 90% recovery, 10-year life, 50% debt

Exhibit 8-2: Delivered CO_2 Cost (15-Year Life)

Type of Plant	Calendar Day CO_2 Output (MMSCFD)	MEA 50 Miles	MEA 200 Miles	MEA 500 Miles	K_2CO_3 50 Miles	K_2CO_3 200 Miles	K_2CO_3 500 Miles
Gas-Fired Power Plant	75	2.42	2.75	3.41	2.25	2.58	3.24
	30	2.78	3.35	4.49	2.60	3.17	4.31
	15	3.33	4.26	6.12	3.09	4.02	5.88
Coal-Fired Power Plant (High Sulfur)	75	1.80	2.13	2.79	1.67	2.00	2.64
	30	2.16	2.73	3.87	2.04	2.61	3.75
	15	2.75	3.68	5.54	2.57	3.50	5.36
Coal-Fired Power Plant (Low Sulfur)	75	1.46	1.79	2.45	1.60	1.93	2.59
	30	1.83	2.40	3.54	1.94	2.51	3.65
	15	2.42	3.35	5.21	2.47	3.40	5.26
Refinery FCCU	30	3.08	3.65	4.79	2.85	3.42	4.56
	15	3.57	4.50	6.36	3.34	4.27	6.13
	5	5.46	7.08	10.32	5.31	6.93	10.17
Gas-Fired Cement Plant	10	3.73	4.90	7.24	2.93	4.10	6.44
	5	5.06	6.78	9.92	4.86	6.58	9.72
	3	6.68	8.78	12.98	6.68	8.78	12.98
Coal-Fired Wet Cement Plant	13	2.50	3.52	5.56	2.65	3.67	5.71
	10	2.83	4.00	6.34	2.93	4.10	6.44
	5	4.09	5.71	8.95	4.20	5.82	9.06
		Purchased at $1/MCF			Purchased at $1.50/MCF		
Ammonia Plant and other High-Purity Sources	30	1.63	2.20	3.34	2.13	2.70	3.84
	15	1.81	2.75	4.64	2.31	3.25	5.14
	5	2.21	3.83	7.07	2.71	4.33	7.57

Based on: 90% recovery, 15-year life, 75% debt

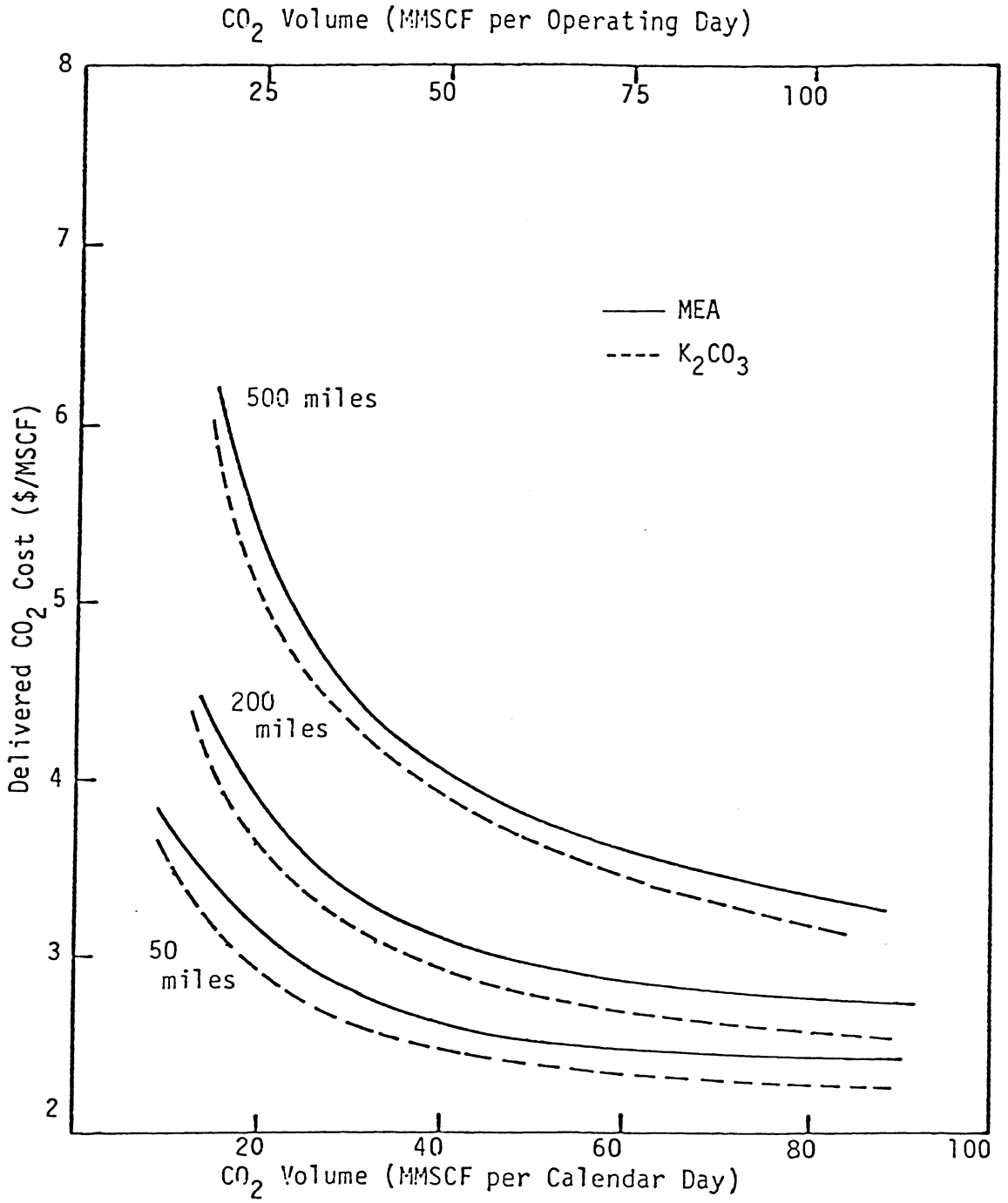


Exhibit 8-3: Delivered CO_2 Cost for Gas-Fired Power Plants

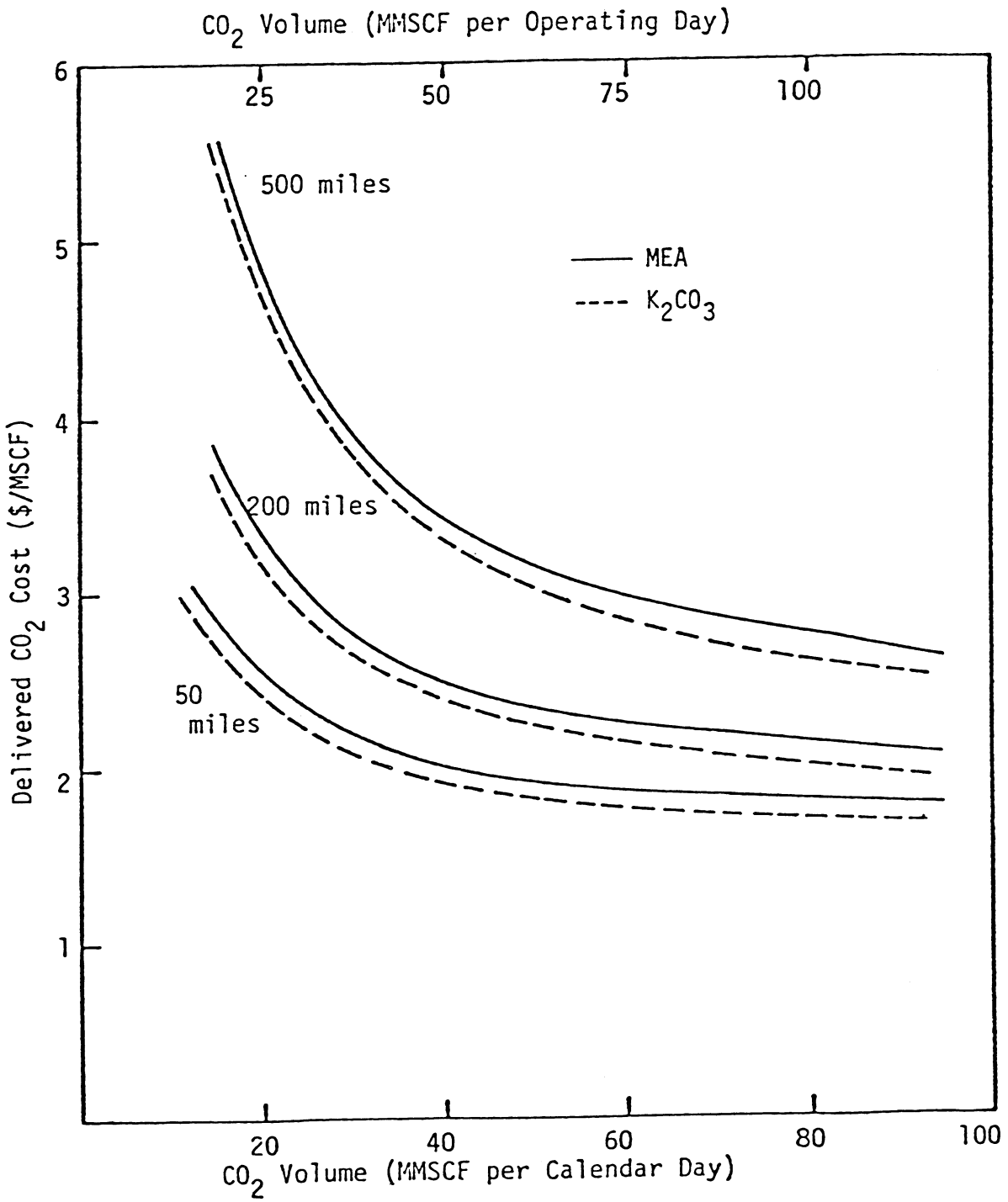


Exhibit 8-4: Delivered CO_2 Cost for Coal-Fired Power Plants (High Sulfur)

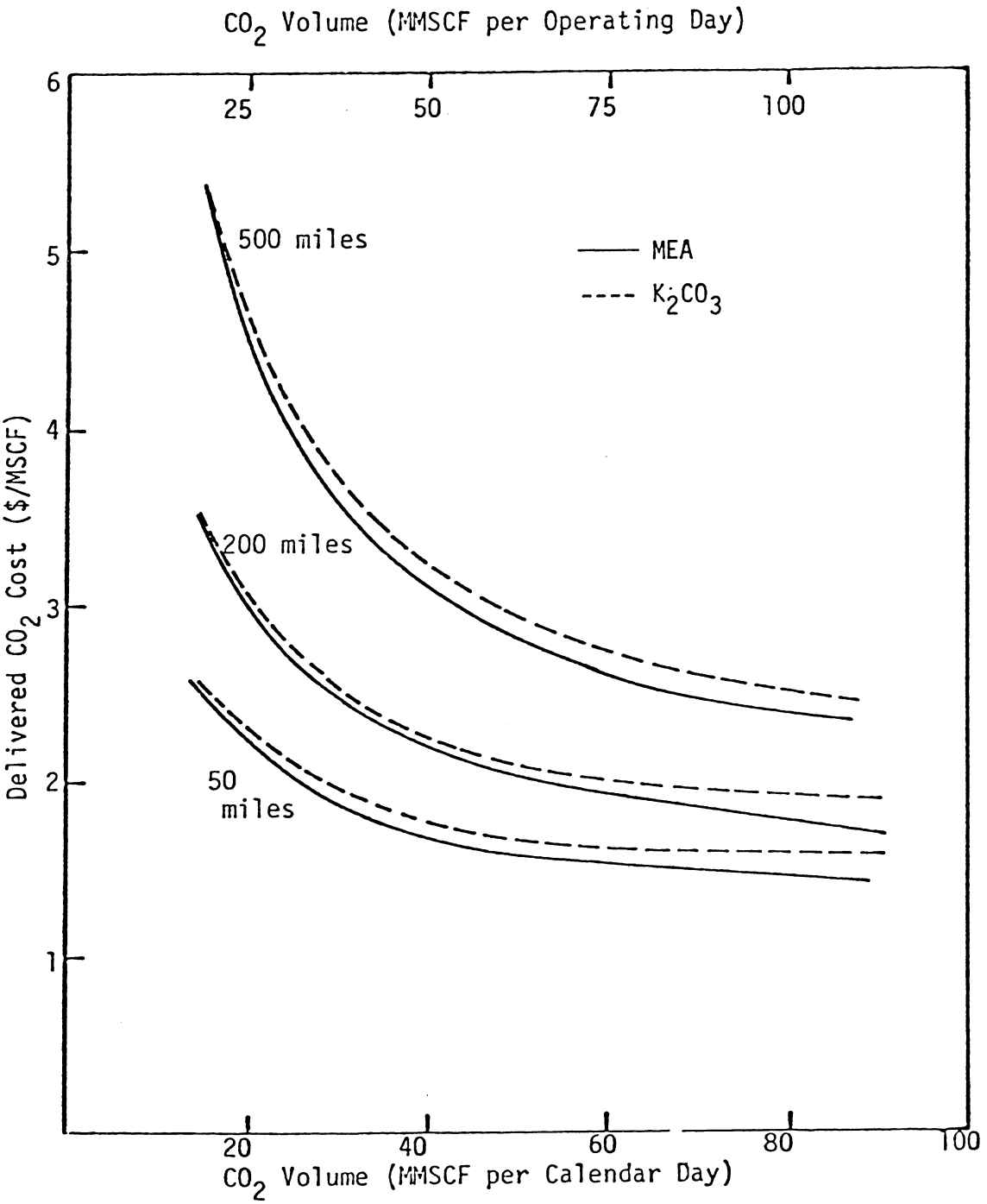


Exhibit 8-5: Delivered CO_2 Cost for Coal-Fired Power Plants (Low Sulfur)

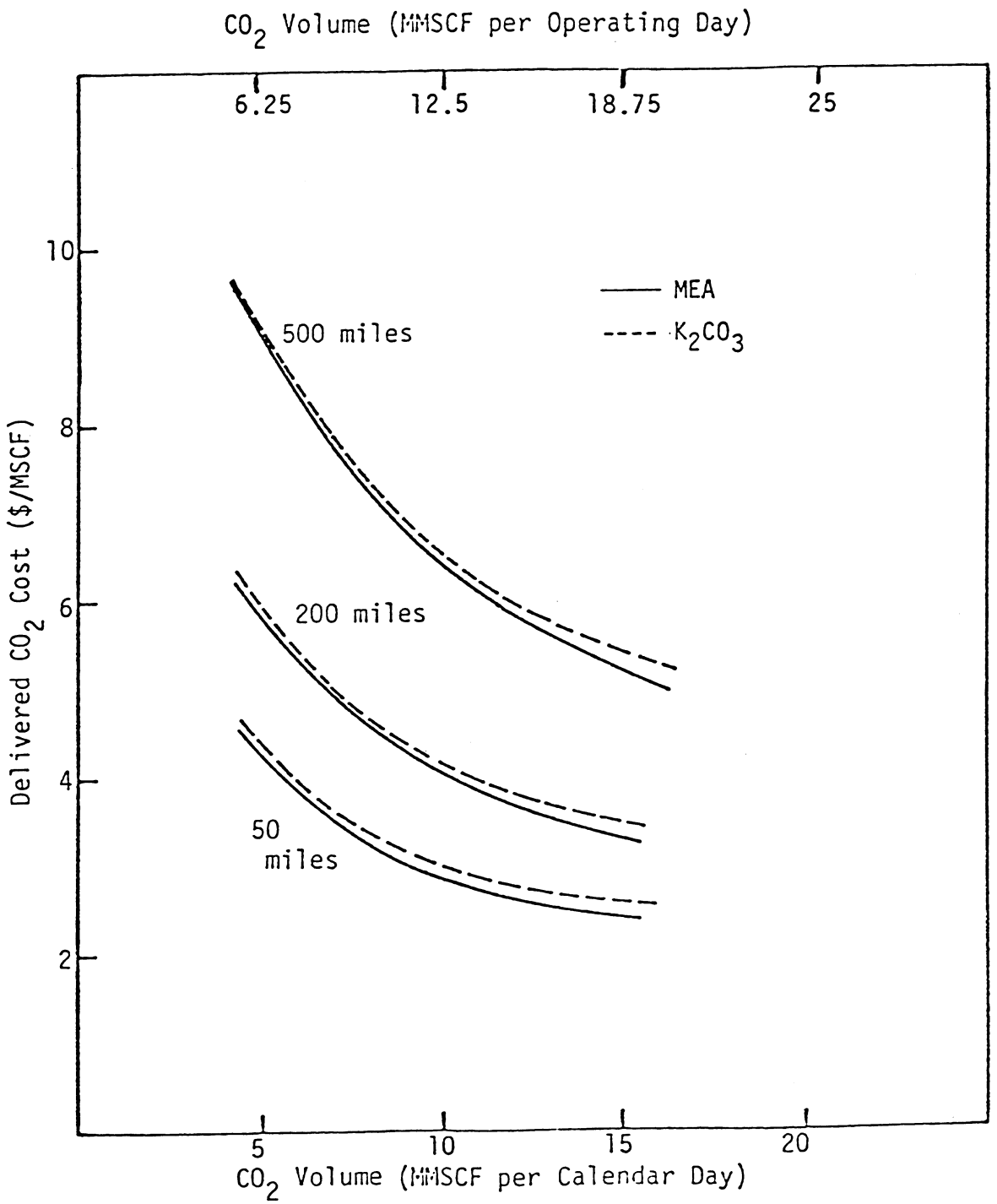


Exhibit 8-6: Delivered CO_2 Cost for Coal-Fired Wet Cement Plants

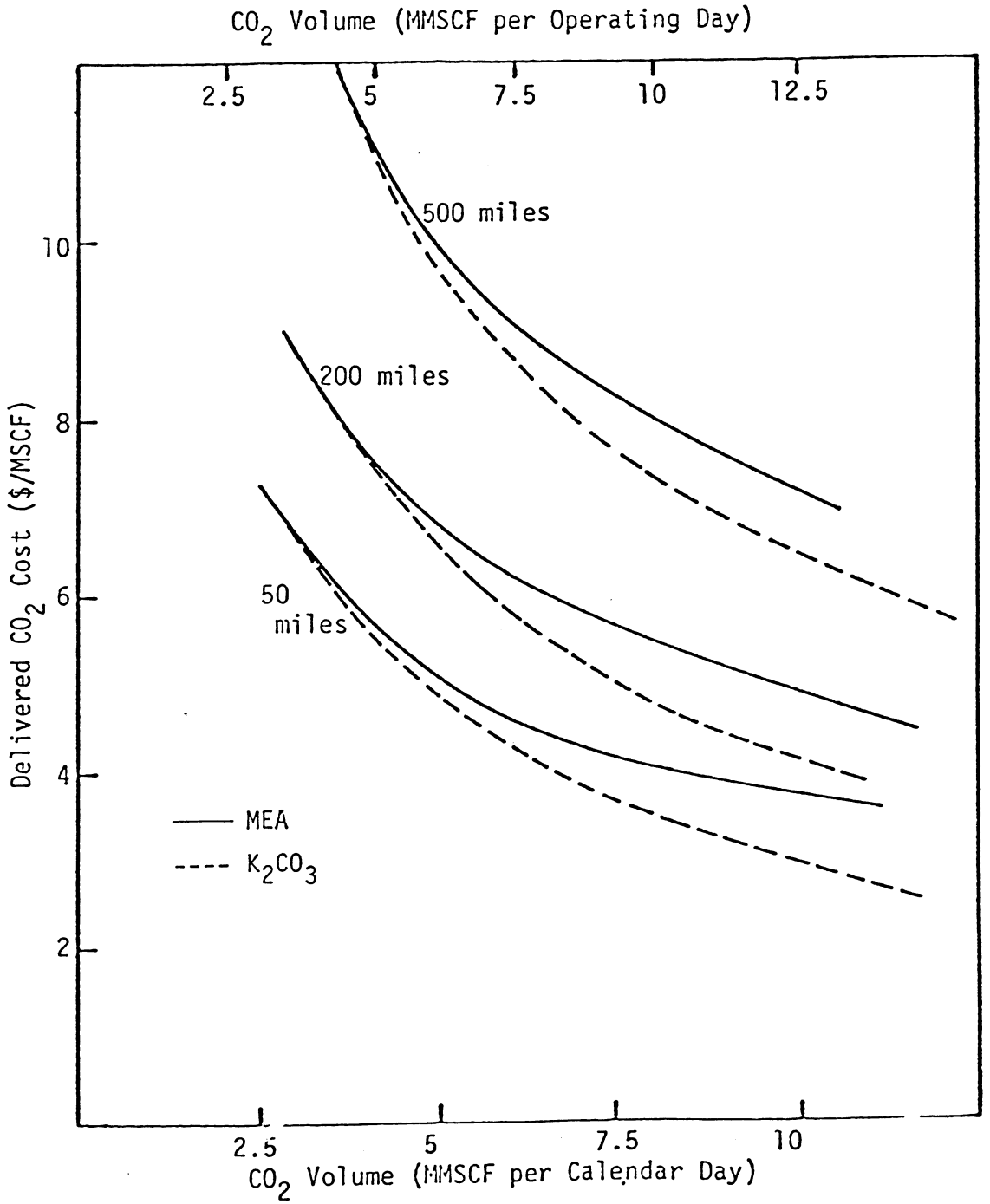


Exhibit 8-7: Delivered CO_2 Cost for Gas-Fired Cement Plants

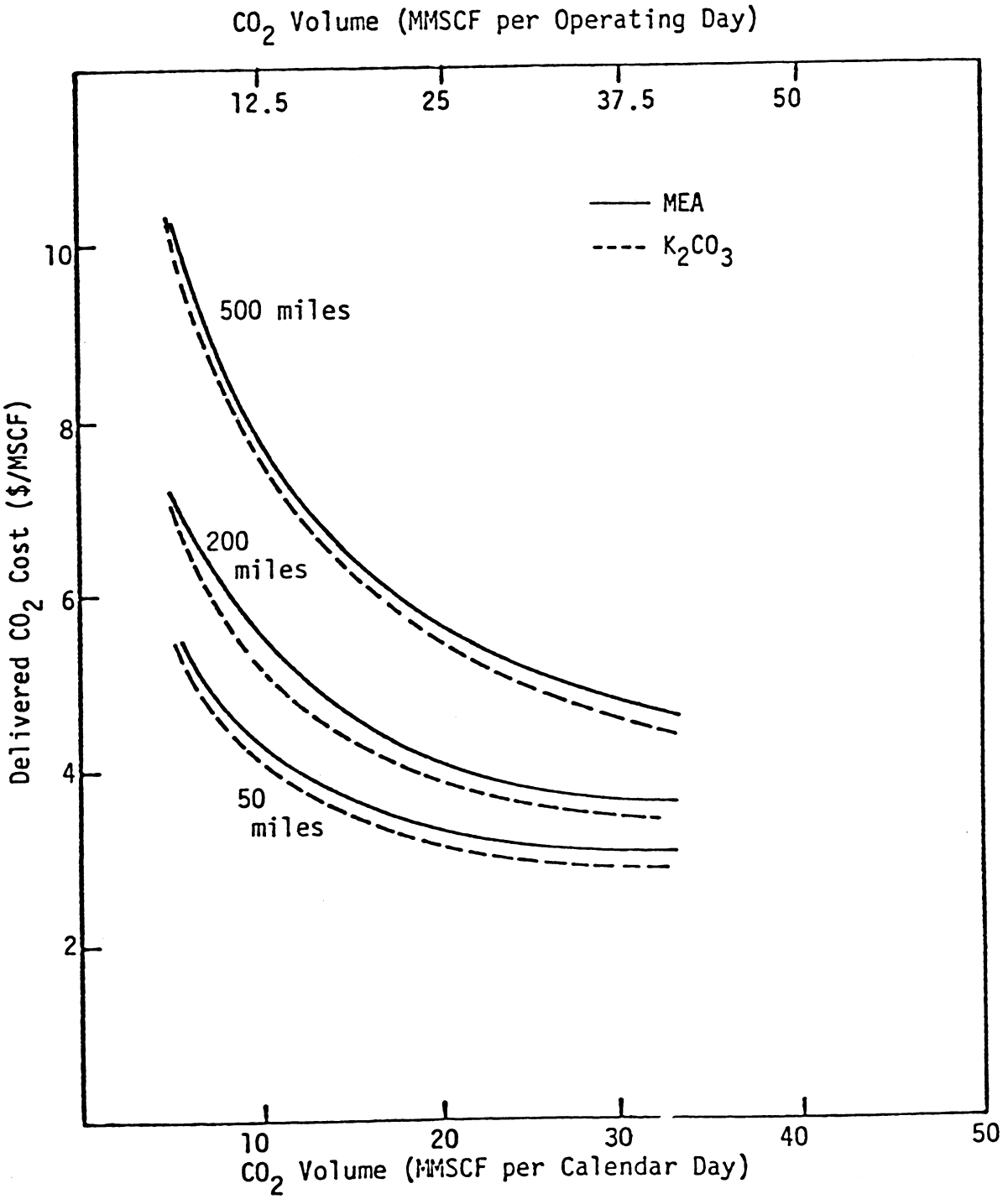


Exhibit 8-8: Delivered CO_2 Cost for Refinery FCCU

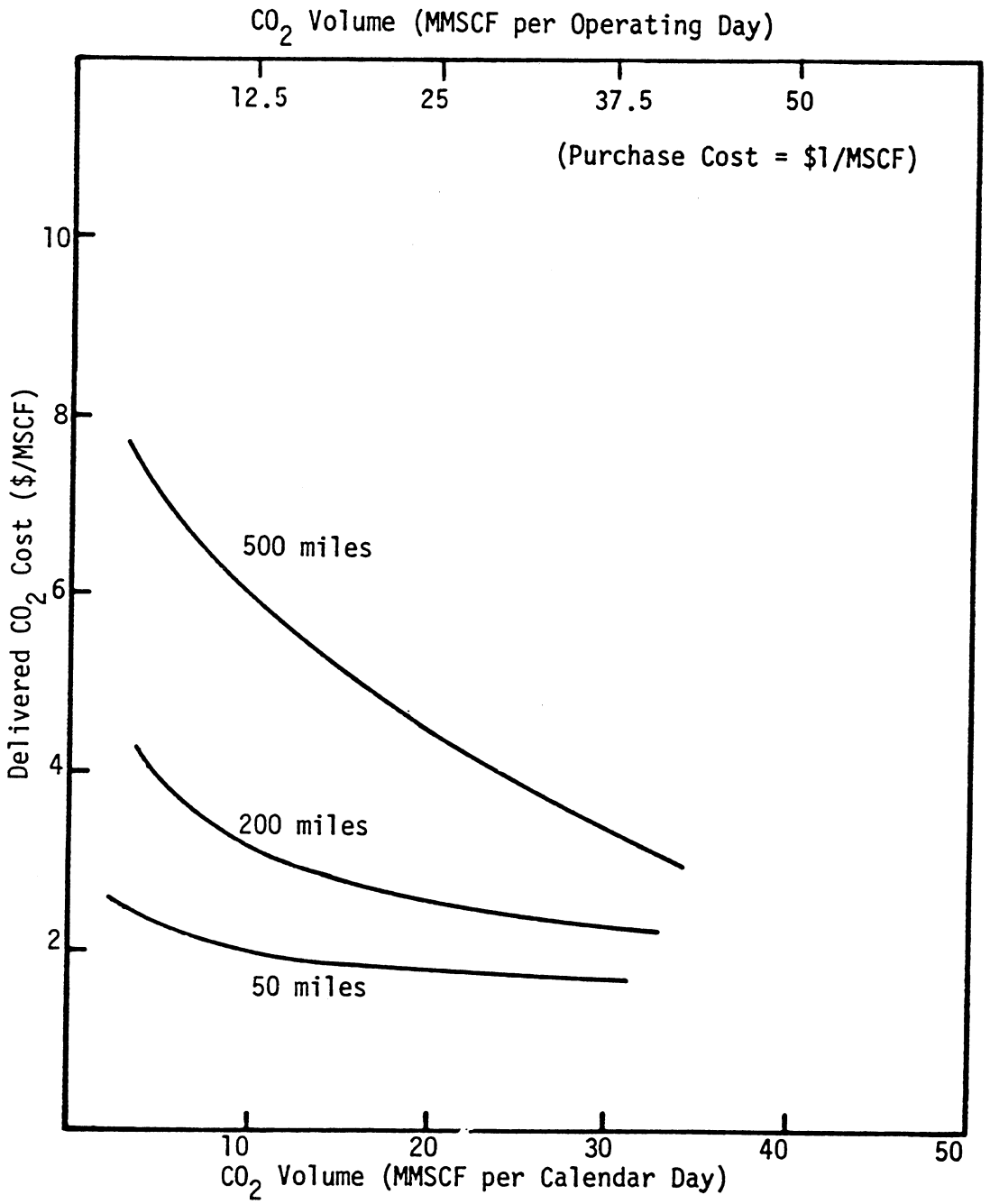


Exhibit 8-9: Delivered CO_2 Cost for Ammonia Plants and Other High Purity Sources

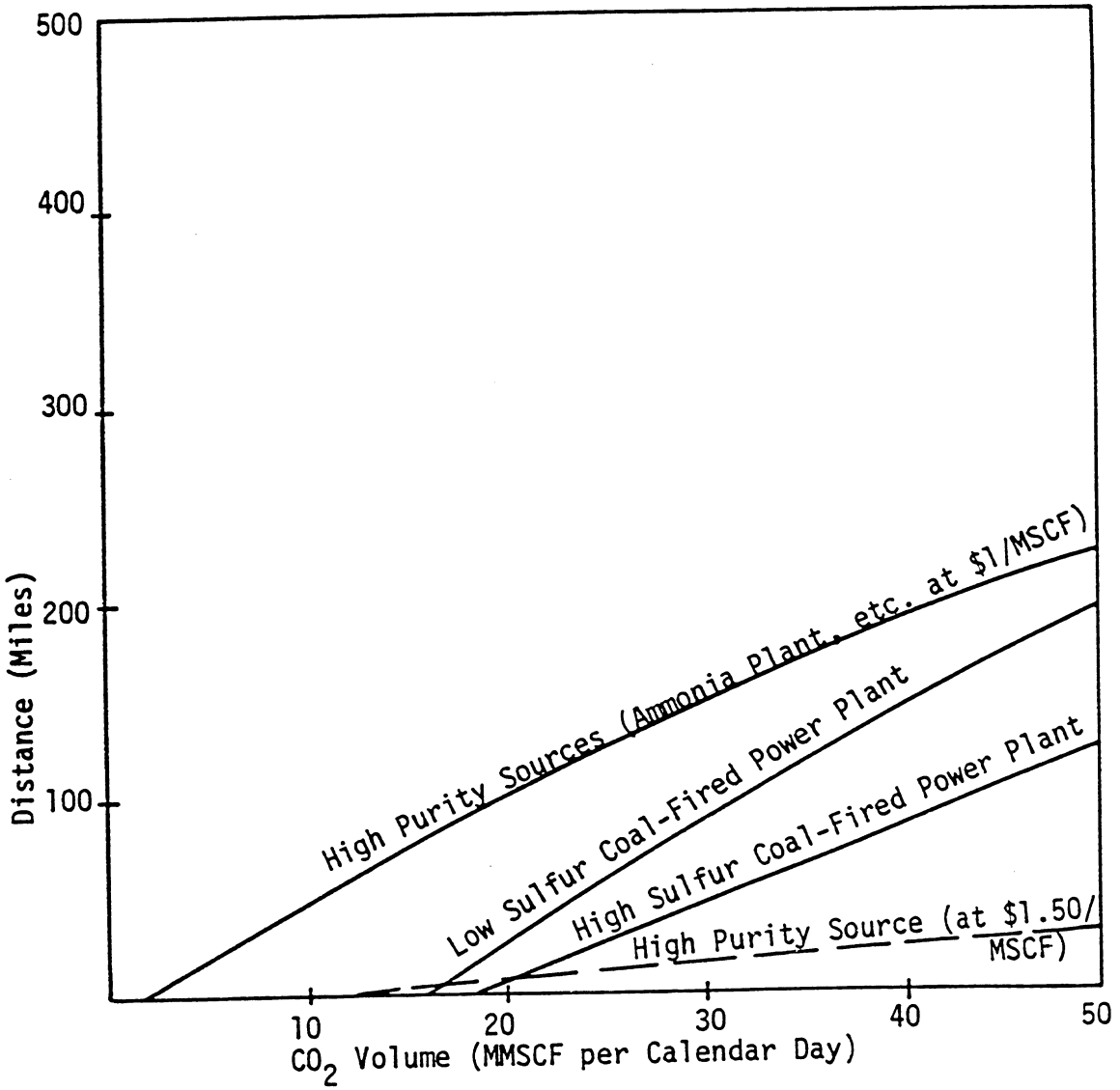


Exhibit 8-10: Maximum Transportation Distance for By-Product CO_2 Delivered at $2/MSCF

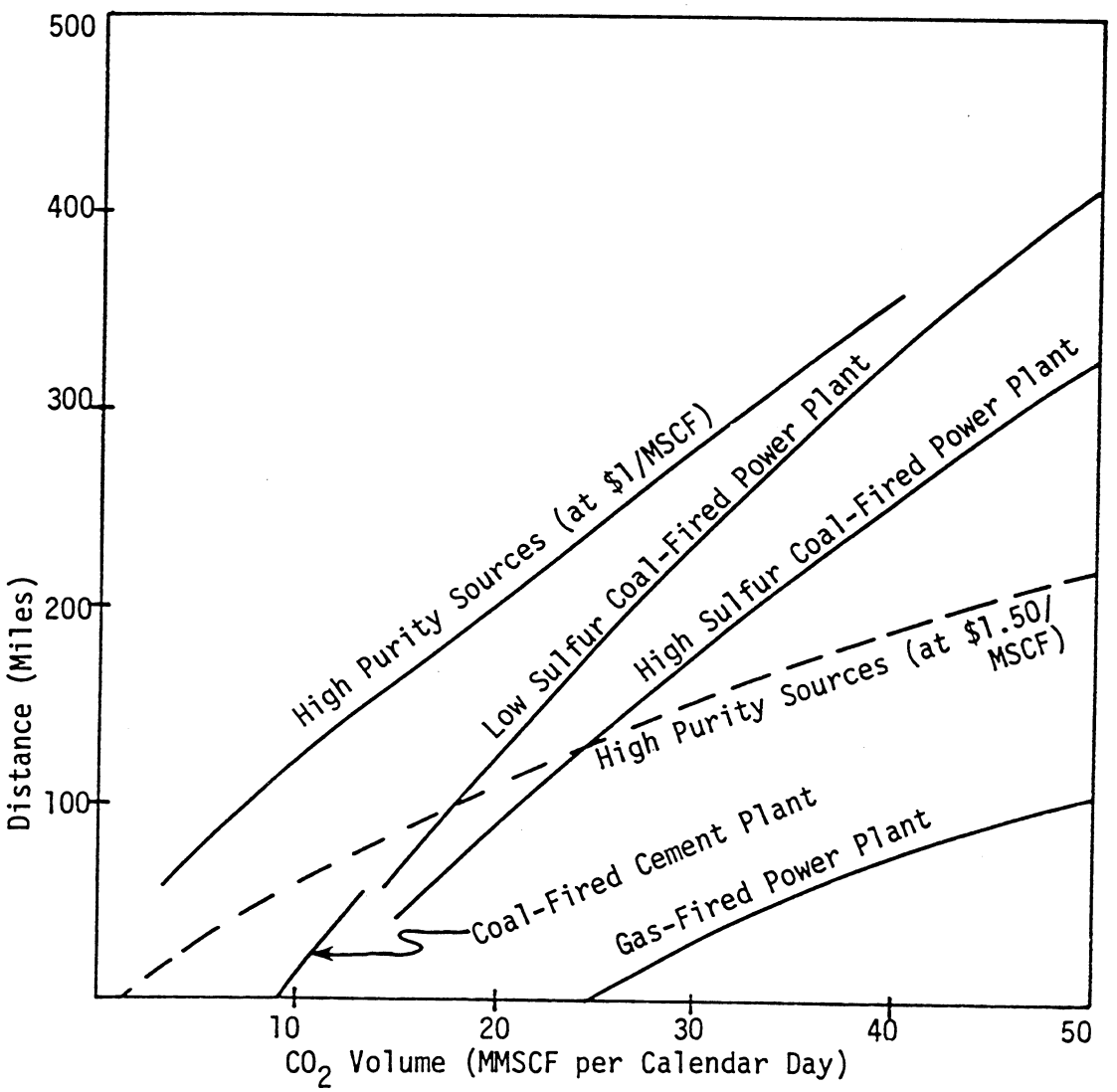


Exhibit 8-11: Maximum Transporation Distance for By-Product CO_2 Delivered at $2.50/MSCF

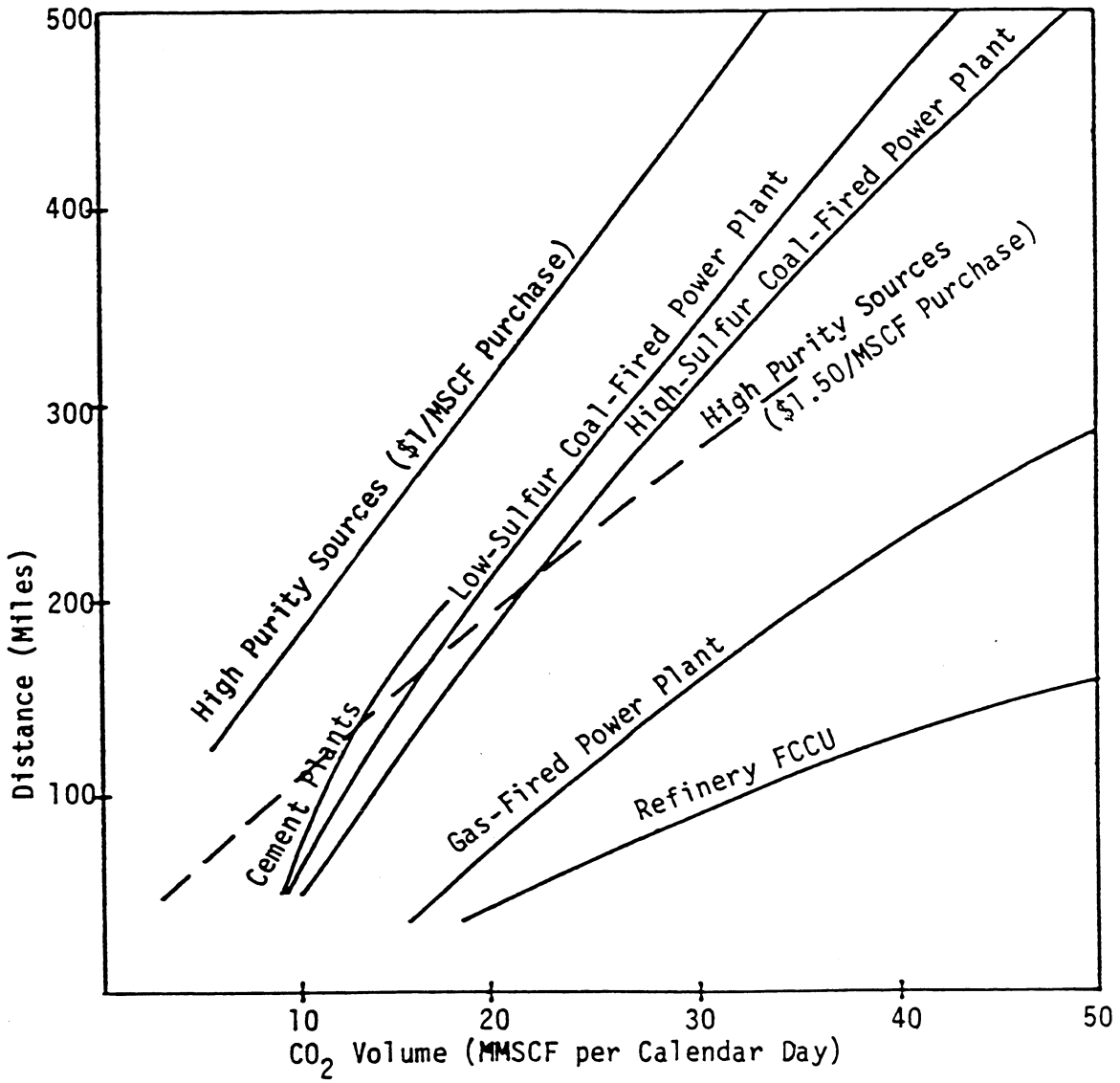


Exhibit 8-12: Maximum Transportation Distance for By-Product CO_2 Delivered at $3/MSCF

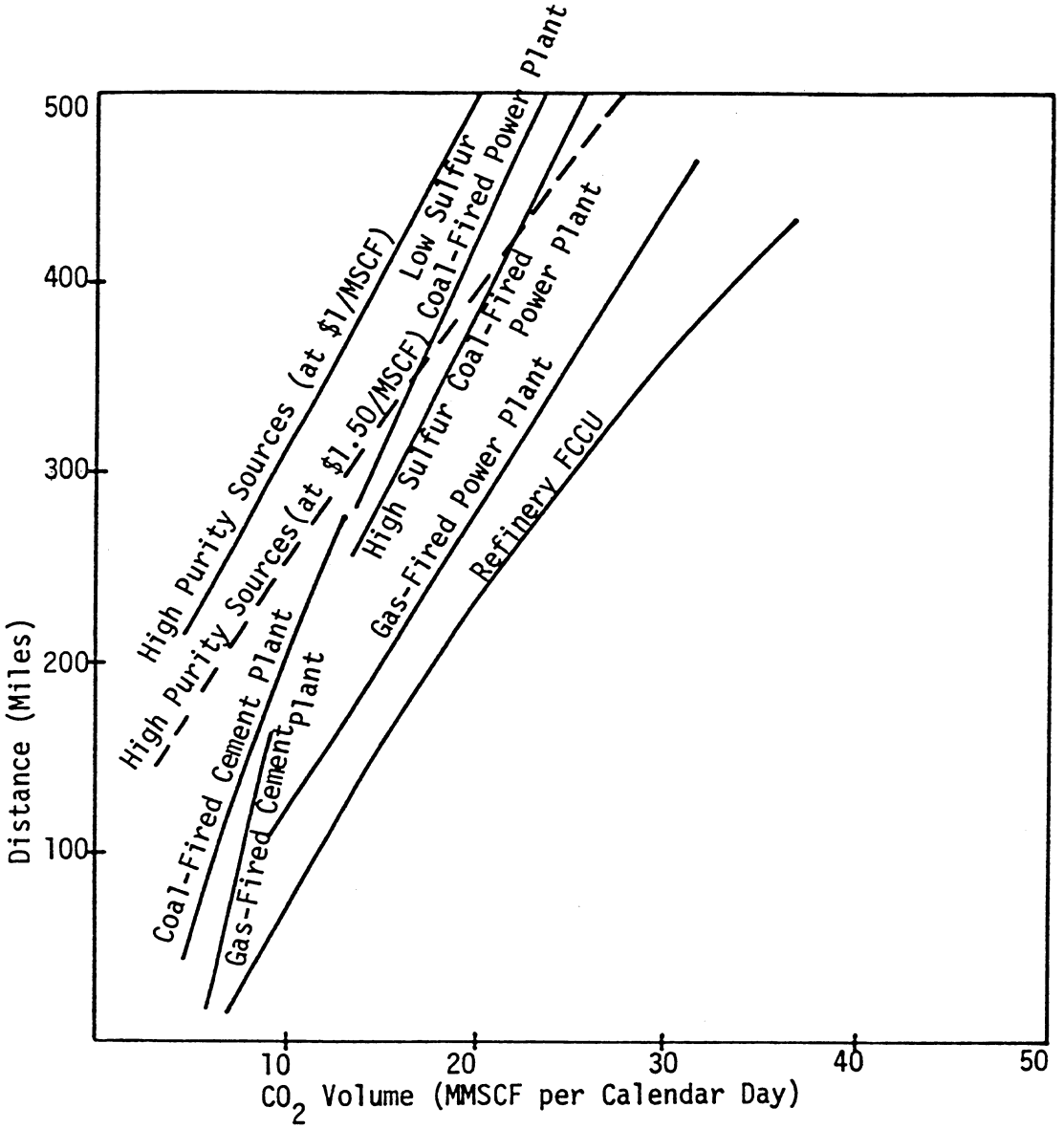


Exhibit 8-13: Maximum Transportation Distance for By-Product CO_2 Delivered at $4/MSCF

Thus, it appears that ammonia plants and other high purity sources can deliver CO_2 more cheaply than other by-product sources (in all cases if the CO_2 can be purchased at $1/MSCF). At a purchase price of $1.50/MSCF, the high purity sources are cheaper at low volumes, but above approximately 15 MMSCFD, the low purity sources are cheaper. Also, the number of high purity sources over 15 MMSCFD is quite low, restricting the availability for large projects to power plants, natural CO_2, or (future) SNG plants.

8.3 VALUE ADDED ANALYSIS

Value added analysis is a graphical technique for comparing cost components and total costs between alternative sources. Exhibits 8-14 and 8-15 show the individual costs for CO_2 supply for two types of source, at different demand rates.

This method of analysis can be used to display the result of the methodology in Section 8.2.1 and can provide indications of the trade-offs between purchase cost, purification cost, and transportation cost (The Exhibits are based on equal transporation distances, while in general the distances would be different for each source).

8.4 TRANSPORTATION MODEL

8.4.1 Methodology

In order to determine the average and maximum costs of supplying the CO_2 demand in a given region, an allocation of sources to serve various demand points is required, together with the total cost of serving each demand point from each source allocated to it. The individual costs can be obtained as described earlier in this Section. Optimization of the supply-demand matching (intended not in any prescriptive sense, but only as a means to determine the demand that can be satisfied at various CO_2 prices) can be achieved by modeling the situation as a classical Operations Research problem known as the Transportation Model.[54]

Several assumptions need to be made:

(a) All the supply from a given CO_2 source can be sold (not necessarily to the same buyer). This assumption implies that for a given source, the CO_2 purification and compression costs do not change as the quantity of CO_2 sold changes.

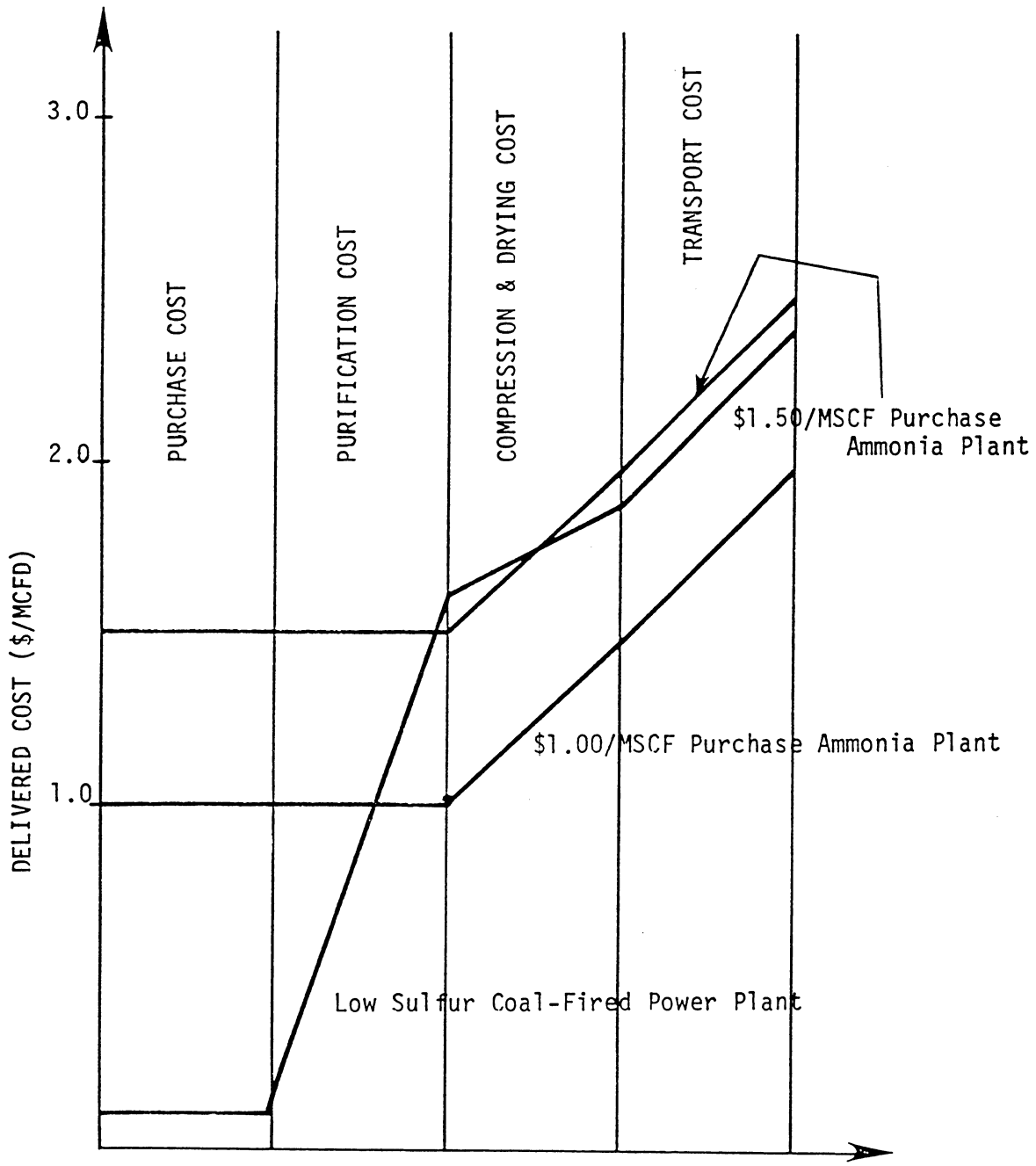


Exhibit 8-14: Value Added Chart for 10 MMSCFD CO_2

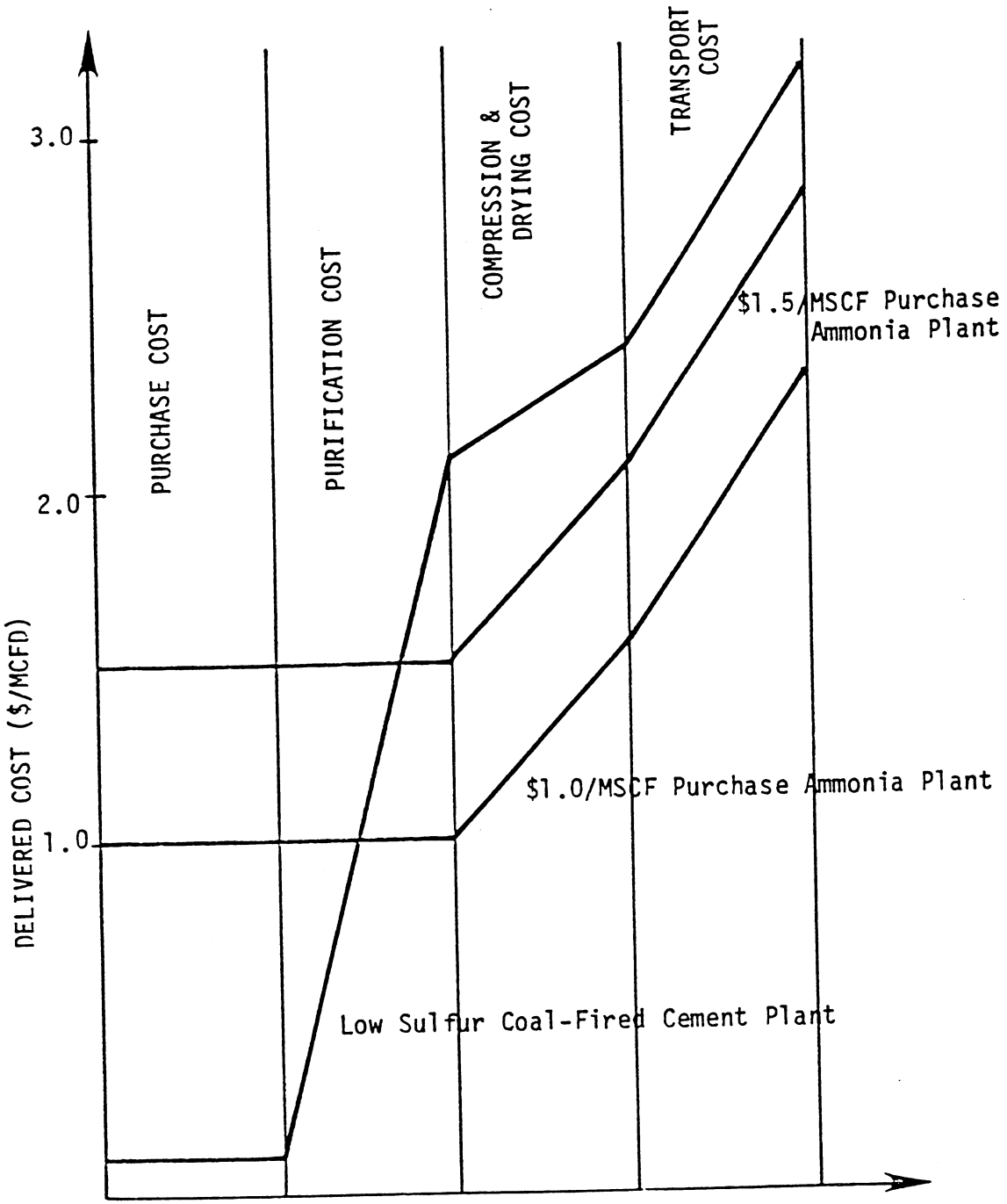


Exhibit 8-15: Value Added Chart for 20 MMSCFD CO_2

(b) The transportation cost is based on either (i) the smaller of the source volume and volume at the demand point , or (ii) the volume of the source.

Case (i) corresponds to the situation where the CO_2 supplied by each source is assumed to be in separate pipelines, trucks, etc.

Case (ii) applies when a source can utilize one pipeline to supply several demand points that are close together.

Results later in this Section will be derived for the first case, since this reduces the size of the problem.

(c) All CO_2 demand is assumed to be located at the center of the county.

(d) In order to reduce the problem to a manageable size, a limit of $2.50/MSCF was set for the maximum cost between supply and demand points. Any connections involving a higher cost were not considered. The cost of natural CO_2 was assumed to be $1.40/MSCF, and the cost from wet-air oxidation $3/MSCF.

(e) Since the costs are based on a given volume (either source or supply volume), they assume that this volume will flow between the source and demand, or the volume will be zero. This condition is not met in the following analysis, since a mathematical method of implementing this condition into the analysis was not readily available. However, the results below indicate that this situation does not arise very often, and even when it does, the input on the average cost should be small.

The method used to solve the problem for the example in Section 8.4.2 is known as the "out-of-kilter" algorithm, and is based on transforming the original problem (a simple linear programming problem) to a network formulation (see Reference 54 for details). A computer program was written to implement the algorithm, and is listed in appendix R, together with the input data used for analyzing the Permian Basin region.

8.4.2 Results

The total supply/demand figures used in the example were:

Total Demand	8220 MMSCFD
By-Product Supply	6724 MMSCFD
Natural CO_2	1150 MMSCFD
Shortage	346 MMSCFD
Wet Air Oxidation	Unlimited supply

When the individual supply/demand constraints were considered, only 5716 MMSCFD of the by-product supply could be used, and 2504 MMSCFD was supplied by wet air oxidation. The average delivered cost was $2.21/MSCF.

The allocation of supply points to the various demands is shown in Exhibit 8-16. A listing of the input volume and cost data is given in Appendix R.

Some of the counties shown as supplied by wet air oxidation could be supplied at a slightly lower cost ($2.50 to $3.00) from various by-product sources. This would not significantly impact the average cost (which may be reduced by a maximum of 8 cents/MSCF), but may change some of the flow patterns. However, the flows indicated here are not meant to indicate actual flows that will occur, but to illustrate the optimum allocations if the Permian Basin region is considered as a whole.

Exhibit 8-16: Supply/Demand Pattern for the Permian Basin Region

DEMAND			SUPPLY		
County, State	Daily Volume (MMSCFD)	Type of Plant	Plant Number	County, State	Volume Used/ Available (MMSCFD)
Hansford, TX	12	Ammonia	68	Moore, TX	7/7
		Ammonia	55	Woodward, OK	5/20
Chaves, NM	33	Wet Air Oxidation	--	--	33
Roosevelt, NM	41	Wet Air Oxidation	--	--	41
Eddy, NM	334	Low Sulfur Coal Power	12	Navajo, AZ	73/73
		Gas Fired Power	530	Seminole, OK	210/210
		Low Sulfur Coal Power	433	San Juan, NM	51/463
Lea, NM	553	Low Sulfur Coal Power	19	Coconino, AZ	378/503
		Gas Fired Power	445	Lea, NM	43/43
		Low Sulfur Coal Power	443	San Juan, NM	132/132
Hale, TX	90	Gas Fired Power	648	Potter & Randall, TX	11/65
		Low Sulfur Coal Power	31	Benton, AR	79/79
Cochran, TX	282	Gas Fired Power	649	Lamb, TX	35/45
		Low Sulfur Coal Power	74	Denver, CO	177/177
		Low Sulfur Coal Power	69	El Paso, CO	70/70
Hockley, TX	269	Gas Fired Power	649	Lamb, TX	10/45
		Gas Fired Power	648	Potter & Randall, TX	47/65
		Low Sulfur Coal Power	645	Potter & Randall, TX	109/109
		High Sulfur Coal Power	383	Henry, MO	103/122
Yoakum, TX	441	Natural Gas Processing	27	Yoakum, TX	112/112
		Low Sulfur Coal Power	433	San Juan, NM	329/463
Terry, TX	8	Wet Air Oxidation	--	--	8
Garza, TX	76	Gas Fired Power	651	Young, TX	67/67
		Gas Fired Power	648	Potter & Randall, TX	7/65
		Wet Air Oxidation	--	--	2
Kent, TX	112	Low Sulfur Coal Power	642	Camp, TX	93/93
		High Sulfur Coal Power	383	Henry, MO	19/122
Stonewall, TX	7	Wet Air Oxidation	--	--	7
Gaines, TX	756	Low Sulfur Coal Power	227	Linn, KS	255/255
		Low Sulfur Coal Power	19	Coconino, AZ	125/503
		Low Sulfur Coal Power	433	San Juan, NM	83/463
		Wet Air Oxidation	--	--	293
Dawson, TX	90	Wet Air Oxidation	--	--	90
Borden, TX	13	Wet Air Oxidation	--	--	13
Scurry, TX	276	Gas Fired Power	661	Titus, TX	276/412
Fisher, TX	18	Cement	135	Nolan, TX	18/21
Andrews, TX	671	Wet Air Oxidation	--	--	671
Martin, TX	7	Wet Air Oxidation	--	--	7
Howard, TX	256	Cement	135	Nolan, TX	2/21
		High Sulfur Coal Power	656	Freestone, TX	15/314
		Gas Fired Power	653	Mitchell, TX	90/90
		Low Sulfur Coal Power	527	Muskogee, OK	149/149

Exhibit 8-16, continued

DEMAND			SUPPLY		
County, State	Daily Volume (MMSCFD)	Type of Plant	Plant Number	County, State	Volume Used/ Available (MMSCFD)
Nolan, TX	41	Cement Gas Fired Power	127 668	Ellis, TX Taylor, TX	6/28 35/35
Winkler, TX	307	Gas Fired Power Wet Air Oxidation	655 --	Ward, TX --	68/68 239
Ector, TX	1692	Ammonia High Sulfur Coal Power High Sulfur Coal Power Gas Fired Power Wet Air Oxidation	62 660 656 646 --	Ector, TX Rusk, TX Freestone, TX Lubbock, TX --	5/5 358/358 238/314 49/49 1042
Midland, TX	130	Ammonia Low Sulfur Coal Power Wet Air Oxidation	52 637 --	Garfield, OK Bexar, TX --	43/43 55/136 32
Coke, TX	126	Cement Cement Gas Fired Power	135 128 663	Nolan, TX Ellis, TX San Saba, TX	1/21 40/40 85/85
Ward, TX	21	Wet Air Oxidation	--	--	21
Crane, TX	1034	High Sulfur Coal Power Natural CO_2	656 --	Freestone, TX --	61/314 973
Upton, TX	8	Natural CO_2	--	--	8
Reagan, TX	23	Natural CO_2	--	--	23
Tom Green, TX	16	Natural CO_2	--	--	16
Pecos, TX	170	Natural CO_2 Natural Gas Processing	-- 23	-- Pecos, TX	130 40/40
Crockett, TX	109	Cement Low Sulfur Coal Power	124 637	Bexar, TX Bexar, TX	28/28 81/136
Shackelford, TX	90	Cement Cement Gas Fired Power	139 127 652	Tarrant, TX Ellis, TX Tarrant, TX	26/26 22/28 42/90
Ford Bend, TX	11	Hydrogen Ammonia	27 63	Harris, TX Galveston, TX	2/13 9/9
Jackson, TX	56	Ammonia Gas Fired Power	69 627	Victoria, TX Ford Bend, TX	5/5 51/249
Refugio, TX	28	Gas Fired Power	607	Nueces, TX	28/56
Willacy, TX	8	Gas Fired Power	603	Hidalgo, TX	8/99
Webb, TX	5	Wet Air Oxidation	--	--	5

9. CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

1. The potential demand for CO_2 for EOR in each of the four regions considered in the study cannot be met by natural sources and high purity by-product sources (such as ammonia plants and ethanol plants), alone.

   A cost comparison (delivered costs) for pure CO_2 versus by-product sources shows that costs for natural CO_2 (or CO_2 purified from natural sources) are almost always lower than those for by-product CO_2 sources. Thus, unless the transportation costs are very high, natural CO_2 is the preferred source.

   However natural CO_2 and high purity by-product sources can supply a maximum of 20 percent of the projected daily demand requirements. Thus, low-purity by-product CO_2 sources are very important.

2. Although on-site generation of CO_2 was shown to be expensive in Section 7, the continued development of these processes may make this source possible in certain particular applications. Favorable circumstances could include using waste fuels in burning and by-product steam for local equipment. The favorable circumstances cited in Section 7 may not be present in the field.

   Wet air oxidation is a promising method for supplying CO_2, especially in an area where there is a local requirement for steam, but the technology is not yet commercially available for use in CO_2 supply.

   A more detailed study of wet air oxidation may be warranted, including coal purchase and transportation costs and the local market for the steam generated by these plants, before a definitive judgement can be made.

3. The total by-product supply in each region from low purity sources such as power plant flue gases is more than sufficient to meet the CO_2 demand. However, the demand should be met at a price that is affordable for profitable oil production.

Assuming an oil price of \$32/bbl, and estimated operation costs of \$18/bbl, the CO_2 delivered cost should not exceed \$14/bbl. Most estimates for the required CO_2 in MSCF/bbl of oil are in the 4 to 8 MSCF/bbl-range. This limits the cost of CO_2 to a range of \$1.75 to \$3.50/MSCF. Conservatively, an attractive price for CO_2 is \$2.50/MSCF. Sections 5 through 8 show compression and drying costs at large plants to be \$0.20/MSCF, the transportation costs to be approximately \$0.22/MSCF for 100 miles, and a by-product CO_2 purchase cost of \$0.10. Thus, the CO_2 purification cost must be less than \$2.00/MSCF for CO_2 by-product sources to be of potential economic interest.

These cost numbers may vary, but the general order of magnitude is correct. As inflation continues the price of oil will also increase. However, as energy prices are tied somewhat to inflation, and as the recovery of by-product CO_2 is energy intensive, it would require special circumstances to change the relative picture of the future. Such circumstances might be rising oil prices, more constant coal prices, and coal (lignite) being used for generating steam which is required for the regeneration of CO_2. In this report however, the present situation will be assumed to apply in the future.

Present technology using by-product sources such as gas-fired boilers produce CO_2 at roughly this cost (\$2/MSCF) or slightly higher (keeping in mind the $\pm$ 30% accuracy of these costs estimates). Current reported charges for CO_2 from high-purity sources such as ammonia plants are roughly \$1.50/MSCF (average). These sources provide CO_2 more cheaply than low-purity sources using present technology - particularly for demand volumes of less than 30 MMSCFD. In the short term such sources will be important. However, low-purity sources will be competitive for large demands, particularly assuming the optimistic designs presented in Section 5.

The potential demand for CO_2 requires an inexpensive CO_2 source. Low-purity sources, such as power plant flue gases, cement plants, and refinery off-gases, have more than sufficient CO_2 to meet the demand. Present technology (e.g., MEA absorption in plate towers) can extract the CO_2. However, if the total delivered cost is restricted to less than \$2.50, then many by-product sources cannot be used, and the total CO_2 supply may be inadequate unless improvements in CO_2 recovery technology are made.

4. Based on present projections and the identified supply and demand, the average delivered cost for CO_2 in the Permian Basin is expected to be \$2.20/MSCF [first quarter 1981 dollars]. This includes natural CO_2, existing by-product sources, and wet air oxidation.

5. The only by-product sources that can potentially provide CO_2 for a delivered cost under \$2/MSCF are coal-fired power plants, and high purity sources such as ammonia plants.

6. MEA processes are apparently cheaper than K_2CO_3 processes for low-sulfur coal-fired power plants and coal-fired wet cement plants, but the difference is only 5 to 10%, which is probably not significant within the accuracy of this preliminary analysis ($\pm$30%). K_2CO_3 processes are apparently cheaper for high-sulfur coal plants (because of their technical advantage over MEA in the presence of sulfur), and for gas-fired power and cement plants (due to the lower steam requirement compared to MEA processes). Again the difference is not significant.

7. For a given source, recovery costs do not vary much with respect to the recovery percentage. (Costs increase about 10% at 60% recovery compared to costs at 90% recovery. A further reduction to 30% recovery does significantly increase the costs). To provide a given output volume of CO_2, there is no significant difference in cost between 90% recovery from a small plant, and 60% recovery from a large plant.

8. Pipelines are the most economical form of transport for large volumes of CO_2 over all distances, and for small volumes (1 to 10 MMSCFD) at small (1 to 20 miles) and large distances (over 150 miles). Truck transport is competitive with pipelines for small volumes over the medium distance range.

   For pilot schemes, either truck or rail transport may be the best method to use, depending on the availability of equipment, rail facilities, and the volumes of CO_2 required.

9.2 RECOMMENDATIONS

1. It is suggested that improvements in the technology may be required for the widespread adoption of by-product CO_2 extraction for EOR.

Several alternatives are presented in this report for extending the technology. Higher active-species concentrations are recommended, as well as the adoption of a vacuum carbonate type process. It is probable that absorbtion columns of types other than plate towers should be used, e.g., packed columns or spray towers. Low cost fuel is particularly important. One possibility is the independent use of lignite coal for regeneration steam. With these improvements, and assuming ready operation with controlled corrosion, the costs for large CO_2 by-product sources were \$0.70 to \$1.30/MSCF. These potential costs are competitively advantageous even with smaller high-purity sources. By-product CO_2 does show the potential low costs needed for widespread adoption, but perhaps only after needed engineering research and development.

K_2CO_3 processes could be improved further, specifically variations of the vacuum carbonate processes. This could reduce steam requirements considerably and might eliminate the need for heat exchangers between the absorber and stripper. Thus, the lower surface area requirements for the reboiler, reclaimers, and heat exchangers could reduce capital costs by more than 50 percent. This would reduce the cost of CO_2 purification considerably, making CO_2 economical for EOR applications.

One further possibility is the simultaneous absorption of SO_2 and CO_2 where SO_2 scrubbing is already mandated. The incremental costs for CO_2 absorption may be lower than separate SO_2 and subsequent CO_2 scrubbing. The actual calculations showed an improved cost structure, but one that clearly depended on the exact rate structure allowed for SO_2 capture in the combined equipment. This apprrach looks promising.

2. Very little information was available on the EOR potential of oil fields in Louisiana and Mississippi. Since these fields are likely to be sources of large amounts of oil suitable for gas miscible displacement, more data should be gathered on them, and the CO_2 supply to these areas should be studied.

3. As the study is generalized in nature and gives estimated cost data within ±30% accuracy, the cost data should be used only for screening purposes and as guidelines. A detailed study would be required to obtain more accurate figures for specific sites and recovery systems.

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