



ENGINEERING HEALTH HAZARD CONTROL TECHNOLOGY  
FOR COAL GASIFICATION  
AND LIQUEFACTION PROCESSES

Final Report

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DISCLAIMER

The Enviro Control Division of the Dynamac Corporation prepared this report under contract No. 210-78-0084 for the National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering. The views expressed and conclusions reached in this document are the result of careful review of the available evidence, and consideration of comments from external reviewers. Mention of company names or products in this report does not constitute endorsement by the National Institute for Occupational Safety and Health or by the Dynamac Corporation.

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## PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to potential hazards at their workplace. The Act also mandates the National Institute for Occupational Safety and Health to conduct research, either directly or by grants or contracts, into areas relating to occupational safety and health.

The purpose of this study is to document current hazard control strategies and technologies used in coal gasification and liquefaction facilities which appear to be partially or wholly effective in preventing potential occupational health hazard exposures. The types of worker protection measures considered include engineering controls; safe work practices; personal protective equipment and clothing; industrial and personal hygiene; and process, workplace, and medical monitoring. A system comprised of most or all of these measures is necessary to provide an acceptable degree of confidence that worker protection can be maintained under both routine and unusual operating conditions.

Although the information presented is based on data from pilot, demonstration, and small scale commercial coal gasification and liquefaction plants, many of the potential hazards and control technologies will be similar to those occurring in large, commercial coal gasification and liquefaction facilities. This document should, therefore, be a valuable reference for researchers and administrators responsible for the development and implementation of occupational health guidelines in both pilot and full scale coal conversion facilities. It is also intended to be helpful in making occupational health considerations an integral part of the development of commercial scale coal conversion technology. In this way, hazards can be identified and effective control technology can be incorporated into the design, construction, operation, and maintenance of commercial coal gasification and liquefaction plants.

## ABSTRACT

The development of commercial coal conversion plants to supplement petroleum and natural gas supplies has engendered concern for the health of workers who will be employed in these plants. These workers may be exposed to toxic materials from leaks and spills from process and waste streams during normal plant operation, and during maintenance. Additional hazards are heat, noise, and the danger of fires and explosions. This report summarizes a survey of engineering controls and work practices used to protect worker health in twenty-one coal gasification and liquefaction pilot plants or semi-works. Sources of exposure, control technologies in use, and the effectiveness of the controls were compiled from observations at the facility, examination of plant layout and process diagrams, and interviews with plant management, engineers, operators, and maintenance workers. The principal health hazards of coal conversion are coal-derived liquids, carbon monoxide, and hydrogen sulfide. The coal-derived liquids are highly aromatic and contain polyaromatic hydrocarbons (PAHs) and aromatic amines which are associated with carcinogenic and mutagenic effects. Although occupational safety and health guidelines used in coal liquefaction plants (and to a lesser extent coal gasification plants) are similar to those used in petroleum refineries, the crude coal-derived liquids and the tars and oils from liquefaction and gasification contain higher levels of toxic and carcinogenic compounds than petroleum crudes. Proper choice of materials of construction and equipment is essential because of the corrosive and erosive nature of process materials and the severe conditions encountered in coal conversion. The objective of this study was to create a data base of hazard control technology options that may be utilized in the construction of future coal conversion plants which provide effective protection for the safety and health of their workers.

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CONTENTS

Disclaimer . . . . .	ii
Preface . . . . .	iii
Abstract . . . . .	iv
Acknowledgements . . . . .	v
I. EXECUTIVE SUMMARY . . . . .	1
A. PURPOSE . . . . .	1
B. APPROACH . . . . .	1
C. FINDINGS . . . . .	2
D. RECOMMENDATIONS . . . . .	3
1. ENGINEERING CONTROLS . . . . .	3
2. WORK PRACTICES . . . . .	4
II. INTRODUCTION . . . . .	5
A. SCOPE . . . . .	5
B. APPROACH . . . . .	6
C. PLANTS VISITED . . . . .	7
D. REPORT ORGANIZATION . . . . .	7
III. ENGINEERING CONTROL MEASURES . . . . .	10
A. COAL GASIFICATION . . . . .	10
1. COAL RECEIVING, STORAGE, AND PREPARATION . . . . .	13
a. Process Description . . . . .	13
b. Hazards . . . . .	13
Spontaneous Combustion . . . . .	13
Inhalation of Coal Dust . . . . .	13
Noise . . . . .	13
Asphyxiation by Inert Gases . . . . .	13
c. Engineering Controls . . . . .	15

CONTENTS (Continued)

2.	GASIFICATION . . . . .	16
	a. Process Description . . . . .	16
	b. Hazards . . . . .	17
	Inhalation of Coal Dust . . . . .	17
	Inhalation of Toxic Gases, Particulates, and Vapors . . . . .	17
	Skin Exposure to Ash . . . . .	17
	Noise . . . . .	17
	Heat Stress . . . . .	17
	Fire and Explosion of Combustible Gases . . . . .	18
	c. Engineering Controls . . . . .	18
	Leaks in Coal Feeding Systems . . . . .	18
	Gasifier Leaks . . . . .	19
	Dilution Ventilation . . . . .	20
	Noise . . . . .	20
	Heat Stress . . . . .	21
	Fire . . . . .	21
	Additional Engineering Controls . . . . .	21
3.	ASH REMOVAL . . . . .	21
	a. Process Description . . . . .	21
	b. Hazards . . . . .	22
	Gas Leakage . . . . .	22
	Dust . . . . .	22
	Skin Contact With Ash Quench Water . . . . .	22
	High Pressure Steam, Air, or Oxygen . . . . .	22
	c. Engineering Controls . . . . .	22
	Gas Leakage . . . . .	22
	Dust Leakage . . . . .	22
4.	PARTICULATE REMOVAL . . . . .	23
	a. Process Description . . . . .	23
	b. Hazards . . . . .	23
	Equipment Leaks . . . . .	23
	Fire and Explosion . . . . .	24
	Noise . . . . .	24

CONTENTS (Continued)

c.	Engineering Controls . . . . .	24
	Cyclone Separator Design . . . . .	24
	Scrubber Design . . . . .	24
5.	TAR REMOVAL . . . . .	25
a.	Process Description . . . . .	25
b.	Hazards . . . . .	25
	Skin Contact . . . . .	25
	Inhalation of Toxic Fumes and Vapors . . . . .	25
	Fire and Explosion . . . . .	25
c.	Engineering Controls . . . . .	25
	Plugged Lines . . . . .	25
	Equipment Leakage . . . . .	26
	Storage . . . . .	26
6.	ACID GAS REMOVAL . . . . .	26
a.	Process Description . . . . .	26
	Benfield Process . . . . .	27
	Stretford Process . . . . .	27
b.	Hazards . . . . .	27
	Toxic Gases . . . . .	27
	Toxic Solutions . . . . .	27
	Other Hazards . . . . .	27
c.	Engineering Controls . . . . .	27
	Construction Materials . . . . .	27
	Tank Covers . . . . .	27
7.	PRODUCT UPGRADING . . . . .	28
a.	Process Description . . . . .	28
	Shift Conversion . . . . .	28
	Methanation . . . . .	28
b.	Hazards . . . . .	28
	Dusts or Gases from Catalyst . . . . .	28
	Toxic and Hazardous Gases . . . . .	28
	Fire . . . . .	28
	Other Hazards . . . . .	28

CONTENTS (Continued)

c.	Engineering Controls . . . . .	29
	Preventing Nickel Carbonyl Formation . . . . .	29
	Loading and Unloading Catalyst . . . . .	29
	Construction Materials . . . . .	29
B.	COAL LIQUEFACTION . . . . .	30
1.	COAL RECEIVING, STORAGE AND PREPARATION . . . . .	30
a.	Process Description . . . . .	30
b.	Hazards . . . . .	30
c.	Engineering Controls . . . . .	34
	Respirable Coal Dust . . . . .	34
	Fire . . . . .	34
	Dust Explosion . . . . .	34
	Noise . . . . .	34
	Inert Gases . . . . .	35
2.	SLURRY MIXING . . . . .	35
a.	Process Description . . . . .	35
b.	Hazards . . . . .	35
	Coal Dust . . . . .	35
	Organic Vapors . . . . .	35
	Inert Gases . . . . .	36
	Skin Contact with Coal Derived Liquids . . . . .	36
c.	Engineering Controls . . . . .	36
	Respirable Coal Dust . . . . .	36
	Organic Vapors . . . . .	36
	Escape of Inert Gas Containing Carbon Monoxide . . . . .	37
	Contact with Coal Derived Liquids . . . . .	37
3.	REACTION AND PRESSURE LETDOWN . . . . .	37
a.	Process Description . . . . .	37
b.	Hazards . . . . .	38
	Liquid and Gas Leaks . . . . .	38
	Skin and Respiratory Exposure . . . . .	38
	Heat Stress and Noise . . . . .	38

CONTENTS (Continued)

c. Engineering Controls . . . . .	38
Organic Vapors . . . . .	38
Contact with Coal Liquids . . . . .	39
Noise from Furnace Burners and Pressure Letdown Valves	39
4. PRODUCT SEPARATION . . . . .	39
a. Process Description . . . . .	39
b. Hazards . . . . .	39
Equipment Leaks and Spills . . . . .	40
Maintenance . . . . .	40
c. Engineering Controls . . . . .	40
Equipment Leaks and Spills . . . . .	40
Maintenance . . . . .	40
5. GAS PROCESSING, RECYCLE, AND SULFUR RECOVERY . . . . .	41
a. Process Description . . . . .	41
b. Hazards . . . . .	41
Hydrogen Sulfide . . . . .	41
Ammonia . . . . .	41
Sulfur Removal Chemicals . . . . .	42
Sulfur . . . . .	42
c. Engineering Controls . . . . .	42
Hydrogen Sulfide . . . . .	42
Molten Sulfur . . . . .	43
6. SOLIDS SEPARATION . . . . .	43
a. Process Description . . . . .	43
b. Hazards . . . . .	43
c. Engineering Controls . . . . .	43
7. PRODUCT STORAGE . . . . .	44
a. Process Description . . . . .	44
b. Hazards . . . . .	44
c. Engineering Controls . . . . .	45
Fire and Explosion . . . . .	45
Leaks . . . . .	45
Tank Cleaning and Spills . . . . .	45

CONTENTS (Continued)

8.	HYDROGEN PRODUCTION . . . . .	46
	a. Process Description . . . . .	46
	b. Hazards . . . . .	46
	c. Engineering Controls . . . . .	46
9.	SUPPORTING OPERATIONS . . . . .	47
	a. Operations and Procedures . . . . .	47
	Plant Utilities . . . . .	47
	Byproduct Recovery . . . . .	47
	Waste Treatment and Disposal . . . . .	47
	b. Other Common Hazards . . . . .	48
	Hot Surfaces . . . . .	48
	Fire and Explosion . . . . .	48
	Process Monitoring and Analysis . . . . .	48
C.	SPECIAL EQUIPMENT AND MATERIALS . . . . .	49
	1. VALVES . . . . .	50
	Lockhopper Valves . . . . .	50
	b. Letdown Valves . . . . .	55
	c. Block Valves . . . . .	57
	2. PUMPS . . . . .	59
	3. THERMOWELLS . . . . .	62
	4. FLANGES . . . . .	63
IV.	WORK PRACTICES . . . . .	64
	A. MAINTENANCE PROCEDURES . . . . .	64
	1. EQUIPMENT ISOLATION . . . . .	65
	2. DRAINING . . . . .	65
	3. CLEANING . . . . .	66
	4. VESSEL ENTRY . . . . .	66
	B. HOUSEKEEPING . . . . .	67
	1. GENERAL PRACTICES . . . . .	67
	2. CLEAN-UP PROCEDURES . . . . .	67

CONTENTS (Continued)

C.	ISOLATION OF WORK AREAS . . . . .	68
1.	RESTRICTED AREAS . . . . .	68
a.	Barricades . . . . .	68
b.	Limited Access . . . . .	69
V.	PERSONAL PROTECTION . . . . .	70
A.	PROTECTIVE CLOTHING . . . . .	70
1.	PROCESS STREAM SAMPLING . . . . .	72
B.	RESPIRATORS . . . . .	73
C.	MISCELLANEOUS . . . . .	74
VI.	ENVIRONMENTAL MONITORING . . . . .	75
A.	AREA SAMPLING AND PERSONAL MONITORING PROGRAMS . . . . .	75
B.	MONITORING RESULTS REPORTED BY FACILITIES . . . . .	77
C.	NIOSH-SPONSORED INDUSTRIAL HYGIENE SURVEY . . . . .	77
VII.	WORKER TRAINING AND PERSONAL HYGIENE . . . . .	81
A.	TRAINING AND EDUCATION . . . . .	81
B.	PERSONAL HYGIENE . . . . .	82
VIII.	MEDICAL SURVEILLANCE . . . . .	85
IX.	RECOMMENDATIONS . . . . .	87
A.	DESIGN AND LAYOUT OF PROCESS AND EQUIPMENT . . . . .	87
B.	EQUIPMENT SELECTION . . . . .	88
C.	MATERIALS OF CONSTRUCTION . . . . .	88
D.	PROCEDURES . . . . .	89
E.	INSTRUMENTATION . . . . .	90
F.	ADMINISTRATIVE MEASURES . . . . .	90
G.	HEALTH AND SAFETY MONITORING PROGRAMS . . . . .	92
H.	RESEACH NEEDS . . . . .	93
X.	REFERENCES . . . . .	96

CONTENTS (Continued)

IX. GLOSSARY . . . . . 102

FIGURES

1 Typical Coal Gasification Schematic Diagram . . . . . 12  
 2 Typical Coal Liquefaction Schematic Diagram . . . . . 31  
 3 Rockwell Coal Lockhopper Valve . . . . . 53  
 4 Everlasting Double-Disc Coke-Oven Valve . . . . . 53  
 5 Everlasting Sliding-Disc Valve . . . . . 54  
 6 Kamyr PD Series Ball Valve . . . . . 54  
 7 Slurry-Letdown Valve . . . . . 56  
 8 Slurry-Letdown Valve and Receiver . . . . . 58  
 9 Through-Conduit Gate Valve . . . . . 61  
 10 Tapered-Plug Valve . . . . . 61  
 11 Locker/Change House . . . . . 83

TABLES

1 Coal Conversion Facilities Visited During the Study . . . . . 8  
 2 Occupational Hazards in Coal Gasification Plants by Process Operation 14  
 3 Major Process Operations in Coal Liquefaction Plants . . . . . 32  
 4 Occupational Hazards in Coal Liquefaction Plants by Process Operation 33  
 5 Summary of Valve Requirements for Coal Conversion Service . . . . . 51  
 6 Comparison of Valve Designs . . . . . 60  
 7 Minimal Protective Clothing Entry Requirement for Process Area . . . 71  
 8 Types of Respirators Used in Coal Conversion Facilities . . . . . 74  
 9 Hazardous Agents Monitored by Thirteen Plants . . . . . 76  
 10 Sampling and Analytical Methods for Hazardous Agent Monitoring . . . 78  
 11 Eight Coal Conversion Facilities Ranked by Geometric  
     Mean of PAH Area Concentrations . . . . . 80  
 12 Eight Coal Conversion Facilities Ranked by Geometric  
     Mean of PAH Concentration for Field Operators . . . . . 80  
 13 Comparison of Plant Medical Programs . . . . . 86



## I. EXECUTIVE SUMMARY

This report summarizes the results of twenty-one surveys of engineering controls and work practices used to protect worker health in coal gasification and liquefaction plants in the United States. Information from discussions of design practices relating to occupational health with two engineering companies is also included. The study was performed for the National Institute of Occupational Safety and Health (NIOSH) under Contract No. 210-78-0084.

### A. PURPOSE

Commercial coal conversion plants are being developed to supplement petroleum and natural gas supplies. These processes utilize finely divided coal as the raw material to produce gaseous and liquid hydrocarbon products. The occupational health hazards known to be present in petroleum refining and coal handling processes and others, yet unknown, may affect the health of workers in coal conversion plants. These workers may be exposed to toxic materials in process and waste streams in the course of normal plant operation, during maintenance, and by leaks and spills. Additional hazards are heat, noise, and the danger of fires and explosions.

In 1978, NIOSH contracted with the Enviro Control Division of the Dynamac Corporation to document and evaluate the controls being used to reduce or eliminate worker exposure to potential health hazards in coal gasification and liquefaction plants. In two concurrent studies, Dynamac performed industrial hygiene surveys for NIOSH at a number of these same plants to identify the hazards present and to assess the danger posed to workers in the coal conversion industry [1,2]. Some information derived from those studies has been incorporated into this report; however, the final reports of each study should be consulted for details concerning industrial hygiene sampling at the coal conversion plants. The primary emphasis of the present report is on the control of health hazards with some treatment on control of safety hazards relating to chemical fires and explosions. The combined objective of the three studies was to help create a data base that designers and operators of future coal conversion plants can build on to provide protection from occupational hazards in the design, operation, and maintenance of present and future coal conversion facilities.

### B. APPROACH

Health hazard control technology information was gathered through site visits to coal gasification and liquefaction plants. At each plant site visit, teams consisting of engineers and industrial hygienists explored the following areas:

- hazardous agents in the plant
- the routes by which workers may be exposed to these agents
- designed or retrofitted engineering controls to reduce worker exposure
- the effectiveness of the controls
- work practices which reduce worker exposure
- personal protection programs
- monitoring programs.

Data on the sources of exposure, control technologies in use, and the effectiveness of the controls were obtained through observations at the facility; examination of plant layout and process diagrams; and interviews with plant management, engineers, operators, and maintenance workers. Information from each facility was compiled in individual site visit reports. These reports and reports of the industrial hygiene surveys were the primary source of information for this document.

To organize the findings of the site visits, coal gasification and liquefaction processes have been broken down into a number of generic process areas. Information on the hazards and controls has been collected for each process area.

### C. FINDINGS

The experimental nature of the pilot and demonstration plants leads to frequent shutdown for repairs and modifications. These conditions, which are not expected to prevail in large-scale commercial plants, lead to an increased frequency of worker exposure to potentially hazardous materials. In spite of the wide range of variability within an operation and among the plants visited, the following general comments may be made:

The principal health hazards of coal conversion are coal-derived liquids, carbon monoxide, and hydrogen sulfide. The coal-derived liquids are highly aromatic and contain polyaromatic hydrocarbons (PAHs) and aromatic amines which are associated with carcinogenic and mutagenic effects. These compounds may pose a health problem through long-term exposures. The presence of high concentrations of carbon monoxide and hydrogen sulfide in the process stream can lead to an acutely hazardous condition during process upsets or repair work.

Many of the occupational safety and health guidelines used in coal liquefaction plants, and to a lesser extent in coal gasification plants, are similar to those used in petroleum refineries. The similarities should be even greater in full scale plants than in pilot plants.

The crude coal-derived liquids and the tars and oils from the liquefaction and gasification processes contain higher levels of toxic and carcinogenic compounds than do petroleum crudes.

The design of process technology and processing equipment can have a major effect in reducing or eliminating exposures. Reduction of exposure results from the elimination of leaks and other uncontrolled discharges and from lowered maintenance requirements.

Proper choice of construction materials is essential because of the corrosive and erosive nature of process materials and the severe conditions encountered in coal conversion. Although research is ongoing in this area, the best available information on reliability and durability is obtained from operating experience in the pilot and demonstration plants; designers should seek this type of information.

The variety of processes, operating conditions, and feedstocks requires numerous facility-specific considerations in controlling worker exposures.

All facilities visited have instituted programs for worker protection which include formal work practice development and documentation, worker training programs, medical surveillance programs, and workplace monitoring. However, the content of these formal programs and the management support for them varied considerably.

A personal hygiene program is critical for minimizing skin contact with coal tars and oils. Hygiene facilities and work practices varied widely among the plants visited.

Little is known about the specific hazards potentially associated with upgrading medium-Btu coal gas to a substitute natural gas (SNG) because of limited operating experience. Severe, unanticipated hazards are considered unlikely, however, since similar upgrading processes are fairly common to the petroleum refining and petrochemical industries.

#### D. RECOMMENDATIONS

The effectiveness of the engineering controls and work practices employed to protect and monitor worker health and safety varied among the coal conversion plants visited. Summarized below are controls and work practices that should be considered in the design of an effective worker protection program. These recommendations result from the observation of both effective and ineffective controls and work practices.

##### 1. ENGINEERING CONTROLS

Equipment, piping, instrumentation, and valves should be designed for maximum reliability. Equipment failures may cause leaks or spills, resulting in worker exposure. Frequent equipment failures increase the exposure of maintenance personnel who must make the repairs.

Various alternatives in the design of health hazard engineering controls should be considered. A change in operating conditions, or of process design, may be more effective than an equipment modification. The use of more than one type of control may be necessary to provide adequate reliability.

Equipment, piping, and instrumentation should be designed to prevent or relieve the accumulation of solids and eventual plugging, and to permit easy cleanout and decontamination, if necessary.

Processing should be conducted in closed systems as much as possible.

A closed drain system should be installed to prevent hydrocarbon emissions when emptying or flushing equipment and piping.

Welded joints should be used wherever possible; the use of flanged and screwed connections should be minimized.

Hazardous gases with poor warning properties, such as carbon monoxide and hydrogen sulfide, should be continuously monitored and high level alarms installed to alert workers.

## 2. WORK PRACTICES

Operators, maintenance personnel and supervisors should be trained to understand that housekeeping is a major factor in hazard control.

Joining flanged connections should be performed only by personnel who have been properly trained and who have the proper equipment.

Safe work procedures should be established for all modes of operation: startup, normal operation, shutdown, and emergency situations.

All equipment essential to the safety of the worker, including relief valves, fire fighting equipment, hazardous atmosphere monitors and alarms, and respirators should be inspected regularly.

Procedures should be instituted for cleaning up spills immediately and for ensuring that process areas are kept clean; workers and first line supervisors should be trained in these procedures and evaluated on their adherence to them.

Contamination should not be carried outside the plant or into the control room, eating areas, or toilet facilities. Housekeeping and personal hygiene measures should be instituted to ensure this.

Workers should participate actively in safety and health programs through joint safety committees, regular training, and interaction with peers and first line supervision.

Plant management should provide active, sincere, and highly visible support of safety and health programs.

Respirator programs should follow OSHA standards or NIOSH recommendations.\*

An industrial hygiene monitoring program should be established to identify significant emission or contaminant sources and the exposure or contamination levels present in the workplace.

A medical surveillance program should be established to include tests and examinations designed specifically to identify any health changes or conditions that are likely to be related to coal-derived materials.

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\* Information on respirator program recommendations and standards can be obtained through the NIOSH Training Course: Occupational Respiratory Protection Course 593 (1977) and OSHA CFR 1910.134.

## II. INTRODUCTION

It has been apparent for several decades that the United States would need to utilize alternate energy sources to supplement or replace traditional petroleum and natural gas supplies. With increased political and economic pressures to develop petroleum substitutes through the 1970's, both government and industry began to explore technologies for producing synthetic fuel from coal. A major concern in the development of a new coal conversion industry is for the health and safety of the workers involved.

The Occupational Safety and Health Act of 1970 established the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health and Human Services (formerly the Department of Health, Education, and Welfare) and the Occupational Safety and Health Administration (OSHA) in the Department of Labor. The Act provides for research, informational programs, education, and training in the field of occupational safety and health and authorizes the development, promulgation, and enforcement of standards.

NIOSH has been given the responsibility to conduct research, experiments, and demonstrations relating to occupational safety and health. As part of this overall mandate, NIOSH began a program to document and evaluate solutions to hazard control problems in 1976. To accomplish one portion of this control technology effort, NIOSH contracted with Enviro Control to study control technologies used to reduce or eliminate worker exposures to potential health hazards in coal gasification and liquefaction plants. In 1978, Enviro Control began to document and assess hazard control technology already in use to protect the safety and health of workers in coal conversion pilot plants. In two concurrent studies for the NIOSH Division of Respiratory Disease Studies, this contractor also performed industrial hygiene surveys at a number of coal gasification and liquefaction plants to identify the types of hazards present and the degree of danger posed to the workers in the coal conversion industry. The objective of these studies was to create a data base of potential hazards and preventive control options which would assist designers of future plants in the protection of their workers' safety and health.

This report presents the findings of the control technology assessment. The industrial hygiene surveys are documented in reports titled: Final Summary Report - Industrial Hygiene Assessment of Coal Gasification Plants [1], and Final Summary Report - Industrial Hygiene Assessment of Coal Liquefaction Plants [2] available from the National Technical Information Service (NTIS)\*.

### A. SCOPE

The health hazards associated with coal conversion plants include inhalation, dermal contact, and ingestion of toxic materials. Also included are physical agents, such as heat, noise, and fire. Exposure to hazardous agents in coal

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conversion plants may be reduced through the use of control technology, which includes engineering controls, work practices, personal protective programs, industrial hygiene programs, and monitoring. All aspects of control technology must be considered and integrated into an optimum control program.

The term engineering control is defined by NIOSH to include control measures, such as: the use of equipment designed to eliminate or reduce an occupational safety or health hazard; the use of add-on control equipment (e.g., ventilation systems); the modification of existing equipment (e.g., the substitution of mechanical seals on shafts for packing in rotating equipment or the use of special metallurgy); changes in the process design (e.g., recycling a stream that was formerly discharged); or changes of process chemistry (e.g., the substitution of mixed xylenes for benzene).

This study examined a wide range of coal conversion processes. The contractor visited gasification plants employing fixed, fluidized, and entrained bed gasifiers, which are designed to produce high-, medium-, and low-Btu gas. Liquefaction technologies studied included catalytic and non-catalytic hydrogenation, as well as donor solvent processes. In addition, the plants visited used coal types ranging from lignite to anthracite as feedstocks.

## B. APPROACH

Information for this study was gathered by visits to coal gasification and liquefaction plants. At each plant the site visit team identified the following factors:

- hazardous agents in the plant;

- routes through which workers may be exposed to these agents;

- engineering controls designed into the process or added later to reduce worker exposure;

- apparent effectiveness of the controls, based on observation of the controls, discussions with relevant personnel, and/or evaluation of plant workplace environmental sampling data and some limited NIOSH sampling;

- work practices which may reduce worker exposure;

- personal protective equipment programs; and

- process, workplace environment, and medical monitoring programs.

A Site Visit Protocol was sent to each facility visited. The protocol explained the purpose of the study and described the types of information sought. After arrangements for the visit had been made, a team (usually consisting of two engineers and an industrial hygienist) performed the survey. Information about the sources of exposure, the control technologies in use, and the effectiveness of the controls was obtained through personal observations of the facility; examination of plant layout, records, and process diagrams; and

through interviews with plant personnel. The personnel interviewed typically included plant management, plant and corporate industrial hygienists, plant safety officers, plant engineers, plant operators, maintenance workers, and employee representatives.

A draft report of the team's findings was reviewed by NIOSH, DOE, and the plant management for technical inaccuracies and/or proprietary information. The reviewers' comments were incorporated, as appropriate, and a final report of the site visit was issued. These reports, which are the primary source of information for the present document, are available through the NITS.

### C. PLANTS VISITED

The primary mission of the pilot and demonstration plants visited was to develop technically and economically viable processes for converting coal into a fuel or chemical feedstock that is an environmentally acceptable alternative to oil and natural gas. To accomplish this goal, many equipment and process design changes were made to test the reliability and costs of the process options. The scope of the present study included not only equipment designed specifically to control potentially harmful emissions, but also modifications of processing equipment which resulted in reduced exposure, even if such changes were not made specifically for occupational health reasons. Twenty-one coal conversion plants and two engineering design and construction companies were visited (see Table 1). Industrial hygiene sampling surveys were performed at eight of these plants as part of the two concurrent NIOSH studies. Summaries of the results of these surveys have been incorporated into the present report where appropriate. The individual reports should be consulted for details concerning the sampling methods and results.

Additional information was gathered by attendance at technical conferences. Topics covered by these conferences fell into four areas: coal conversion processes, instrumentation and control, valves, and industrial hygiene findings.

Proceedings of the symposia and conferences attended and the papers presented are identified in the references section of this report [57-69].

### D. REPORT ORGANIZATION

Section III is a discussion of the engineering control measures found in the various coal conversion facilities. Typical processing steps used in coal gasification plants are delineated in Part A; however, no single gasification plant may have all the of steps described. Part B is a discussion of direct coal liquefaction processes presented in the same manner. Special equipment and materials of construction for certain critical components of coal gasification and liquefaction plants are discussed in Part C.

Chapters IV through VIII are an assessment of nonengineering controls for the reduction or prevention of worker exposure to hazardous agents. Chapter IX presents recommendations for measures to protect worker health and safety which should be considered in the design and operation of coal conversion facilities.

TABLE 1

## Coal Conversion Facilities Visited During the Study

Plant Reference	Process Characteristics	Coal Input (tons/day)	Products	In operation during visit
<u>GASIFICATION</u>				
3	Entrained flow, slagging ash, high pressure, two-stage	120	High-Btu gas	no
4	Fixed-bed, dry ash, low pressure, two-stage	75	Low-Btu gas, tar, oil	yes <sup>a</sup>
5	Fixed-bed, dry ash, single-stage	50	Low-Btu gas	no
6	Fixed-bed, dry ash, two-stage	72	Low-Btu gas, tar, oil	yes
7	Entrained-flow, slagging ash, atmospheric pressure, two-stage	120	Low-Btu gas	yes <sup>a</sup>
8	Fluidized-bed, high pressure	72	High-Btu gas	no
9	Fixed-bed, slagging ash, pressurized	25	Medium-Btu gas	yes
10	Fixed-bed, dry ash, medium pressure (200-300 psi), airblown	1 (ton/hr)	Low-Btu gas	yes
41	Entrained-flow, slagging ash, high pressure	135	Medium-Btu gas	no
42	Fluidized-bed, agglomerating ash, pressurized, single-stage	15	Medium-Btu gas	no <sup>b</sup>
43	Molten-media (salt), pressurized	1 (ton/hr)	Low-Btu gas	no
44	Entrained flow	3/4 (ton/hr)	High-Btu gas, Benzene, Toluene, Xylene	no

TABLE 1 (Continued)

## Coal Conversion Facilities Visited During the Study

Plant Reference	Process Characteristics	Coal Input (tons/day)	Products	In operation during visit
<u>LIQUEFACTION</u>				
9	Non-catalytic hydrogenation, high pressure	5 (lb/hr)	Distillate products	no
13	Non-catalytic hydrogenation, high pressure	50	Solid or Liquid fuels	yes <sup>a</sup>
14	Non-catalytic, donor solvent hydrogenation, high pressure	20	Heavy distillate	yes <sup>a</sup>
15	Non-catalytic, donor solvent hydrogenation, high pressure	250	Transportation fuels, Boiler fuels	yes <sup>a</sup>
16	Ebulating-bed, catalytic hydrogenation, high pressure	600	Transportation fuels, Fuel oil	yes <sup>a</sup>
17	Non-catalytic hydrogenation, high pressure	6	Solid fuel	yes <sup>a</sup>
45	Fixed-bed, catalytic hydrogenation, high pressure	750 (ton/hr)	Heavy industrial liquid fuel	no
73	Low-temperature (900° F) coal pyrolysis	25	Char, Liquids, High-Btu gas	no
75	Non-catalytic hydrogenation, high pressure	50 (lb/hr)	Solvent refined lignite	no
<u>ANALOGOUS PROCESS</u>				
46	Synthesis gas (steam reforming) from natural gas, high pressure	-	Anhydrous Ammonia	yes

a: Indepth industrial hygiene survey conducted during this site visit.

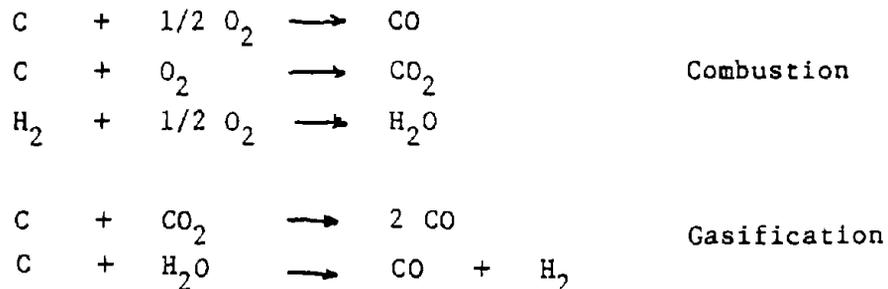
b: Indepth industrial hygiene survey conducted a later date.

### III. ENGINEERING CONTROL MEASURES

In the following presentation, engineering controls relating to gasification processes and liquefaction processes are treated separately. Each processing step is divided into three sections: a generic process description; a discussion of the safety and health hazards associated with the area; and a description of the engineering controls used to mitigate those hazards. Special equipment or materials of construction are discussed in Part C.

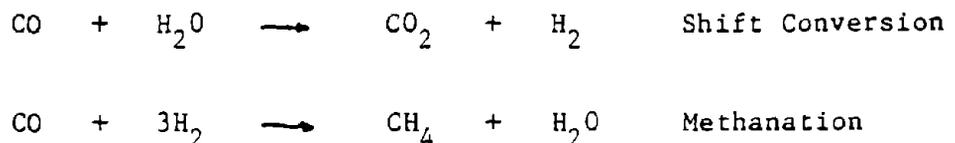
#### A. COAL GASIFICATION

This section focuses on engineering features of coal gasification plants which have been found useful or necessary for controlling the exposure of workers to toxic materials and other hazardous agents. A wide variety of coal gasification processes exist, but in all plants the basic chemical process is the same: carbon is combined with steam and either air or oxygen to generate a combustible gas. The general gasification reaction involves a combustion (exothermic) step and a gasification (endothermic) step as follows:



The value of this gas as a fuel is a function of the carbon monoxide and hydrogen it contains. The product is either low- or medium-Btu gas depending on whether air or oxygen is used in the process. If air is used, the concentration of the carbon monoxide and hydrogen is diluted by the nitrogen present, and thus the energy content per unit volume is reduced.

Medium-Btu gas can be processed to produce a high-Btu gas which can be substituted for natural gas: the carbon monoxide to hydrogen ratio is adjusted by shift conversion; these gases are then catalytically combined under high temperature and pressure to generate methane in a highly exothermic reaction:



Although this process is costly and involves substantial energy losses, the resulting gas is equivalent to natural gas and can be distributed through the existing natural gas pipeline network.

A number of different engineering designs for gasifying coal exist in varying states of commercial readiness. These concepts vary both in fundamental operating parameters, such as pressure and temperature, and in engineering features, such as designs for gasifier coal feed and ash removal. Plants that produce high-, medium-, and low-Btu gas were included as part of this study. The designs that were surveyed included three types of coal beds (fixed, entrained, and fluidized) and both dry and molten (slagging) ash removal techniques. Table 1 provides descriptive information on the plants visited.

Since no large-scale plants have yet been built in this country, the only operational data available come from small scale process development units, pilot plants, and small commercial units. These plants ranged in coal usage from 10 to 120 tons of coal per day (tpd). Many of the pilot plants visited simply burned product, byproduct, and waste streams to dispose of these materials; because the plants were small, some facilities, such as hydrogen generation, sulfur removal, and wastewater treatment, were provided by adjacent commercial plants. Commercial scale coal conversion plants (20,000 tpd) will up-grade, store, distribute products and byproducts, and recover other byproducts from the wastewater. Commercial plants will also be self-sufficient, providing their own utilities. Because of these and other differences, commercial operations probably will present hazards and sources of exposure not found in the pilot and demonstration plants visited. However, severe, unanticipated hazards are unlikely, since many of the auxiliary processes will be analogous to existing installations e.g., in petrochemical complexes.

Unlike pilot plants, in which changes to equipment and operating procedures are routine, commercial plants are built with the goal of stable, continuous operation. This difference could affect worker exposure in two contradicting ways. Maintenance operations at a commercial facility should be less frequent and more routine, reducing this source of exposure. However, small problems, such as leaks of toxic or hazardous gases or liquids, (particularly from low pressure systems) which do not threaten the operation of the plant, are likely to be tolerated in a commercial facility. This is especially true if servicing the problem will reduce the production rate for a short time. Specialized safety requirements will be required for operation and maintenance of commercial plants.

The discussion of engineering controls for coal conversion plants has been organized by unit operations. Coal gasification processes discussed in this section have been divided into a sequence of unit operations. All plants can be described by linking together a number of these operations, although any given plant may not include all of them. Figure 1 is a schematic diagram of unit operations for the coal gasification system.

Each of the following sections is divided into three parts: 1) a brief description of the operation or chemical processes, 2) a discussion of associated hazards, and 3) a discussion of the engineering controls which were found in operation during the site visit or planned for future installation. Where appropriate, additional information is included from visits to coal conversion plants made as part of other studies.

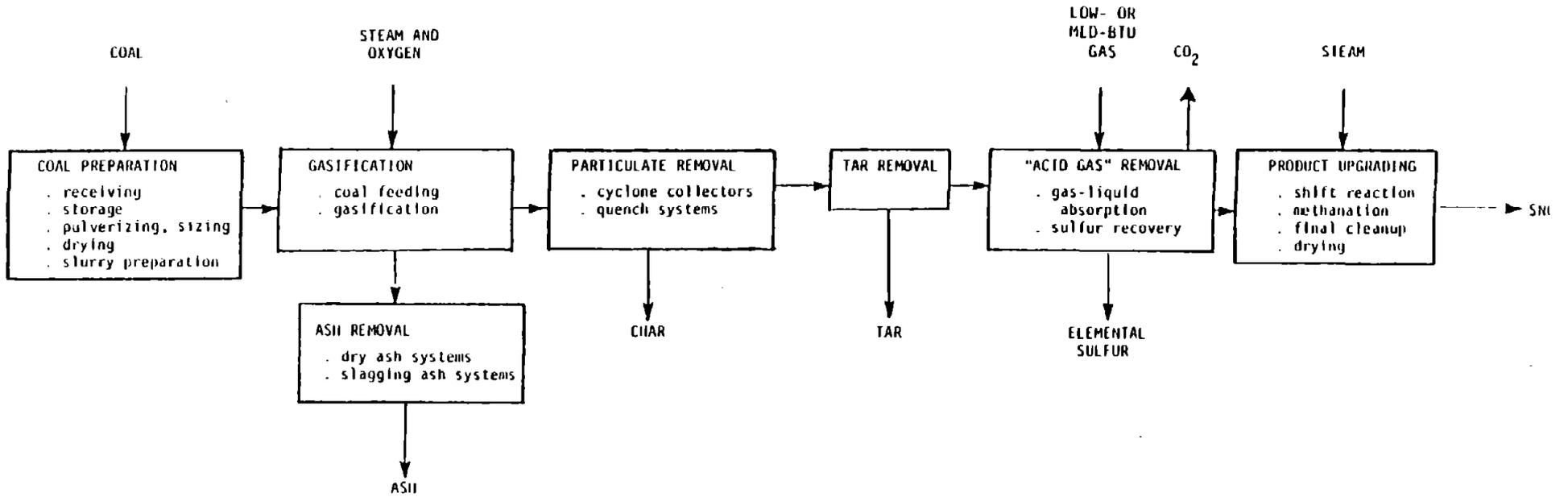


Figure 1. Typical Coal Gasification Schematic Diagram

There is a certain amount of overlap between the unit operations. Not only are hazards, such as worker exposure to product gas, common to several processing stages; but many controls, such as the use of welded joints, are also appropriate for several operations. In addition, the severity of a hazard common to several operations can vary from operation to operation. There are also many problems and controls which are relevant to only one process. Table 2 is a summary of the potential occupational exposures in coal gasification plants by unit operations.

## 1. COAL RECEIVING, STORAGE, AND PREPARATION

### a. Process Description

Coal is generally transported and received in bulk quantities delivered to the facility by truck, rail, conveyor, or barge. Transfer from the carrier to the storage area may be done by conveyor, stacker-reclaimer, haulage trucks or loaders, or pneumatically (for finely ground, prepared coal). Raw coal may be stored in open piles or enclosed in silos.

Generally, coal preparation for gasification processes will include one or more of the operations of pulverizing, grinding, and drying. Prepared coal will be stored in closed bins or silos prior to use. The amount of preparation, size, and moisture reduction will depend on the process in which the coal is used.

### b. Hazards

#### Spontaneous Combustion

Storing and processing coal by grinding, pulverizing, and drying operations pose the possibility of spontaneous combustion in storage areas and process equipment, and the possibility of coal dust explosions. Coal, and particularly lignite, can react with air while in storage, providing enough heat to eventually cause combustion. In general, the greater the surface area of the coal, the more likely it is to combust spontaneously. The presence of noncarbon impurities can also contribute to this process. Spontaneous combustion of stored coal can produce a complex mix of smoke, carbon monoxide, and coal tars.

#### Inhalation of Coal Dust

In reducing the coal to the proper size, crushing, grinding, and pulverizing operations produce dust. In some gasification processes finely ground coal dust is required as the feed. The potential for worker exposure to and inhalation of this dust is high in these operations. Drying the coal also may release coal dust to the atmosphere.

#### Noise

Due to the enormous scale of the equipment and the feed rates needed, high noise levels will occur, particularly in the size reduction and coal loading and unloading operations.

#### Asphyxiation by Inert Gases

Blanketing stored material with an inert atmosphere, such as nitrogen and flue gas, is used to prevent fire and explosion in the coal preparation section. Leaks of these gases into the workplace may accumulate in low or unventilated areas, with the possibility of asphyxiation of workers in these areas.

TABLE 2

## Occupational Hazards in Coal Gasification Plants by Process Operation

HAZARD	PROCESS OPERATION						
	Coal Preparation	Gasification	Ash Removal	Particulate Removal	Tar Removal	Acid Gas Removal	Product Upgrading
Noise	x <sup>a</sup>	x	- <sup>b</sup>	-	-	-	x
Fire	x	x	-	x	x	-	x
Heat	-	x	-	-	-	-	x
Coal Dust	x	x	-	-	-	-	-
Steam	-	x	x	-	-	x	x
Catalyst Dust	-	-	-	-	-	-	x
Product Gas	-	x	-	x	x	x	x
Methane	-	-	-	-	-	-	x
Hot Ash and Dust	-	-	x	x	-	-	-
Tars and Oils <sup>c</sup>	-	x	-	x	x	-	-
Carbon monoxide	x	x	x	x	-	x	-
Hydrogen Sulfide	-	-	-	x	x	x	x
Gas-liquor	-	-	-	x	x	-	-
Inert Gases (asphyxiation)	x	x	-	-	-	-	-
Nickel Carbonyl	-	-	-	-	-	-	x
Cryogenic Temperatures	-	-	-	-	-	x	-
Hydrogen Cyanide	-	-	-	x	x	x	x

a x: hazard is associated with the process operation

b -: hazard is not associated with the process operation

c Contains polynuclear aromatic hydrocarbons and aromatic amines

### c. Engineering Controls

Coal storage piles and bins are located at a safe distance from the plant [3]. To reduce the likelihood of spontaneous combustion in the coal storage piles, a first-in, first-out system of coal storage is employed. The piles are compacted by front-end loaders to reduce voids (and the included oxygen) [4]. Anthracite coal is less friable (but more expensive) than lower rank coals and presents a smaller coal dust hazard [5]. Upon transfer into the plant, coal is unloaded in a closed, ventilated area to reduce the spread of dust. Dust drawn off by the ventilation is removed from the air stream by cloth filters [6,7]. Water and detergent sprays may be available to agglomerate dust and for use in case of fires [5,6]. Coal is also wet down to control the dust [7]. All ventilation air passes through baghouse filters to remove the coal fines [4,7]. Blowout panels are installed in the baghouse to release the pressure in case of a dust explosion [7,8].

Conveyor belts and other coal transport devices are enclosed to control the dust and reduce noise levels [4,5,8]. The use of rubber materials in the transport system minimizes noise problems [5]. Transfer points in the coal transport system are covered with cloth covers to control coal dust generated at the transfer point [9]. The use of nitrogen blanketing to control the fire hazard has been proposed for a plant using lignite, since this type of coal has a greater tendency toward spontaneous combustion [7]. In this plant, thermocouples are located in the bin to detect heat build-up so that measures can be taken to prevent or control fires at an early stage [7]. Stainless steel may be used to reduce corrosion and maintenance requirements at points where acid gases are handled [7].

In one plant, all coal handling equipment was enclosed and under negative pressure to prevent dust from escaping into the workplace. Unfortunately, a vibrating feeder in this system had a tendency to clog. When this happened, the cover of the feeder had to be removed and worker exposure to dust and noise was increased [4].

Additional control measures needed will depend on the nature of the coal preparation activities. When feasible, the use of pre-sized coal avoids the hazards of pulverizing in the plant [5]. In pulverizing operations, the coal may be mixed with water to control dust and reduce the noise level associated with pulverizing; however, the need to dry the coal introduces other potential hazards associated with high temperatures [3]. Coal fines have a greater tendency towards spontaneous combustion and explosion and should, therefore, be stored separately [4].

In handling pulverized coal, the level of oxygen must be held below 15% to prevent explosions [8]. However, high levels of dust may cause high maintenance requirements for oxygen analyzers [7].

In one plant all seals on the coal pulverizer are blanketed with nitrogen to reduce the possibility of air contacting the hot coal [7]. Furthermore, the process is computer controlled; if a problem develops, the system is shut down automatically using techniques which are applied to commercial utility boilers.



## 2. GASIFICATION

### a. Process Description

The gasifier is a closed vessel in which coal is reacted in an oxygen-poor environment. In all gasifiers, the inputs are coal, steam, and air or oxygen, which provide the carbon, hydrogen, and oxygen needed for the gasification reactions. The general reaction steps were described earlier in this section. The gasifier output streams are the product gas (including impurities) and ash or slag, which is withdrawn from the bottom of the gasifier. Useful fuel gases produced during gasification include carbon monoxide, hydrogen, methane, and other hydrocarbons. The gas exiting from the gasifier also contains other compounds, which have no useful fuel value. These components may include any or all of the following: hydrogen sulfide and other sulfur compounds; ammonia, hydrogen cyanide, and organic nitrogen compounds; and tars. The composition of the gas produced is determined by the coal used, the temperature of gasification, and the design of the gasifier.

Three significant engineering features distinguish gasifier designs: the operating pressure, the nature of the coal bed, and the temperature. Operation may be at sub-atmospheric, atmospheric, or at elevated pressures. The advantages of high pressure operation are: higher gas production rate, increased methane production, elimination of the need to pressurize the gas at a later stage, and increased gas production per unit volume of gasifier. Low pressure gasifiers have the advantage of lower cost but this may be offset by the lower capacity.

There are also three types of bed-characterized gasifier designs: fixed bed, fluidized-bed, and entrained-flow.

In the fixed-bed gasifier, a grate supports a bed of coarse coal. Oxygen and steam pass up through the bed, and ash falls through the grate for removal. Rotating grates and stirrers have been added to some fixed-bed gasifiers to break up coal agglomerates formed by caking coals.

In the fluidized-bed gasifier, fine coal is used and the gas passing through the fluidized coal bed lifts these fine particles in a "boiling" action. The increased surface area of the coal exposed by this action enhances the rate of chemical reaction and gasification. The use of caking coals in this type of bed may be limited.

In the entrained-flow gasifier, any coal can be utilized, including caking coal. As in fluidized-bed gasifiers, fine particles of coal are carried into the vessel with the oxygen and steam. The particles have a much shorter residence time in the portion of the bed which might be considered to be fluidized. The product gas is high in particulate matter, since much of the feed material is entrained in it.

Several distinctions may also be made on the basis of temperature. Gasifiers may operate above or below the melting point of the ash. Slagging gasifiers operate above the ash melting point; the ash is removed as a molten slag which

is solidified prior to disposal. Dry ash gasifiers operate below the melting point of the ash and the ash is removed as a solid. Slag usually is discharged directly into a water quench tank, but ash may be handled dry or sluiced with water to a disposal pond. The ash melting temperature depends on the composition of the coal mineral matter; in general, high levels of alkali metals tend to form low melting ashes. Fluxing compounds may be added to aid this process.

## b. Hazards

### Inhalation of Coal Dust

Coal dust may escape during the gasifier feeding operation. It could also be accompanied by inert gas if such gas is used to blanket the coal going to the gasifier. However, the hazards of dust inhalation or asphyxiation are generally not as great here as in the coal receiving and preparation processes because of the need to maintain a closed-system operation at the gasifier.

### Inhalation of Toxic Gases, Particulates, and Vapors

As the coal devolatilizes, particularly in low temperature, fixed-bed gasifiers, various gases and vapors of tars and oils produced in the gasifier are carried out with the product gas in a manner roughly analogous to a coke oven. The gases and vapors contain not only hydrocarbons (methane, ethane, and PAHs), but other species, such as hydrogen sulfide, carbonyl sulfide, carbon monoxide, ammonia, and hydrogen cyanide. Low temperature fixed-bed gasifiers tend to produce more complex organic compounds, such as PAHs. High temperature, fluid bed or entrained gasifiers, operating above about 1500° F (815° C), essentially break down all organics to methane and carbon monoxide. Particulates entrained in the gas contain inorganic compounds which may include toxic trace elements (e.g., arsenic, beryllium, nickel, and cadmium). Leaks of these toxic gases and particulates into the workplace may result in worker exposure. This hazard is more likely with high pressure gasifiers than with those operating at atmospheric pressure, because a much greater leakage rate would be produced by the higher pressure differential.

### Skin Exposure to Ash

Dry ash gasifiers may use water to slurry the ash. Repeated skin contact with this ash slurry may cause dermatitis. Slagging gasifiers pose little danger due to dust from the solids; however, ash handled in dry form may allow exposure to trace elements in the ash and thus present an additional hazard. Components of the ash can include essentially any element or compound (as the oxide, silicate, or other mineral form) with a relatively low vapor pressure at the gasifier conditions.

### Noise

Noise is generated by the gases flowing through pipes, valves, and other equipment and by compressors used to pump the gases to the gasifier. Noise in this area is normally less of a problem than in coal preparation, however.

### Heat Stress

Temperatures within the gasifier may approach 2000° F (1093° C) for the slagging operation. Some types of gasifiers require manual determination of the coal level through "poke holes." Extensive poking may be required to break up coal bridges which form within the gasifiers. Toxic gases escaping from the poke holes and heat (radiant and sensible) from the gasifier are potential hazards.

### Fire and Explosion of Combustible Gases

The product gases exiting the gasifier are both hot and highly combustible. If these gases contact air through leaks out of or into the system, fire or explosion could result.

#### c. Engineering Controls

The most persistent hazards associated with the gasifier are leaks which expose workers to coal dust, toxic gases, tars and oils which contain PAHs and trace elements. Leaks can occur at any gasifier inlet or outlet (coal lockhoppers, ash lockhoppers, pokeholes, etc.), as well as at valves, flanges, and seals. In general the most effective engineering control is the maintenance of a closed or sealed system. The integrity of the system will be disrupted during coal feeding, maintenance, and during poking operations.

### Leaks in Coal Feeding Systems

The most common technique for feeding coal into the gasifier is through lockhoppers. Lockhoppers typically consist of a chamber with an upper sliding valve connected to a coal hopper and a lower sliding valve which empties into the gasifier. The lockhopper, generally located at the top of the gasifier, is filled with coal and sealed. A pressurizing gas, such as nitrogen [9], carbon dioxide, or steam [8] is introduced to increase the pressure in the lockhopper above that of the gasifier. This prevents blowback of the hot product gas into the lockhopper. The bottom valve is opened to release the coal, then closed to reseal the lockhopper. The gas inside the sealed lockhopper is purged and discharged to the flare system [9]. Lockhopper valves are interlocked so that the lockhopper cannot be pressurized if the upper valve does not seat properly, nor can it be depressurized or opened if the bottom valve does not seat properly [6,8,9,10].

Sealing and wear problems in lockhopper valves are frequent due to abrasion and solids buildup. They can be reduced by flushing the particulate matter from the valve seat with nitrogen before it is closed [9]. In one system, three knife valves are used, with the bottom two valves operating in conjunction with each other [6]. In another system, a variable speed auger, operating above gasifier pressure, provides continuous rather than batch feed from the lockhopper to the gasifier [10]. At a third facility, coal from the bunker is fed into a drum which rotates to drop the coal through a knife gate valve [4]. The knife valve closes and the drum rotates to accept another load of coal. The gate valve opens before the loaded drum rotates to avoid an accumulation of coal particles in the knife valve which would reduce its effectiveness. A vent line to the roof exhausts gas released when the knife valve is opened. Gas escaping through the coal bunker is exhausted through a baghouse. Finally, the drum rotation is alternately clockwise and counter-clockwise to produce an even feed into the gasifier. This reduces maintenance and poking requirements, produces a level coal bed, and results in more uniform operation.

Worker exposure can also be reduced with alternative designs for the coal feeding system. In one system, coal fines are mixed with tar from the product gas stream [10]. The mixture is forced through an extruder into the lockhopper. The extruder pressure is higher than that of the the gasifier, preventing backflow of lockhopper gas. Within the lockhopper, a mechanical chopper breaks up

the extrudate into lumps small enough to be fed into the gasifier. This system may reduce the handling and disposal problems associated with fine coal and heavy tar during operation. However, there is additional potential for skin contact with tar during maintenance operations.

Coal may also be mixed with water to form a slurry which is then pressurized to the system pressure [3]. The slurry is dried at this pressure and injected into the gasifier. In this way the exposure of workers to dust is minimized. However, it is more difficult to monitor the amount of coal fed to the gasifier than with lockhopper systems. Additional exposure problems may arise during shut-down and maintenance when coal slurry lines become plugged.

Carbon monoxide, escaping from the gasifier during coal feeding operations in one plant, normally accumulated in the bunker (which was remote from the process area) and was exhausted through a baghouse. However, when the filter plugged, gas backed up through the coal handling equipment into the workplace. Changing the filters more frequently solved this problem [4]. A monitoring system to detect an unacceptable pressure drop would be a useful backup control.

Product gas leaks in the vicinity of lockhoppers are monitored by carbon monoxide detectors [6]. Gas escaping from the upper portions of the gasifier contains a higher percentage of PAHs than gas from other portions. Auxiliary ventilation may be used to remove the dust and toxic gases [6,9].

#### Gasifier Leaks

Besides coal feeding operations, manual poking to determine fire-bed depth or to break up any coal agglomeration also disrupts the integrity of the system. During poking, steam venturi injectors are used to prevent product gas from escaping into the workplace [4,6]. These must be carefully adjusted to eliminate backflow of steam into the workplace. In one installation, the steam is injected along a tangent to the poke hole and, to assure proper steam flow, the injectors are operated for two minutes before the poke hole is opened [4].

When poke holes are located at the floor level, the covers are sealed and unsealed by means of kick locks which can be operated by foot. In this way the worker does not have to put his face near the hole during poking operations [4,5]. In one plant, leakage of product gas around the poke hole covers was controlled by using braided asbestos gaskets [4]. Gasket integrity is checked periodically with carbon monoxide monitors.

In general, hazards associated with leaks are minimized by maintaining the integrity of the closed system. Welds should be used in place of flanged fittings at as many points as possible [7]. In one installation, carbon monoxide leaks at flanges in the gas line could not be eliminated by replacing gaskets or by re-torquing the flange bolts; the improperly sized flanges were easily warped. Therefore, metal boxes were welded around each flange to prevent toxic gases from escaping into the work area [6].

The degree of hazard depends, in part, on the pressure at which the system is designed to operate. In one system, the gasifier operates below atmospheric pressure, preventing the escape of gases into the workplace [7]. However, the low pressure creates a problem associated with potential leakage into the system; the introduction of additional oxygen could cause an explosion. Detectors

have been installed in this system to monitor the level of oxygen in the product gas [7]. Low pressure systems, if properly maintained will present a lesser hazard associated with leaks than systems operating at high pressure. Another control measure is the use of a low sulfur coal, such as anthracite, which inherently reduces the problem of exposure to hydrogen sulfide [5]. The use of anthracite also reduces the amount of tar generated. Unfortunately, the main commercial attractiveness of gasification processes is the ability to use low quality feedstocks

When fixed-bed gasifiers are equipped with moving grates for ash removal and/or stirrers for breaking up agglomerations of coal, the seals for these shafts are potential sources of toxic gas emissions. In time, the harsh environment within the gasifier can lead to wear and scoring of the shafts. This problem is especially severe for stirrers that not only rotate but also move in the vertical plane. Leakage at the bottom of the gasifier, where the shaft rotating the ash grate enters the vessel, is also possible, but at this point the gas should consist primarily of air and steam [10].

The following steps were used to prevent leaks at one gasification plant [5]:

Rough spots on pokehole covers and fire doors were smoothed to provide a better seal with the gasifier body.

The faces of the slide valve body were filed smooth.

Care was taken to ensure that the flange bolts were tightened evenly.

The flange between the top and middle sections of the gasifier was seal welded.

The coal feed downlegs were welded to the top of the gasifier.

#### Dilution Ventilation

Dilution ventilation is an important adjunct to leak control for reducing the over-all worker exposure to toxic gases associated with coal gasification. In one installation, fans on the roof of the facility above the coal feeding bunkers operate constantly at low speed [5]. When monitors in this area detect carbon monoxide levels exceeding 50 ppm, the fans switch to high speed to exhaust the gas. One problem with this design is that the resulting suction may pull gases from the gasifier into the workplace; sufficient makeup air is, therefore, essential. In one instance, when the gasifier was in a banked mode, outside air pulled in through a gasifier vent caused a small explosion within the gasifier.

#### Noise

High noise levels are generated at the poke holes where steam jets are used to prevent gasifier products from entering the workplace [6]. Coal feeding equipment is another source of noise. These noise sources can be reduced through the use of mufflers [6]. Air blowers should be carefully balanced to reduce further contribution to the general noise level. However, the use of personal noise protection may be the only effective means for controlling exposure to sources of noise, such as the steam venturis (see Section V).

### Heat Stress

Another hazard associated with poking and other gasifier operations is exposure to heat. Where manual poking is performed, water cooling may be only partially effective and the temperature of the outside surface of the gasifier may be as high as 266° F (130° C) [6]. In other cases, there may be no water cooling jacket at all [10]. The use of additional heat shielding and/or insulation on the gasifier may be necessary to reduce the level of heat stress.

### Fire

In one facility it was reported that a fire occurred when a stainless steel expansion joint ruptured. The escaping hot product gas ignited upon contact with the air. Corrosion was the probable cause of the rupture; this incident emphasizes the need to use or develop materials resistant to specific environments [3]. Other measures taken to minimize injury to workers and damage to equipment in the event of fire or explosion include: installation of channels to divert blowout to areas outside the building [3], blowout vents [6], steel floorplates to isolate the hazard [3], physically separating stair wells from hazardous areas [3,9], and providing emergency backup power to operate the cooling system in the event of power failure [7].

### Additional Engineering Controls

Some additional engineering considerations helpful in reducing worker exposure to the above hazards include the following:

- use of equipment with low maintenance requirements to reduce worker exposure to tars, gases, etc., during maintenance and repair work,

- use of explosion-proof electrical equipment [4,5],

- installation of carbon monoxide detectors in all areas where leakage of product gas is a possibility,

- location of pumps on lower levels of the gasifier structure for safe maintenance during operations [3],

- selection of remote measuring devices and techniques, such as nuclear level detectors [3,8] and radiometric temperature measurements [3], to minimize maintenance requirements in commercial plants,

- operation of control valves from a central control room [7], and

- ventilation designed to handle remote, potentially stagnant, areas of the plant [9].

## 3. ASH REMOVAL

### a. Process Description

Ash formed in the gasifier contains the mineral matter present in the coal feedstock as well as various amounts of unreacted carbon. Ash may be removed from a coal gasifier in either a solid or molten state, depending on the operating temperature. If it is removed in a molten state, additional burners may

be required at the gasifier exit to prevent cooling and solidification which would plug the opening. Molten ash, or slag, is dropped into a water bath where it is cooled and solidified before removal.

In dry ash removal systems, ash is removed through a lockhopper system. For dry ash systems, there may be an emergency quenching device in the ash pit in case hot coals are accidentally discharged. Wet ash systems discharge the ash into a quenching vessel. It is then transported for disposal as a slurry.

#### b. Hazards

##### Gas Leakage

In general, the hazards associated with ash removal processes are minimal. However, sizable leaks could result in the escape of significant quantities of toxic gases. There is the possibility of product gas leakage at the ash lockhoppers; but because ash is removed from below the combustion zone, the escaping gas will consist primarily of steam and oxygen [11].

##### Dust

Ash handled in dry systems can present a dust hazard. Inhalation of the ash dust may expose workers to silica, toxic trace elements, organic materials, and adsorbed toxic gases contained in the ash.

##### Skin Contact With Ash Quench Water

Wet ash systems and slagging gasifiers pose little danger due to dust. However, some coal ash may contain relatively high levels of soluble oxides, particularly alkaline components, which will be leached into solution by the quench and transport water. This water then becomes alkaline and may cause dermatitis if constant skin contact is required. Slag does not present this danger since it is in a glassy state and has negligible solubility in water.

Under operating conditions such as startup and shutdown, or under heavy coal fines load, especially for fixed-bed gasifiers, char may be discharged with the ash. Tar, oil, and trace elements may be adsorbed onto the char because most chars will have large surface area. Although the char may be inert, the adsorbed materials could be easily leached from the resulting solids and remain in the quench water [12].

##### High Pressure Steam, Air, or Oxygen

In pressurized gasifiers, malfunction of the ash discharge system may result in the discharge of high pressure steam and air or oxygen.

#### c. Engineering Controls

##### Gas Leakage

Attempts to use a mercury seal at one plant generated mercury vapor in the workplace [10]. This seal was replaced with an automatically tensioned, packed seal, but the gas leakage was still not entirely eliminated.

##### Dust Leakage

Worker exposure to dust is minimized in slagging gasifiers [3,7,9]; the size of the smallest slag particles is well above the respirable range [7]. The inhalation hazard is reduced if the ash is moistened by the incoming steam [5].

A wet ash removal system, in which the ash falls into a water-filled pan, is an effective method for controlling exposure to ash dust from dry-bottom gasifiers [4,6]. In one system the following steps were taken to reduce plugging in the wet ash removal system, thus reducing maintenance requirements which could increase skin contact [6]:

an internal worm-and-gear drive for the ash hopper dump gate, which plugged frequently, was replaced with an external drive

a wet ash chute that had a tendency to become plugged was replaced with an auger

because of the abrasive nature of the ash, deterioration of metal parts caused numerous problems; these were apparently solved by replacing chains and sprockets with belt drives

In another system, a remote, chain-operated slide valve was installed to dump the ash, so that the operator could stay clear of escaping feed gas during the dumping operation [5].

At one slagging gasifier, two slag lockhoppers are used on alternating 4-hour schedules. In this installation, a slag agitator is used to break up strands of molten slag. In addition, grids installed over the exit ports to the lockhoppers prevent plugging if a slag "ball" should form [3]. With this ash removal system, the slag must be kept hot enough to shatter upon contact with the quench water. Two additional burners (a slag-heating burner and a slag-tap burner) were added to maintain the necessary temperatures [3]. The use of ball valves on each slag lockhopper provided better seals than the slide valves which were originally installed [3].

#### 4. PARTICULATE REMOVAL

##### a. Process Description

Hot gas exiting the gasifier contains particles of ash and unreacted coal, as well as oil and tar vapors and other compounds that must be removed. As the gas cools, some of the vapors condense to form aerosols that must also be removed. The particulate-laden gas passes through a cyclone collector in which the large particulates are separated from the gas. Depending on the carbon content, material may be either disposed of or recycled to the gasifier.

Quenching devices also remove particulate material from the gas stream. These devices also cool the gas and condense water and some tar vapors. In some commonly used venturi scrubbers, the scrubbing fluid (liquor) is atomized to maximize the surface area. The effluent from the scrubber contains tar and solids. After it is cooled and the solids and tars are removed, the "liquor" is often recycled through the quench system.

##### b. Hazards

###### Equipment Leaks

The primary hazards are exposure to particulates, gas-liquor, and hot product gas due to leaks, poorly seated valves, or erosion of pipe walls.

### Fire and Explosion

The hot product gas and entrained vapors can easily ignite on exposure to atmospheric oxygen.

### Noise

Since large volumes of gas are moving through pipes and equipment, noise levels may be high.

## c. Engineering Controls

### Cyclone Separator Design

In the case of physical separators, such as cyclone collectors, particulate material may be deposited on the seat of the dust unloading valves. Leaks of product gas can then occur through the improperly sealed collector. In one plant, a pneumatically operated knife valve installed behind the two dump valves eliminated the leakage [6]. At another, the cyclone can be flooded with water to seal off the gasifier when it is not producing gas [5].

Exposure to dust from the cyclone collector is of particular concern where the dumping operation is manual [6]. This hazard can be eliminated by recycling the char to the gasifier [3,7]. However, recycling can increase the hazard of fire. At one plant, a fire occurred when an expansion joint on the char recycle line ruptured and the hot char contacted outside air; a more corrosion-resistant material was required [3]. At another facility, an inert nitrogen atmosphere is maintained in the char bin [7]. In this latter plant the fans in all primary air lines have dampers to control the flow of air such that if the char return line becomes plugged the amount of air flowing into the gasifier will still be regulated for proper combustion [7].

The cyclone collector can be designed to operate inside the gasifier [3]. Internal operation reduces the hazards associated with cyclone leakage; however, this approach requires that the collector be designed to withstand the severely corrosive conditions found inside the gasifier in order to minimize the required maintenance.

### Scrubber Design

In many installations, venturi washers and scrubbers are used to remove both particulates and tars from the product stream [3,7,9,10]. The principal hazards associated with these operations include leaks of product gas and leaks of gas-liquor; the latter would be most likely at the seals of the gas-liquor pumps [11]. The gas-liquor is recycled through the wash system so that, if leaks are eliminated, exposure will be minimal. Clean, low-Btu gas at one plant is resaturated with this heated gas-liquor to increase its Btu content before being fed to a gas turbine [10]. Because the product gas is not only cleaned but also cooled by these quench devices, continuous operation is critical. A failure of the pumps would cause heating of all equipment downstream of the washers, as well as contamination with tars and solids. In one system, an increase in temperature caused by a pump failure will trigger an automatic shutdown of the entire system [7]. Another plant design includes an emergency water injection system so that gasifier operation can be maintained in the event the cooling system fails [11]. Spare pumps may be provided for critical operations to allow gasification to continue during maintenance or to permit a controlled shutdown, in the event of an emergency [3].

In the particulate removal system of one gasifier, it was found necessary to use stainless steel, fiberglass piping, and epoxy coatings because of corrosion problems in venturi scrubbers, demisterizers, and piping systems [7].

## 5. TAR REMOVAL

### a. Process Description

Gas produced at temperatures below about 930° F (500° C) will contain tar and oils. Such temperatures are typically found in the upper zone of a fixed-bed gasifier. Systems operating at higher temperatures produce much less tar and oils. Many of the processes described as methods for the removal of solid particulate matter from the gas stream in the preceding section, also remove tar and oils. In particular, the various devices for contacting the gas with a quench or wash fluid will remove both solid particulates and tars. These processes cool the raw gas, condensing excess water and some tars. This fluid is then separated; tars and oils are recycled to the gasifier or stored for reuse or disposal, and the "liquor" which remains is recycled.

Tar is sometimes removed from the product gas by electrostatic precipitators. These devices also remove other particulate matter. Successful operation of electrostatic precipitators requires that the temperature of the gas be less than 800° F (426° C), yet hot enough to maintain the tar in a fluid state so that it can flow out of the precipitator without plugging.

### b. Hazards

#### Skin Contact

The primary hazard associated with this process area is skin contact with such materials as PAHs, aromatic amines, and phenols. These exposures may occur during routine maintenance activities, during shutdowns to clean equipment and lines plugged by condensed tar, and during the cleanup of spills.

#### Inhalation of Toxic Fumes and Vapors

An additional hazard is the inhalation of gases, such as CO, H<sub>2</sub>S, and HCN, caused by leaks of gas and hot liquor into the workplace.

#### Fire and Explosion

There is a slight risk of fire and explosions.

### c. Engineering Controls

#### Plugged Lines

Accumulations of tar condensates tend to plug equipment and lines. The system must be opened to correct this problem, thereby introducing the potential for worker exposure to the tars and oils. In one facility using an electrostatic precipitator, maintenance requirements were reduced by increasing the diameter of the pipe through which tar-containing gas is withdrawn from the gasifier; steam tracing was also installed to keep the temperature high enough to maintain the flow of tar [6]. At another gasifier, it was found unnecessary to insulate or steam trace lines to the electrostatic precipitator to achieve the proper tar flow because the light tar/oil byproduct produced by gasification

of bituminous coal was fluid at normal operating temperatures [4]. Both of the gasifiers discussed above are fixed-bed installations in which gas is withdrawn from both the top and bottom of the gasifier. The top gas, taken from the cooler portion of the gasifier, contains tars and oils and is cleaned in an electrostatic precipitator. The hotter, bottom gas contains very little tar but is high in particulate material. Solids are removed from the bottom gas and it is then combined with top gas which has passed through the precipitator. In one of these installations, the combined stream is passed through a second electrostatic precipitator, or deoiler [4]. Again, insulation or steam tracing was unnecessary to maintain proper tar flow due to the light nature of the tar-oil. These systems are started using coke in one plant [6] and anthracite in the other [4], and then converted to coal after steady operating conditions are achieved. The electrostatic precipitators are bypassed during the start up so that they will not be plugged by the dust produced.

The Lurgi system includes a ram to clean accumulated condensed tars in the line between the gasifier vessel and the water quench spray. This is intended to reduce maintenance requirements; however, material condensing on the ram may be forced back through the packing into the workplace.

The engineering controls related to systems using a liquid wash are discussed in Section III,A,4.

#### Equipment Leakage

Proper system design will minimize leakage of crude gas, hot liquor, and tars. The most likely leak point for the quench fluid is the recycle pump. Paved areas under probable leak points should be dished and/or curbed to contain spills. Some plant designs include a covered spill collection system beneath the tar separation area; liquids collected are pumped back into the tar separator.

#### Storage

Steam tracing has been installed on lines and tanks used for the collection and storage of the tars and oils [4,6]. In one installation, tars and oils removed from the process stream are stored in temporary tanks; the oils are pumped directly to a boiler where they are burned to generate steam [4]. This minimizes handling requirements. The tars are pumped to separate storage tanks. Tar-resistant, rubber gaskets have been installed between the tanks and the tank tops to prevent tar and oil seepage and emissions of vapors into the workplace.

## 6. ACID GAS REMOVAL

### a. Process Description

For gasification processes using high sulfur coal, the product gas will contain significant quantities of hydrogen sulfide which must be removed. This is especially true if the gas is to be upgraded to pipeline specifications since sulfur compounds will poison the methanation catalyst. Additionally, environmental pollution specifications often require sulfur removal. Hydrogen sulfide may be converted directly to elemental sulfur using the Stretford process, or the acid gases may be removed from the product stream by a gas-liquid absorption technique, such as the Benfield process, for later conversion to elemental sulfur using, for example, the Claus process.

### Benfield Process

In the Benfield process, gas flowing upward through a reactor is contacted with a hot potassium carbonate solution flowing downward. Hydrogen sulfide and carbon dioxide are absorbed by the solution. The later is regenerated by passing through a second reactor, counter current to a rising flow of steam. The acid gas is separated from the steam and sent to a sulfur recovery unit, while the regenerated potassium carbonate solution is recycled to the first reactor.

### Stretford Process

The Stretford process is used in many plants to recover elemental sulfur from hydrogen sulfide. In this process the acid gas is washed countercurrently with a solution containing anthraquinone-disulfonic acid (ADA), sodium metavanadate, citric acid, and sodium carbonate. Hydrogen sulfide is absorbed by the solution which is then pumped to oxidizer tanks. In the oxidizers, air is blown through the liquor to produce elemental sulfur and to reoxidize the solution for recycling. The air also carries the sulfur to the top of the tanks by froth flotation. The sulfur is recovered by filtration.

#### b. Hazards

##### Toxic Gases

The principal hazard associated with sulfur removal processes is inhalation exposure to carbon monoxide and hydrogen sulfide.

##### Toxic Solutions

Thermal and chemical burns or toxic effects may result from skin contact with process solutions and inhalation of associated vapors.

##### Other Hazards

Lesser hazards include: exposure to high pressure steam, cryogenic temperatures, refrigerant gases, noise, and the possibility of fire.

#### c. Engineering Controls

##### Construction Materials

Few of the plants surveyed had a sulfur removal process in operation. At one installation, it was necessary to install stainless steel pumps and valves because of the alkaline nature of the sulfur removal solution.

Many sulfur removal processes are commercially proven and can be expected to operate reliably when proper gas stream cleanup precedes the unit. Exposure to carbon monoxide and hydrogen sulfide is minimized by locating sealed equipment out-of-doors or in separate structures. In one installation, the Stretford absorber and slurry tanks are outside [4], and in another, the gas quench, gas liquor, and sulfur removal process areas are located in open structures outside of the gasification building [10].

##### Tank Covers

Carbon monoxide concentrations measured near open-topped slurry tanks at one plant were consistently greater than 300 ppm as a result of the degassing of the process constituents. After tank covers were installed, carbon monoxide levels were reduced to less than 10 ppm. [5].

## 7. PRODUCT UPGRADING

### a. Process Description

The cleaned product gas may be upgraded to pipeline specifications by treatment with two additional processes: shift conversion and methanation.

#### Shift Conversion

In the shift conversion process, carbon monoxide and steam are converted to hydrogen and carbon dioxide by a series of reactions. Cobalt-molybdenum catalysts on an alumina base are commonly used since these catalysts are not poisoned by the presence of sulfur compounds, viz., hydrogen sulfide, in the gas. Therefore, the shift reactors can be placed before sulfur removal in the process stream. Periodic regeneration of the catalyst with a steam-air mixture is required [12]. A portion of the raw gas is passed through the shift-conversion reactor and the remainder is mixed with the shifted gas to achieve a hydrogen to carbon monoxide ratio of 3:1 as feed to the methanation step.

#### Methanation

The methanation process is a catalytic reaction which combines carbon monoxide, carbon dioxide, and hydrogen to generate methane. Raney nickel is the most common catalyst used. The reaction is highly exothermic, liberating as much as 10% of the total energy content of the methane produced. The excess heat must be removed; at elevated temperatures carbon monoxide and methane decompose to carbon. The catalyst is inactivated by the deposition of carbon upon it.

### b. Hazards

#### Dusts or Gases from Catalyst

Normal operation of the shift and methanation units should be relatively free of hazards. There is the potential for worker exposure to catalyst dust during the loading and unloading of the reactors. Exposure to nickel carbonyl from the methanator could be a serious problem because of the high toxicity of the compound; however, formation of nickel carbonyl can be prevented by correct operating practices and good process control, and does not occur under normal operating conditions.

#### Toxic and Hazardous Gases

The principal hazard for workers is exposure to raw gas at high temperatures and pressures. Potential operating problems include plugged catalyst beds and lines and leaking valves and pumps which could release gases, such as carbon monoxide, methane, and hydrogen, into the workplace at high temperature and pressure. However, the frequency and severity of such leaks should be less than that for the upstream processes, due to the single phase and relatively pure nature of the feed stream.

#### Fire

Because of the high temperatures there is a danger of fire if a leak develops.

#### Other Hazards

Other hazards include heat stress, high pressure steam leaks, and noise.

### c. Engineering Controls

#### Preventing Nickel Carbonyl Formation

The formation of nickel carbonyl during startup and shutdown can be prevented by ensuring that carbon monoxide does not contact the nickel catalyst while the temperature of the catalyst is below 500° F (260° C). The procedure, in one plant, is to fill the methanation reactor with nitrogen before startup, then switch to hydrogen as the unit approaches the operating temperature. In addition, gas entering the methanator is heated to a temperature high enough to prevent the formation of nickel carbonyl. At shut-down, the reactor is flooded with nitrogen to displace carbon monoxide from the vessel as it cools [11].

#### Loading and Unloading Catalyst

To avoid dust problems, an ejector or blower should be used to move the dust to a collection system during periods of loading and unloading. Because of its reactive nature, the spent nickel catalyst from the methanation reactors must be loaded and unloaded either in water or in a reducing atmosphere [11].

#### Construction Materials

Materials used for piping and equipment for the shift-conversion process must be able to resist the highly corrosive nature of the product gas which contains hydrogen and hydrogen sulfide at high temperature and pressure. At one plant visited, titanium-stabilized stainless steel was used for heat exchangers and pipework, and catalyst vessels were made of refractory-lined carbon steel, sprayed internally with alumina [11].

## B. COAL LIQUEFACTION

Several coal liquefaction processes have reached the stage of development at which demonstration or commercial scale facilities are technically feasible. These processes all operate by dissolving coal in a process derived solvent and adding hydrogen to increase the hydrogen to carbon ratio. The result is that the coal "molecules" (generally high molecular weight, low hydrogen components) are converted to lower molecular weight species, having a higher hydrogen to carbon ratio than the coal. The hydrogenated components are predominately liquids but do contain some gaseous compounds, such as lower alkanes and alkenes. After the initial dissolution step, further refining (or hydrotreating) is necessary to produce fuels or synthetic crude comparable to petroleum derived fuels and crude.

Five processes have been tested in pilot plants: Exxon Donor Solvent (EDS), Liquid Solvent Refined Coal (SRC-II), Solid Solvent Refined Coal (SRC-I), H-Coal, and Consol Synthetic Fuel (CSF). Each achieves liquefaction of the coal by a slightly different route. Site surveys at facilities operating these processes were conducted during this study. General process characteristics on each site are given in Table 1. The two most similar are SRC-I and SRC-II which are variations of the same basic process. (SRC-I is considered a liquefaction process even though the product is a solid. SRC-II was developed from the SRC-I process.)

The pilot plants surveyed did not contain all of the operations that must be performed in commercial plants. For example, one pilot plant had no wastewater treatment system, three had no sulfur recovery unit, and none generated hydrogen by gasification of the unreacted coal, an operation necessary to the economics of the commercial processes.

A block diagram of a typical liquefaction process is shown in Figure 2. This identifies the major operations carried out in the pilot plants, and other support operations which a commercial facility will require. Typical unit operations and conditions used in the various liquefaction processes surveyed are listed in Table 3. A summary of hazards, by unit operation area, is presented in Table 4. The processes, hazards, and controls for each major unit operation are discussed in the following text.

### 1. COAL RECEIVING, STORAGE AND PREPARATION

#### a. Process Description

Coal preparation for liquefaction may include any or all of the following: receipt of coal from a mine or coal preparation plant, transfer to onsite storage areas, storage of the coal, preparation of the coal for the liquefaction process, and storage of prepared coal prior to its entry into the process stream. These steps have been discussed in Section III,A,1.

#### b. Hazards

Hazards associated with coal preparation are related to the nature of the coal and to the operations being performed. Coal is combustible and friable, and preparation for commercial liquefaction processes requires large equipment.



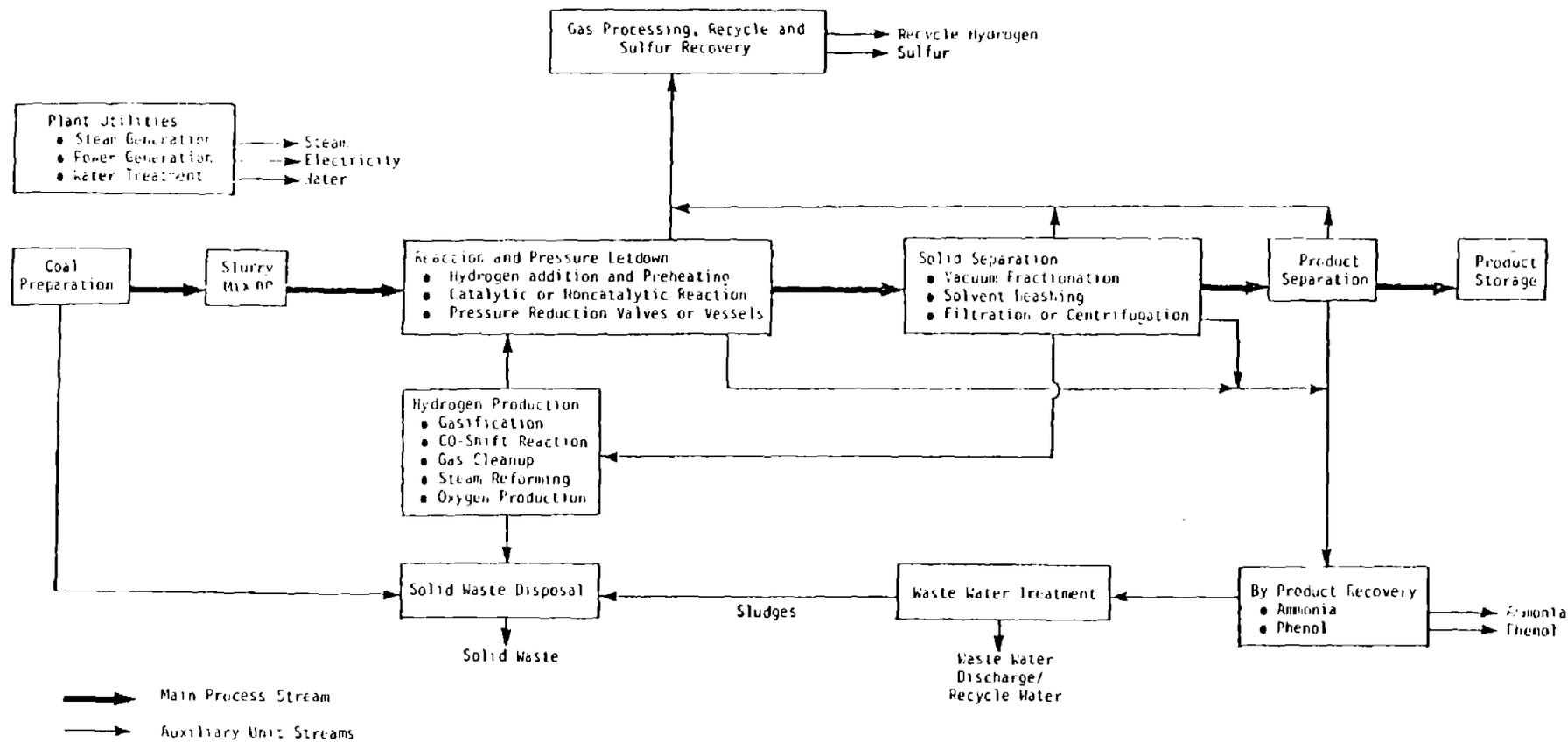


Figure 2. Typical Coal Liquefaction Schematic Diagram

TABLE 3

## Major Process Operations and Operating Parameters of Coal Liquefaction Plants

PROCESS UNIT AND PLANT CHARACTERISTICS	TYPE OF PROCESS				
	H-Coal	CSF	EDS	SRC-I	SCR-II
Coal Preparation	x	-	x	x	x
Noncatalytic Coal Hydrogenation	-	-	x	x	x
Catalytic Coal Hydrogenation	x	x	-	-	-
Catalytic Solvent Hydrotreatment	-	-	x	-	-
Fractionation	x	x	x	x	x
Carbonization	-	x	-	-	-
Residue Separation	Vacuum Stripper/ Flaker belt	Precipitation	Vacuum Stripper/ Flaker belt	Filtration/ Deashing	Vacuum Stripper/ Flaker belt
Design Capacity	200 tons/day (syncrude mode)	20 tons/day (revamped)	250 tons/day	6 tons/day	50 tons/day
Feed Coals Used	Lignite/ Subbituminous	Lignite/ Subbituminous	Subbituminous/ Bituminous	Subbituminous/ Bituminous	Subbituminous/ Bituminous
Reactor Type	Ebullated-bed	Stirred-tank extractor/ Ebullated-bed catalytic hydrogenator	Tubular plug flow	Vertical tubular plug flow	Vertical tubular plug flow
Temperature °F	850	750-850	850	800-875	800-850
°C	450	400-450	450	425-475	425-450
Pressure psig	up to 3000	450 - extractor 3000-3500 - hydrogenator	2000+	2500	1500-2050
Residence time	no information	30 minutes - extractor	40 minutes	10 to 60 minutes	60 minutes

TABLE 4  
Occupational Hazards in Coal Liquefaction Plant by Process Operation

	Coal Preparation	Slurry Mixing	Reaction and Pressure Letdown	Gas Processing Recycle and Sulfur Recovery	Solids Separation	Product Separation	Product Storage	Hydrogen Production
Respirable Coal Dust	x	x	-	-	-	-	-	x
Inhalation of Organic Vapors	-	x	x	-	x	x	-	x
Contact with Process Materials	-	x	x	-	x	x	-	x
Inert Gases	x	x	-	-	-	-	-	x
Fire and Explosion	x	x	x	x	x	x	x	x
Noise	x	-	-	-	-	-	-	-
Burns	x	x	x	-	x	x	-	x
Hydrogen Sulfide	-	-	-	x	-	-	-	x
Carbon Monoxide	x	x	-	-	-	-	-	x
Gas Processing Chemicals	-	-	-	x	-	-	-	x
Ammonia	-	-	-	x	-	-	-	x

Hazards which are encountered during coal preparation include respirable coal dust, the potential for fire and explosion, noise, and dangers from inert gases. These hazards are the same as those encountered in preparing coal for gasification and have been discussed in Section III,A,2.

### c. Engineering Controls

Engineering controls are essentially the same as those used in gasification processes. Specific examples observed at liquefaction facilities follow.

#### Respirable Coal Dust

In any operation involving the transfer, size reduction, or drying of coal, there is a potential for producing respirable coal dust. Covered rail cars and conveyors reduce the emission of coal dust during transport [15]. During unloading operations, water-spray dust suppression systems can control dust [15]. Dust collection systems are used to pneumatically transport dust to cyclones, baghouses, or wet dust collection systems [14,15,16]. In addition, coal dust in gases used to provide inert atmospheres and to dry the pulverized coal can be cleaned using venturi scrubbers or baghouses [14,15,16].

#### Fire

Fire can occur spontaneously during storage of raw and prepared coal or during grinding and drying if oxygen is present. Nitrogen [15,16] or combustion gases with a low oxygen content [13,14] can be used to provide an inert atmosphere. Inert combustion gas may be used for pneumatic conveying of pulverized coal [14]. During crushing and drying, it is necessary to limit both the oxygen content and the temperature to prevent ignition. Limits of oxygen of 0.5 to 1.0% [13,14] and 8% [15,16] have been used; either alarms and/or automatic shutdown systems are activated when the prescribed limit is exceeded. The actual limit selected depends on specific plant operations and practices. Generally, coal dust can ignite when the oxygen content exceeds 15%. Temperature probes in the storage bins also can provide warning of potential spontaneous combustion [16].

#### Dust Explosion

Coal dust explosions can occur when the oxygen content of the gas exceeds 15% [14]. To prevent explosions during grinding, systems using oxygen sensors have been installed to shut down the mill or to limit the oxygen to a predetermined level [13,14]. Damage can be limited, if the preventive systems fail, by providing blow-out panels in storage bins, baghouses, and other equipment [14,16]. It is not adequate merely to blanket the coal (raw or pulverized) in storage silos with an inert gas; the gas must also be sparged into the mass of coal to displace oxygen in the interstitial spaces.

#### Noise

Equipment used in size reduction generally produces very high noise levels. Changes in operating conditions, such as speed or throughput, can reduce the noise, but this approach is not always compatible with production or economic goals. Design changes or enclosing the equipment in insulating compartments can reduce noise levels in specific instances, but this approach is not always feasible, especially on a retrofit basis. The equipment should be somewhat oversized to allow for slower operation, and space for enclosures should be allowed in designing full scale facilities.

### Inert Gases

Inert gases used to prevent fire and explosion during coal processing and storage introduce the danger of asphyxiation to workers. The two gases most frequently used are nitrogen and combustion or flue gases. The latter may also contain carbon monoxide and thus pose an additional danger of carbon monoxide poisoning. Where transfer facilities are located below ground, such as coal receiving hoppers or feed bins [14,16], provisions for ventilating the area to prevent the accumulation of inert gases are necessary. This can be accomplished by mechanical ventilation [14] or coincidentally with the dust collection system [16]. Fixed monitoring systems for carbon monoxide and/or oxygen content may also be desirable because of the poor warning properties associated with asphyxiation.

## 2. SLURRY MIXING

### a. Process Description

All direct coal liquefaction processes include mixing feed coal with a recycle solvent. Variations between processes relate to factors such as the size and moisture content of the feed coal, temperature and physical properties of the solvent, coal-to-solvent ratio, and methods of feeding the coal and of keeping it suspended in the recycle solvent. Generally, the dried and pulverized coal is transported to the mixing vessel under an inert atmosphere and introduced into the vessel through a device such as a rotary airlock or a screw conveyor. In some cases, undried coal may be fed to the slurry mixing vessel so that the slurry mixer serves as a dryer as well. The coal is uniformly distributed in the solvent by mechanical agitation inside the vessel. Some form of recycle pumping system may be required to resuspend coal which settles to the vessel bottom. The slurry is also pumped to the next process step.

### b. Hazards

Generally, the coal is finely ground and the solvent is at a temperature above 392° F (200° C). Hazards include inhalation of respirable coal dust, organic vapors, inert gases, and coal derivatives, and skin contact with coal-derived liquids, such as heavy fractions containing PAHs and aromatic amines.

### Coal Dust

The potential for inhalation of coal dust is similar to that associated with coal preparation operations, although there may be fewer sources of exposure.

### Organic Vapors

Certain chemical species in coal liquids are particularly hazardous because they may be toxic and they may have carcinogenic or mutagenic properties. Examples are PAHs, aromatic amines, and benzene.

The recycle liquid is hot, usually 392° F (200° C) or greater, and vapors may be released at atmospheric pressure. The slurry mix tank is closed and not pressurized; nevertheless, it can be assumed that vapors may escape into the atmosphere. Inhalation of these vapors can lead to systemic exposure of workers to potentially toxic compounds.

### Inert Gases

Inert gases used to blanket or transport the coal to the slurry mix tank may escape. As with coal preparation, they present the hazard of asphyxiation or carbon monoxide poisoning, although to a lesser degree than in the coal preparation section.

### Skin Contact with Coal Derived Liquids

Worker contact with coal-derived liquids can occur if leaks develop or material is spilled. Maintenance work on vessels, pipes, pumps, and other equipment can also result in skin contact.

## c. Engineering Controls

### Respirable Coal Dust

Since slurry mixing is usually performed in a closed system, the release of respirable coal dust probably will be an unusual occurrence in this operation. Dust may be released from a failure in the integrity of the coal dust feed system or during maintenance operations.

Rotary valves for feeding coal to the slurry mix tank have been used successfully [13,14,15]. The shaft openings of the rotary valves of the EDS facility are nitrogen-purged to keep coal dust out of the packed seals, and the discharge side of the rotary valve is vented to a baghouse to control emissions [15]. If it is necessary to control residual dust in equipment during maintenance, a combination of local or dilution ventilation and personal protection seem to be logical methods.

### Organic Vapors

Escape of organic vapors from the mix tank, agitator shaft, and pump shafts may be prevented in several ways. EDS, H-Coal, and SRC-II all use vent gas scrubbers to recover organic vapors for recycle to the process [13,15,16]. This acts as a control system to prevent the escape of vapors into the work place from the mix tank, manways, and agitator shaft by keeping the tank void volume below atmospheric pressure. Condensed water from the scrubber is processed in the sour water treatment system to remove ammonia and hydrogen sulfide; non-condensable gases are flared. In the EDS plant, double mechanical seals with a circulating seal oil system are used to control organic vapor emissions from the shaft of the mixer [15]. At the CSF plant, 15 psig inert gas pressure is maintained in the mix tanks to prevent the formation of an explosive gas mixture [14].

The abrasive nature of the coal slurry causes significant problems, including pump seal failure and subsequent leakage around pump shafts. Durametallc double mechanical seals have performed well on the slurry mix circulating pumps for the CSF process. However, erosion problems occurred when similar seals were used on the slurry mix tank agitator [14]. In the H-Coal process, Ingersol-Rand plunger pumps are used to pump the slurry to the reactor. Packing failures occur every three or four days from solids entering the seals [16]. Durametallc double mechanical seals flushed with lubricating oil at the SRC-I facility require maintenance about every three months [17]. Plunger pumps, used to transfer the slurry from the mix tank, are a source of organic liquid and vapor exposure due to packing leaks in the EDS plant. Packing life

has been extended to 15-20 days by use of a flush oil system and careful plunger alignment [15]. In the SRC-II process, plunger pumps which are sealed with an oil-flushed stuffing box leak vapors into the pump shed. This hazard can be reduced by installing a local exhaust ventilation system or by better pump packing, seal design, and installation. Leakage through the seals and packing can be controlled by a system in which these fluids are collected and transported through drainage lines to sealed containers [15].

#### Escape of Inert Gas Containing Carbon Monoxide

Combustion gas containing carbon monoxide may be used to provide an inert atmosphere for the pulverized coal being transported to the slurry mix area. If leaks are present in the system, local exhaust ventilation will be necessary to remove the leaking gas from the workplace until the leaks are closed. Continuous monitoring for carbon monoxide is advisable if such leaks occur frequently.

#### Contact with Coal Derived Liquids

The recycle slurry solvent is a coal-derived liquid which contains PAHs, aromatic amines, benzene, toluene, xylene, and other potentially dangerous compounds. Since the system is closed, exposure to these substances will occur only during maintenance or because of leaks and spills. Prompt correction of leaks, cleanup of spills, and the use of personal protective equipment can minimize worker exposure to these and other coal derived materials. Monitoring and alarm systems may be effective warning devices for airborne components.

### 3. REACTION AND PRESSURE LETDOWN

#### a. Process Description

This section includes operations such as pressurizing and preheating the coal slurry, introducing hydrogen into the slurry, and catalytic or noncatalytic liquefaction of the coal by chemically adding hydrogen; followed by a series of pressure letdown, separation, and cooling steps.

The coal slurry is preheated in all processes. Generally, recycle hydrogen or make-up hydrogen is added to the pressurized coal slurry prior to its entry into the slurry preheater. Additional hydrogen may be added after the preheater as well. The CSF process makes no hydrogen addition either before or after the preheater [14]. Instead, hydrogenation is performed after the coal has dissolved.

Following the preheater, the slurry/hydrogen mixture enters a hydrogenation reactor; it may contain a catalyst or may rely on the catalytic effect of the coal mineral matter to accomplish hydrogenation and dissolution of the coal. Both fixed and ebullating beds are in use. Typical reactor conditions are 2000 to 3000 psig, 800° to 850° F (426° to 454° C), and 30 minutes residence time; these conditions vary depending on the type of coal used and the products desired. The slurry leaving the reactor contains hydrocarbon gases, hydrogen sulfide, unreacted hydrogen, other gaseous contaminants, liquefied coal, unreacted coal, and mineral matter. A series of pressure letdown, cooling, and phase separation operations produce several major process streams. These can include: gas streams containing hydrogen, hydrogen sulfide, C<sub>1</sub> to C<sub>4</sub> hydrocarbons, ammonia and other components;

light liquid hydrocarbons; heavy hydrocarbon liquids; sour water; and a slurry containing the unreacted coal, and mineral matter. Part of the slurry stream is recycled with make up solvent (obtained from a downstream fractionation unit) to the slurry mix tank. In the CSF and EDS processes, the recycle liquid is a separately hydrogenated, middle distillate [14,15].

## b. Hazards

### Liquid and Gas Leaks

The reactor section of the liquefaction plant is a closed system which operates at high pressure and temperature. Under normal operation, hazard sources include minor leaks of liquids and gases around pump shafts, valve stems, and pipe flanges; these may rapidly decay into major leaks. A major leak would force a shutdown of the operation.

Since this section is at very high pressure, the potential for leaks is greater than in the slurry mix section. Temperatures are also higher and, because the process material has not yet been refined, much of it is volatile. Volatile components of material leaking through flanges and seals will immediately flash to the atmosphere. This flashing presents a greater risk of inhalation of organic vapors than at the slurry mixing section. High pressure emissions from small sources, such as leaks, may form an aerosol, even if the vapor pressure of the emitted material is low. Material remaining after the leaked liquid has lost its volatile components is a high boiling fraction known to contain carcinogens, such as PAHs. These compounds present the danger of both inhalation and skin exposure.

### Skin and Respiratory Exposure

High temperature, high pressure, and three-phase flow presents a singularly difficult set of conditions for operating equipment. Mechanical stress points, such as seals, gaskets, flanges, pumps, pipe elbows, and let-down valves or orifices, are much more likely to fail. Maintenance and repair of this equipment can lead to significant risk of skin and respiratory exposure, as well as thermal burns.

### Heat Stress and Noise

Areas near the gas-fired burners are potential sources of heat stress, particularly if the space is enclosed. High fuel and air flow rates are needed to heat liquids to the desired temperature at the required rate. Noise from these high volume air and gas flows can be excessive. Noise is also generated at the valves and flash drums in the pressure letdown units.

## c. Engineering Controls

### Organic Vapors

Since the reactor section is designed to be a closed system, organic vapors can be discharged to the atmosphere only from leaks, spills, or during maintenance. (Pressure relief valves are usually vented to a flare.) Proper preventive maintenance of shaft seals and valve stems will reduce or eliminate these sources. Injection of a high temperature lubricant into the packing of pressure letdown valve stems can prevent sticking and keep out solids [15]. Pump shaft leaks were controlled, in one case, by flushing seal oil into the pump shaft packing or seals [16].

high pressure flange leaks are prevented by using metal ring gaskets with high pressure ring joint flanges. Misalignment of the flanges and incorrect or uneven torquing are reported to be a major cause of flange leaks [15]. Gaskets and flange faces must be clean and unmarred, the faces must be aligned properly, and the bolts tightened in the proper sequence to the correct torque. Employees should be trained to ensure that correct techniques are used. \*

#### Contact with Coal Liquids

Contact can be prevented by controlling and eliminating leaks. In addition, when vessel maintenance is necessary, prior flushing of the vessel interior, use of ventilation or supplied air respirators, and personal protective equipment are required. In some cases, equipment can be redesigned to reduce maintenance. For example, frequent cleaning to remove solids which collected in the dissolver bottom was eliminated by redesigning the dissolver with a conical bottom. This change reduced the required maintenance, and thus reduced the potential for exposure due to maintenance operations [17].

#### Noise from Furnace Burners and Pressure Letdown Valves

Major noise sources in the reactor area are from the high airflow at the burners and from the turbulence at the pressure letdown valves. Noise from these sources was significantly reduced by installing mufflers on the burners to reduce the air flow noise and by covering the slurry letdown valve with an acoustical wrapping [15].

### 4. PRODUCT SEPARATION

#### a. Process Description

The streams leaving the pressure letdown vessels of the reactor section can be grouped into three categories: 1) gas streams, including fuel gases and unreacted hydrogen; 2) aqueous waste streams; and 3) hydrocarbon liquid streams which must be processed further to produce liquid fuel products. In general, there are three or more liquid hydrocarbon streams to be processed, ranging in composition from crude naphtha to high boiling range residuals which contain unreacted coal and mineral matter.

Product separation is accomplished by fractional distillation to produce the desired product slate. These operations are carried out at successively lower pressures, usually starting at somewhat above atmospheric pressure to separate the lighter hydrocarbons, and ending with vacuum fractionation to produce either the solid SRC-I product or vacuum bottoms which may contain unreacted solid matter. Additional operations, including critical solvent deashing, may follow vacuum fractionation.

#### b. Hazards

Hazards in the product separation section are primarily from leaks, spills, and maintenance or repair associated with three phase flow, and include inhalation of organic vapors and dusts and dermal contact with coal-derived liquids. Ideally, product separation should be performed in a totally closed system; however, the characteristics of the material being processed and the nature of specific pieces of equipment result in the release of process materials to the work area.

Conditions encountered in the EDS, H-Coal, and SRC-II processes are more severe than in the other methods, because the solids are not separated from the coal liquids before fractionation. They are removed in the vacuum bottoms stream and are, therefore, more concentrated than in the upstream sections. The vacuum bottoms pumps, a particularly important source of leaks, are discussed in Section III,B,6: Solids Separation.

#### Equipment Leaks and Spills

Leaking pump seals and packing were sources of exposure to coal liquids at each of the five pilot plants. While these leaks are generally small, they can present a long term source of exposure if not corrected promptly. A leak measured in grams per day or week usually does not require immediate shut down of the plant, but the total emission from a number of uncorrected small leaks can present a greater risk potential from long term exposure than that from a major leak which requires immediate counter measures.

#### Maintenance

Maintenance of pumps, valves, pipes, and vessel interiors presents the possibility of inhalation and dermal exposure to coal-derived liquids and vapors.

### c. Engineering Controls

#### Equipment Leaks and Spills

Control measures for leaks from pump shafts, valves, and flanges have been discussed in previous sections. Methods for preventing events which require high maintenance efforts should be developed as an effective means of reducing exposure to coal liquids. As an example, flushing vacuum bottoms lines with solvent after use or heat tracing them reduced the incidence of plugging. Similarly, designing pipelines to minimize erosion at elbows and valves reduces the possibility of leaks and spills due to wear. Design considerations can include both the geometry of the piping system and the materials of fabrication. Both approaches were used at the EDS pilot plant: a short, stainless steel elbow in the line from the preheater to the vacuum tower eroded and was replaced with a long sweep elbow lined with an alumina castable refractory [15]. Changing materials to avoid corrosion due to chlorides originating in coal is another way to avoid excessive maintenance [13,15,17].

#### Maintenance

Pumps, valves, and piping exposed to liquids carrying solids require more frequent repairs than other units in this section because of the abrasive nature of the slurry. In addition, pumps and lines carrying the vacuum bottoms are subject to plugging if the material solidifies or if solids accumulate. This can occur if the temperature is too low or if the lines are not flushed with a solvent after shutdown. For normal maintenance, precautions such as flushing vessels, columns, lines, and pumps with a suitable solvent to remove residual coal liquids prior to service may be practical in many (but not all) situations. Ventilating vessels prior to worker entry and providing adequate personal protective equipment, such as gloves, impervious outerwear, and respirators, are necessary measures to prevent inhalation or contact.

## 5. GAS PROCESSING, RECYCLE, AND SULFUR RECOVERY

### a. Process Description

Many gaseous components are formed during the liquefaction of coal. These can include C<sub>1</sub> - C<sub>4</sub> hydrocarbons, hydrogen sulfide, carbon disulfide, carbonyl sulfide, water, carbon monoxide, hydrogen cyanide, and/or ammonia. During each stage of pressure reduction and subsequent fractionation, these low boiling or non-condensable gases are separated from the liquid. Some of the gas streams produced during product separation are of little value as fuel and are flared.

The unreacted hydrogen stream is separated first and treated to remove hydrogen sulfide, ammonia, water, and condensable hydrocarbons. It is then recycled to the process with make-up hydrogen added. Gases from each of the phase separation operations are cooled to remove condensables; water scrubbed to remove ammonia; combined for acid gas removal; and, finally, may be used as fuel in the plant or sold as LPG or fuel gas.

The acid gases are hydrogen sulfide and carbon dioxide. (In direct liquefaction processes, hydrogen sulfide will predominate except in the off-gases from the gasification of the residue.) Hydrogen sulfide can be removed by processes such as Rectisol<sup>R</sup>, using methanol, or Selexol<sup>R</sup>, using diethanolamine as absorbents. The desulfurized gas then is returned to the plant as a fuel gas or recycled to the process. The hydrogen sulfide rich liquid is regenerated, usually by heating, to release the hydrogen sulfide. The latter is then converted to elemental sulfur using, typically, Stretford and Claus processes. Sour water, condensed from the gas streams, and water used to scrub ammonia from the gases also contains hydrogen sulfide. These streams are first stripped of ammonia which is either recovered or incinerated. Hydrogen sulfide, recovered by acidifying the ammonia-free water, is combined with hydrogen sulfide from the desulfurization operation.

### b. Hazards

Hazards associated with gas processing and recycle include exposure to: hydrogen sulfide; ammonia; chemicals, such as methanol or diethanolamine used in the sulfur removal and recovery processes; and molten sulfur.

#### Hydrogen Sulfide

Hydrogen sulfide presents the greatest potential hazard. Although its concentration in the process gas streams is only a few percent, concentration in the gas exiting the desulfurization unit may approach 90%. It is toxic (with poor warning properties) and corrosive in the presence of moisture. Under certain conditions, it may form an explosive mixture with air.

#### Ammonia

Ammonia is less toxic than hydrogen sulfide and has much better warning properties. It can cause irritation of eyes and breathing passages at low to moderate concentrations. The potential hazards due to ammonia will depend on

its disposition. If it is incinerated in a boiler, there will be little danger of exposure other than by leaks. If it is recovered as an aqueous solution or as anhydrous ammonia, greater possibilities for spills or vapor discharges exist.

#### Sulfur Removal Chemicals

Chemicals used in the sulfur removal/recovery units may include methanol, mono- or diethanolamine, vanadates, and various proprietary formulations. A certain amount of handling is necessary in adding make up solutions to the systems and discarding spent material or bleed streams. Exposure to these materials can occur during such material handling operations.

Emissions from leaks of pumps associated with the sulfur removal/recovery units not only contain the chemical agents in the solution but can also contain hydrogen sulfide.

#### Sulfur

Sulfur recovered from the Stretford process is in the form of a froth and poses no significant hazard. However, the output of the Claus process is molten sulfur which may cause burns from spills until the sulfur cools.

### c. Engineering Controls

#### Hydrogen Sulfide

In a commercial facility, the pipelines carrying hydrogen sulfide from the sulfur removal unit to the sulfur recovery unit would be heated by steam or electrical tracing and insulated [15]. This would prevent condensation of moisture and eliminate the need to dry the stream in order to prevent corrosion.

Seals on the compressor which delivers the hydrogen sulfide can be purged with nitrogen so that any hydrogen sulfide leaking past the seal can be picked up by the nitrogen and sent to the flare [16].

At the H-Coal facility, the gas purification area has monitors which sound an audible alarm if hydrogen sulfide is detected. Operators also carry personal hydrogen sulfide monitors with audible alarms. Five minute emergency air packs are strategically located within the area and Scott<sup>R</sup> Air Packs are located nearby. The five minute air packs are for escape only while the Scott<sup>R</sup> Air Packs are for repair purposes [16].

Leaks will pose minimal danger to workers except for the hydrogen sulfide rich stream in the sulfur removal unit. In the H-Coal pilot plant, the rich diethanolamine pumps have single mechanical seals with a slip stream from the pump discharge used as a seal flush to prevent hydrogen sulfide release [16].

Operating temperatures and pressures are significantly lower in the gas purification section than in the main process sections. Similarly, the chemical and abrasive properties encountered in the coal liquefaction units are absent. In view of these differences, control of leaks in this section should be simpler than in the main plant.

### Molten Sulfur

If the Claus process is used for sulfur recovery, molten sulfur will be discharged. In the reaction to produce sulfur, sulfur dioxide is produced. The tail gas from the Claus plant can contain sulfur dioxide or a mixture of sulfur dioxide and hydrogen sulfide. This gas may require incineration to eliminate hydrogen sulfide. In addition, gas discharged with or dissolved in the sulfur will require removal by ventilation to the outside; flaring may be necessary if hydrogen sulfide is present.

## 6. SOLIDS SEPARATION

### a. Process Description

Various methods for removal of unreacted coal and mineral matter have been tried in the coal liquefaction pilot plants. Filtering, centrifuging, and settling have been used with varying degrees of success. Vacuum fractionation or solvent de-ashing seem to be leading candidates for commercial scale use. Vacuum fractionation is used in the EDS, H-Coal, and SRC-II, pilot plants. The vacuum bottoms containing the unreacted coal and mineral matter is solidified on a water cooled steel belt for disposal. In a commercial facility these vacuum bottoms would be pumped directly to a gasifier for the captive production of hydrogen.

If solvent de-ashing is used, the phase containing the solids will be removed at an earlier stage in the process by centrifuging or filtering. However, vacuum fractionation still will be needed. In this case, both the solids removed by the de-ashing step and the vacuum bottoms go to the gasifier for hydrogen production. Solvent de-ashing processes are proprietary and little information has been published on them.

### b. Hazards

Hazards associated with solids separation and disposal by vacuum fractionation are essentially the same as those encountered in product separation: inhalation of organic vapors and dusts and dermal contact with coal derived liquids. In addition to the hazards resulting from leaking seals and packing, pumps and lines carrying the vacuum bottoms are subject to plugging if the material solidifies. This can occur if the temperature is too low or if the lines are not flushed with a solvent after shutdown. Disassembly of the equipment for cleanout then becomes necessary, resulting in potential exposure of maintenance workers to coal derived materials.

### c. Engineering Controls

Control measures for this section are essentially the same as those needed for product separation (Section III,B,4). However, due to the high solids content of the feed to the vacuum fractionation tower and the vacuum bottoms stream, erosion of equipment is a more serious problem, particularly where seals on pump shafts are concerned.

The vacuum bottoms recycle pump in the EDS plant has double mechanical seals with a seal oil system [15]. Also in the EDS plant, the vacuum bottoms are pumped at 600° F (315° C) to the belt cooler by a screw pump. Hydrocarbon vapors escape through the pump packing [15].

The three pilot plants that use vacuum fractionation to separate the solids solidify the vacuum bottoms on a water cooled metal belt. Since the lightest organic component of the vacuum bottoms has a boiling point in the range of 750-800° F (398-426° C), a hydrocarbon aerosol is generated in this process. In one case, the fumes are withdrawn and sent to a high energy venturi scrubber using heated water in a once-through mode of operation [15]. In the second case, the belt is enclosed in a hood and an induced draft fan collects the hydrocarbon vapors and dust, and discharges them to a baghouse [16]. In the third case, there is also a hood over the belt but a steam eductor is used to remove the fumes. However, this latter technique has been reported to be inadequate [13].

## 7. PRODUCT STORAGE

### a. Process Description

The product storage area consists of various types of tanks, piping manifolds, pumps, steam lines, fire detection and extinguishing systems, leak containment structures, etc. Products which are stored in the tanks range from volatile naphthas to heavy distillates. In the case of SRC-I, the main product is a solid fuel.

Storage conditions vary depending on the type of product. Floating roof tanks are used to store lighter liquid products. Other products may require an inert atmosphere in the head space. Internal steam heating coils are necessary for highly viscous fractions which must be prevented from solidifying. Solid products may be stored in open piles or in covered silos.

A system of piping, pumps, and valves provides for the transfer of materials to and from the tanks and between tanks when necessary. Large tanks are diked to contain the contents in the event of leakage; smaller tanks may be diked in material-compatible groups. Tanks are vented to prevent pressure build up or tank collapse when pumping out. A vapor recovery system may be required on these vents to reduce worker exposure at tank farms and to comply with environmental regulations. Bottom drains provide for the removal of sediments or water which may separate out during storage. There also are provisions for cleaning the tank interiors.

### b. Hazards

Major hazards associated with the product storage area are fire and explosion resulting from leaks or spills. Since relatively few workers are routinely in this area, there is less opportunity for routine worker exposure to process materials than in the operating plant. In addition, storage areas are normally outside and open.

Tank cleaning and maintenance operations present the potential for inhalation of vapors and of skin contact with coal liquids. Workers may have to enter tanks to remove solids which have settled to the bottom of the tanks. Stirring the solids during this removal may increase the release of vapors into the tank environment. Exposure to product materials also can occur if a tank overflows or tank contents are mistakenly drained onto the ground.

### c. Engineering Controls

#### Fire and Explosion

Controls for fire and explosion fall into two categories: preventing the occurrence from happening and extinguishing the fire once it has occurred. Flame arresters are used to prevent flash back of fire from outside the tank. Blanketing the head space with nitrogen prevents an explosive vapor/air mixture from forming and lessens the danger of ignition by static electricity. Explosion-proof motors and electrical equipment are used throughout the unit. In the event of a tank fire, foam or water applied as fog is used to extinguish tank fires. Fire-water monitors are located throughout the EDS plant and the fire fighting equipment available is capable of producing either fog or direct water streams [15].

#### Leaks

Conditions encountered in the product storage area are less severe than in the main plant. Generally the product streams to and from storage tanks will be at lower temperatures than in the main plant and storage pressures will be at or near atmospheric. No abrasive slurries will enter this area; as a result, leaks from pumps and fittings should be minimal, using well-known technology.

Methods for the control of leaks from pumps and fittings are similar to those practiced in the plant proper. The use of nitrogen or inert gas flush to prevent leaks may be a feasible leak control method. This technique was discussed in Section III,B,2 for rotary and feed valves.

#### Tank Cleaning and Spills

Tanks should be designed to minimize the need for worker entry for cleaning and maintenance. At the SRC-II plant [13] material from the filtration area had been stored in the heavy oil tanks during maintenance periods. As a result, a heavy tarry material, difficult to remove through the drains, accumulated and worker entry was required to clean the tanks, resulting in worker exposure to process materials. If required, special surge tanks may be designed which are easier to empty, clean, and maintain.

Placement of the drains is important. The naphtha tank for the SRC-II plant must be drained daily to remove water. This drain discharges directly to the ground and as a result the ground is saturated with oil [13]. Relocation of the drain to avoid release of oil with the water or directing the drainage to the wastewater disposal unit could solve this problem. A properly designed water separator upstream will also reduce the amount of the water going to storage.

When worker entry is essential for tank cleaning or for maintenance, procedures to minimize exposure should be strictly followed. At the SRC-I plant, tanks

are cleaned and steamed prior to maintenance [17]. High pressure water or water/detergent jets may be used for cleaning, to flush the removable hydrocarbons from the surfaces; steam flushing may further reduce hydrocarbon accumulations. The tanks should be thoroughly ventilated before entry and personal protective clothing and respirators and non-sparking tools should be used.

Spills can also occur by overfilling a tank, or by opening drain valves leading to open lines. Overfilling can be prevented by level indicators and automatic warning/shutdown systems. Strict adherence to procedures and the use of lockable valves will prevent inadvertent discharges from tanks.

## 8. HYDROGEN PRODUCTION

### a. Process Description

This area includes the gasifier, oxygen production, carbon monoxide shift, gas cleanup, and reforming operations needed to produce hydrogen for the liquefaction process. Hydrogen is produced by the same method used for medium-Btu gas except that after hydrogen sulfide has been removed, the gas is reacted with steam to convert carbon compounds to carbon dioxide liberating hydrogen.

Vacuum bottoms or filtered unreacted coal, together with supplemental coal, is gasified with steam and oxygen to produce a mixture of methane, carbon monoxide, hydrogen, carbon dioxide, and various impurities, such as hydrogen sulfide, carbonyl sulfide, hydrogen cyanide, and ammonia. The gas may go through a carbon monoxide shift reactor to optimize the hydrogen to carbon ratio. Particulates and condensable organics are removed by water scrubbing. Hydrogen sulfide is removed by an acid gas removal process leaving only methane, carbon monoxide, carbon dioxide, and hydrogen as components. This mixture then is steam reformed to convert all of the reduced carbon (methane and carbon monoxide) to carbon dioxide and hydrogen. Finally carbon dioxide is absorbed in an ethanolamine scrubber and pure hydrogen is left.

### b. Hazards

Hazards associated with this section have been discussed in detail in the preceding section on coal gasification (Section III, B). The only units not covered are the steam reforming and the carbon dioxide removal units [13]. Steam reforming is essentially the same type of operation as CO-shift and methanation: a catalytic reaction carried out in the gas phase with a solid catalyst. It poses the same hazards as those operations. Carbon dioxide removal operation is similar to the acid gas removal discussed in Section III, B,5; however, no hydrogen sulfide is involved and, therefore, the associated hazards are significantly reduced.

### c. Engineering Controls

The controls needed for the gasifier operation have been discussed in the preceding section and earlier in this section in "Gas Processing, Recycle, and Sulfur Recovery," Section III,B,5.

## 9. SUPPORTING OPERATIONS

### a. Operations and Procedures

Supporting operations include plant utilities, byproduct recovery, and waste disposal. These units will closely resemble their counterparts in petroleum refineries and petrochemical plants. The major differences are due to the nature of coal-derived materials which, in general, contain more aromatic and polynuclear compounds than petroleum-derived materials.

#### Plant Utilities

A treatment plant is necessary for the preparation of cooling and process water. This will not differ significantly from existing industrial water treatment plants. In general, material handling operations for the solid and liquid additives will need to be controlled.

Steam is required for process use and possibly for onsite generation of electricity. Boilers probably will be fired with process generated fuel gas which is clean and sulfur free. These units are comparable to existing boiler facilities and pose no unusual hazards.

#### Byproduct Recovery

Byproducts from coal liquefaction are sulfur, ammonia, and phenol. Sulfur recovery from the gaseous streams was discussed in Section III,B,5. Ammonia and phenol are recovered from sour water streams. Ammonia is recovered by stripping. Solvent extraction is a preferred method of phenol recovery. The primary hazards associated with these processes are the potential for contact with sour water or inhalation of vapors from it. The sour water produced in coal liquefaction contains hydrogen sulfide, ammonia, hydrogen cyanide, and coal-derived organics; some of these organics are known to be carcinogens.

Control measures include prevention of leaks by regular maintenance, rapid cleanup of spills, and prevention of contact and inhalation. These are not high pressure or high temperature processes. Although the liquids are corrosive, they are not abrasive, so leak control is simpler than in the main process units.

#### Waste Treatment and Disposal

Solid, liquid, and gaseous wastes require disposal. Generally, practices used in petroleum and petrochemical plants can be applied with some modifications. Solid wastes are produced in process water and wastewater treatment and in hydrogen production. Spent catalyst may also be a solid waste. Sludges from boiler and cooling tower water treatment will not differ from those encountered in petroleum and petrochemical plants. Sludges from wastewater treatment may contain residual organics from the coal liquids and prevention of worker contact may be necessary. In particular, sludges and waste oils from oil skimmers or dissolved air flotation units will contain process organics and may require treatment as process materials. Depending upon their characteristics, sludges from wastewater treatment may either be landfilled or disposed of as hazardous wastes.

Ash or slag produced during hydrogen production has been discussed in Section III, B for coal gasification processes. Spent catalyst from the liquefaction reaction has been exposed to process materials and may contain residual organics. Prevention of contact and inhalation of vapors is, therefore, required during removal and disposal.

Waste gases are of two types: 1) gases which are formed during processing but have no value as fuel; and 2) gases vented from process vessels during process upsets. Both should be vented directly to the flare system through closed conduits and should, therefore, pose little hazard to plant personnel.

#### b. Other Common Hazards

Some hazards are present throughout the coal liquefaction plant. Control measures for these common hazards in various plant locations will be similar across the plant. Some may be due to specific conditions prevailing in the plant and others to particular activities being undertaken.

##### Hot Surfaces

Most of the piping and vessels contain material at high temperatures. Steam is transported through lines to its point of use. Insulation is applied to most lines; however, the optimum economic insulation thickness does not necessarily result in a surface temperature near ambient conditions. Thermal burns can result from contact with both insulated and uninsulated equipment. Locating piping where contact is not possible or installing shields to prevent contact will reduce the probability of burns.

##### Fire and Explosion

A second source of burns is from fire and explosion. Leaks and spills release flammable vapors which can be ignited by sparks. Explosion proof electrical equipment and non-sparking tools reduce the probability of burns from fires and explosion. Emergency procedures should be well thought out and appropriate training given for their implementation.

##### Process Monitoring and Analysis

Process control will be largely automatic with instrumentation for monitoring temperatures, pressures, and flows. Automatic analytical equipment can perform required process control analyses in many instances. Some analyses, however, can not yet be reliably automated. Examples are product stability, slurry density, and viscosity [13,14]. For such parameters, samples must be obtained by plant personnel. This sampling can result in worker exposure unless sealed and flushable sampling systems are installed.

### C. SPECIAL EQUIPMENT AND MATERIALS

The hazardous nature of the gases, liquids, and particulates associated with coal conversion processes necessitates the use of reliable process equipment to assure the integrity of the system and hazard containment. Failure of moving parts in pumps and valves, or erosion and corrosion of stationary process lines and vessels, jeopardize worker health and safety. In coal conversion, processes these equipment problems are highly probable due to the erosive nature of the coal and ash (hardness as high as 8-9 on the Moh's scale) and the corrosive nature of the gases. Where high temperature and pressure and three phase flow conditions prevail, valve and pump designs and materials of construction used for conventional process applications are not satisfactory.

The types of wear experienced by equipment used in coal conversion processes are defined as follows [19]:

corrosion - deterioration of materials due to chemical action.

erosion - wearing away due to high velocity flow.

abrasion - mechanical wearing away of material by high velocity solids forced by gravity and/or fluid flow.

galling - wearing away of a material by another material moving over it, combined with a force normal to the worn material.

Emissions of hazardous gases can result from erosion and corrosion of valve and pump seals and shafts, and from leaks in gasketing materials. High pressures and high temperatures, coupled with the erosive and abrasive properties of the solids and slurries, necessitate the consideration of special wear-resistant materials for construction. Special points of concern for process performance and worker protection are lockhopper valves, slurry feed pumps, high and low pressure letdown valves, block valves for flow isolation, flanges, and thermowells. Pilot plants are currently experimenting with new equipment designs and materials of construction which will perform satisfactorily in the processes, and provide longer periods of service without maintenance. Extended maintenance-free performance in most or all of these areas is probably essential for viable commercial production.

The erosive nature of slurries and liquors containing solids, and the corrosive nature of wet acid gases, such as hot hydrogen sulfide, require the use of steel alloys containing at least 30% chromium for some services. In certain applications, low percentage cobalt-based alloys are preferable (these perform better than high cobalt alloys). Chloride stress cracking may occur at lower temperatures, near the dew point of water, due to the formation of hydrochloric acid. Hydrogen embrittlement and cavitation may weaken equipment which may result in gas leaks from equipment; air or oxygen leaks into equipment, and liquid leaks; in some cases the leaking materials may be flammable [18].

Equipment common to all coal conversion plants include centrifugal and/or reciprocating pumps operating at high and low pressures; high and low pressure

valves and flanges; coal feeding mechanisms, such as lockhoppers; process instrumentation; heating furnaces; piping; and miscellaneous tanks and storage bins. In many processes, liquids containing solid particles (slurries) are pumped and, in some instances, liquids, solids, and gases may be present in the same stream. In addition to erosion, corrosion, and hydrogen embrittlement, the equipment is subject to thermal stress due to expansion and contraction. Gasketing materials suffer degradation and eventual failure. In pilot plants built to date, much of the pumping equipment, valves, packings, etc., have been standard commercial items. Use of these items has clearly demonstrated the need for improved equipment fabricated to meet the unique demands of process streams in coal conversion plants [18].

## 1. VALVES

Table 5 describes the operating parameters and wear considerations for various valve types used in coal conversion processes [19].

Corrosion and erosion problems are very severe in the solvent recovery area at the SRC plant. Since high metal loss rates have been observed during extended periods of solids-free operation, corrosion rather than erosion is the probable cause for this loss. The main replacement metal for these corroded parts is 316 stainless steel and the use of this alloy has resulted in vastly improved operating life. There are some indications that 316L stainless may be superior to 316 stainless. The various Hastelloys<sup>R</sup> and Incolloys<sup>R</sup> are also being considered as replacement metals for equipment in this area [13].

Attempts to overcome valve erosion problems included flame coating valve stems with tungsten carbide, Stellite<sup>R</sup>, or other materials. In the SRC Plant, coating of one problem valve was unsatisfactory and solid tungsten carbide valve stems were installed. Although this valve stem was resistant to erosion, it was brittle. If forced from alignment by solid particles, the stem broke, requiring shutdown and replacement [18].

### a. Lockhopper Valves

Valves used for lockhopper service must be capable of handling char and ash. For this service, high alumina ceramic valve components are recommended because they retain their form when exposed to very erosive solids at high temperatures. Valve internals which should be made of this material include seats, sealing discs, stop rings, and springs. Ceramic materials have proven to be superior to tungsten carbide coated stainless steel parts [20].

Design factors which affect the performance of lockhopper valves are the flow-path, the seals between the seat and the body and between the seat and the closure member, the sizing of the actuator and linkages, thermal considerations, and quality control in valve design, and construction. Valves designed to operate under critical tolerances should not be selected for solids service as they are more apt to fail due to misalignment [21].

The valve flowpath must allow an unobstructed flow through the valve body, minimizing contact with valve seats and bearings. Pockets where solids could accumulate should be avoided. If this is impossible, a purge system should be

TABLE 5.

Summary of Valve Requirements for Coal Conversion Service [19]

Valve Type	Pressure Range (psig)	Temperature Range (°F)	Media Handled	Relative Ranking of Wear Considerations
Solid Feed Lockhopper	10-1500	Ambient-850	Coal and/or limestone	1) Abrasion 2) Galling 3) Hot Hardness
Hot, Dry Solids Removal Lockhopper	10-1500	600-1800	Char, ash	4) Erosion 5) Impact
Slag/Slurry Removal Lockhopper	10-1500	450-1000	Water-quenched or slurried char, ash, slag	1) Erosion 2) Impact 3) Hot Hardness 4) Abrasion
Slurry Letdown	600-3000 ( $\Delta P$ across valve: 500-2000)	750-950 (at inlet)	Hydrocarbon-based solvent, 15-40% coal, char, or ash (by weight). Dissolved gases possible	1) Erosion 2) Impact 3) Corrosion 4) Abrasion
Slurry Block	150-3000	150-500 750-950	Hydrocarbon-based solvent, 15-40% coal, char, or ash (by weight). Dissolved gases possible	1) Erosion 2) Impact 3) Corrosion 4) Abrasion
Hot, Dirty Gas Control	50-500 ( $\Delta P$ across valve: 5-50)	1000-1750	Syn-fuel gas 0.1-2 grains per scf of char solids	1) Erosion 2) Corrosion 3) Hot Hardness 4) Abrasion

employed to direct the accumulating debris to the valve outlet. Clearances between movable valve parts must be properly designed to avoid erosion and abrasion; the particles must flow freely through the clearance or be excluded from the space between the mating parts. Most abrasion and erosion in lockhopper valves result from the grinding of coal particles between the movable parts of the valve rather than from abrasive impact of the coal particles against the material surfaces [21].

An important feature for valves controlling the flow of solids is to have a seal that ensures continuous contact between the seat and the closing member to prevent particles from becoming entrained between the moving part and the valve body. This force can be provided by a spring or by a differential pressure in the valve [21].

External leakage problems usually result from the accumulation of fine particles under the valve packing or from the distortion of the valve body joints due to thermal expansion during service [5].

Actuators and linkages from lockhopper valves must be designed to transmit forces large enough to operate the valve properly, even when solid particles cause friction or block movable parts. Usually this requires an over-sized actuator. Linkages used to transmit the force must be designed to handle the full force of the actuator. Ideally, a lockhopper valve controller should vary the force of the actuator to provide only the force required to operate the valve or automatically purge the valve to facilitate valve operation [21].

Lockhopper valves often fail because of improper or infrequent maintenance, or because they do not meet the manufacturer's specifications. To prevent these problems, valves must be thoroughly inspected and tested when purchased; all maintenance should be well documented. The effectiveness of service activities can be monitored and improved upon by keeping valve maintenance records [21].

Most lockhopper valves tested have incorporated Stellite<sup>R</sup> 6 as the sealing surface, and this has usually proven to be adequate. When slags and ashes contain solids which are harder than this alloy, cermets and ceramic materials, such as silicon nitride, tungsten carbide, silicon carbide, and boron carbide, are recommended for use as materials for the sealing surfaces [21].

Testing performed in the State-of-the Art Lockhopper Valve Testing and Development Project showed four valves which had potential for satisfactory service as lockhopper valves. These valves, the Rockwell Coal Lockhopper Valve, the Everlasting Double-Disc Coke-Oven Valve, the Everlasting Sliding-Disc Valve, and the Kamyr PD Series Ball Valve are illustrated in Figures 3 through 6. The variations among these valves demonstrate that no single valve type is uniquely suitable; but rather it is the specific adaptations made on the valve which determine suitability for servicing solids at elevated temperatures [21].

Tests of the Everlasting Double-Disc Coke-Oven valve showed that with several design modifications the valve performs satisfactorily as a lockhopper valve at temperatures of 300° F (150° C) and 600° F (315° C). The valve could perform well in handling solids with hardness similar to that of aluminum oxide if more wear-resistant mating surfaces were used for the seat and disc. Recommended improvements include redesigning the valve joints to

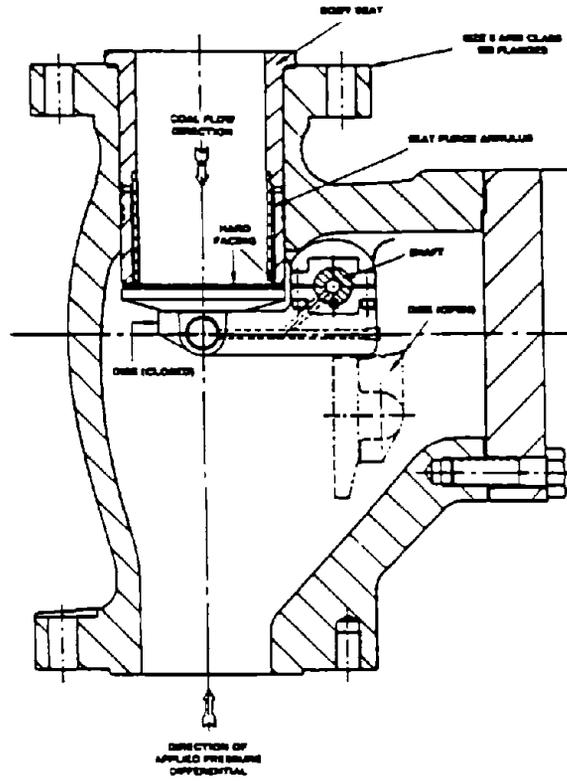


Figure 3. Rockwell Coal Lockhopper Valve [21]

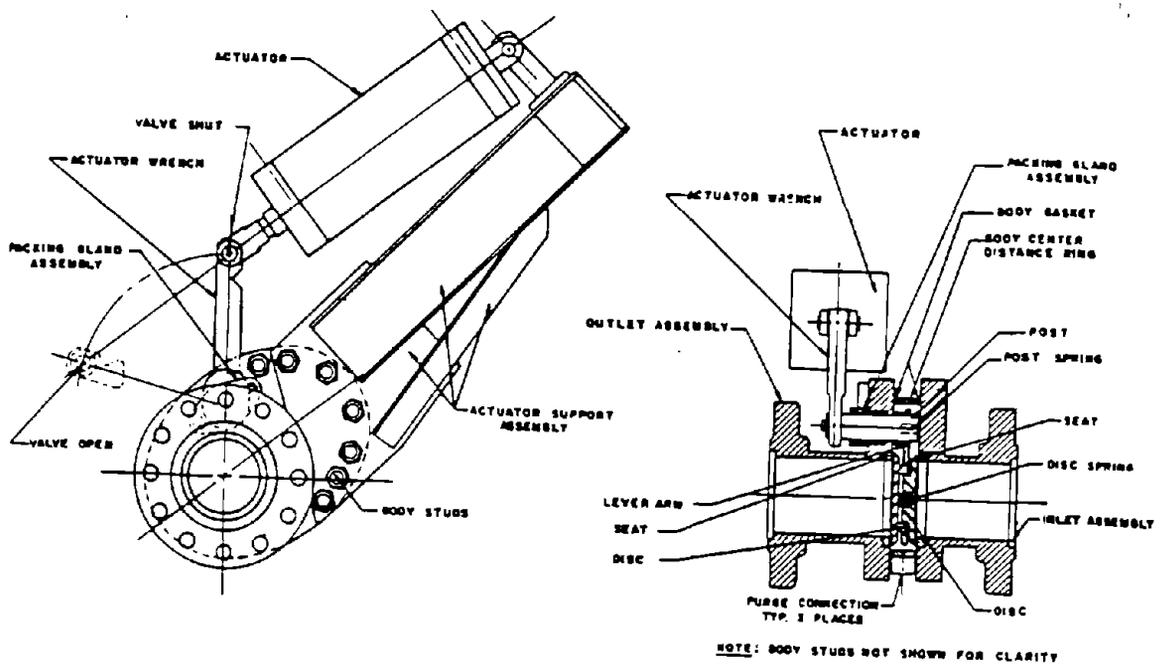


Figure 4. Everlasting Double-Disc Coke-Oven Valve [21]



reduce the effect of thermal expansion, improving the valve purge system, and increasing the spring force which pushes the disc against the surface of the seat to minimize the accumulations on the disc face [22].

The Everlasting Sliding Disc Valve performed well when tested for potential use in lockhopper service. Several problems were encountered with the actuator lever arm, but these could be corrected by increasing the disc spring preload force to prevent accumulation of solids in the recess. Valve operation was not affected by elevated temperatures. With the use of an automatic purge system, this valve would be very appropriate for lockhoppers [23].

#### b. Letdown Valves

The problems associated with letdown valves for coal liquefaction are erosion, flashing, and cavitation which result from the high pressure drop and particle entrainment in the process flow [24]. One approach to designing an erosion resistant valve is to use a streamlined angle valve with a special valve trim material. It was reported that this valve design is superior to the conventional 90-degree pattern angle valves. The streamlined angle valve has a vertical valve inlet and a horizontal hardfaced trim assembly outlet consisting of a plug and seat retainer (Figure 7). The valve is being tested using both conventional and experimental trim materials [24].

When angle control valves were inadvertently installed backwards at the SRC installation, an increase in the service life of these valves by several orders of magnitude was observed [18]. Bituminous Coal Research found that the backward installation of an angle control valve reduced the swirling flow at the valve trim. The experimental valve did not need to be repaired or replaced during the equivalent of two weeks of service [25].

The SRC plant is testing a Willis valve to let down the slurry from 2000 psig to 900 psig. This valve is designed so that there is a wiping action between the two plates that control the flow through the valve. These plates are optical finish flat with orifices that operate on a counter-rotation system to control the flow. Because of the close fit, there is little or no opportunity for the slurry to damage the faces of this type of control valve. However, because of the hardness of coal, the orifices, which are located in the sliding sections of the valve, wear quite rapidly. Two additional valves which are being considered for use as control valves are a microfluted trim valve and a solid tungsten carbide control valve which uses a special grade of carbide with as low as 1.5 percent binder [13].

A study was conducted at Battelle Columbus Laboratories to determine the most erosion-resistant material for trim components in high pressure letdown valves. The criteria for selection were that the materials must be erosion-resistant and be commercially available now or in the near future. The test simulated typical letdown conditions: 650° F (343° C) and letdown from 2000 psi. The slurry consisted of unfiltered product dissolved in anthracene oil [26]. Results of the tests showed that consolidated diamond, chemical vapor deposited (CVD) SiC, and K 701 grade of cemented carbide to have experienced erosion. Materials which performed less well in testing include cast tungsten carbide, Al<sub>2</sub>O<sub>3</sub>-TiC machining grade ceramic, and CVD TiB<sub>2</sub> and LSR-1 TiC type coatings.

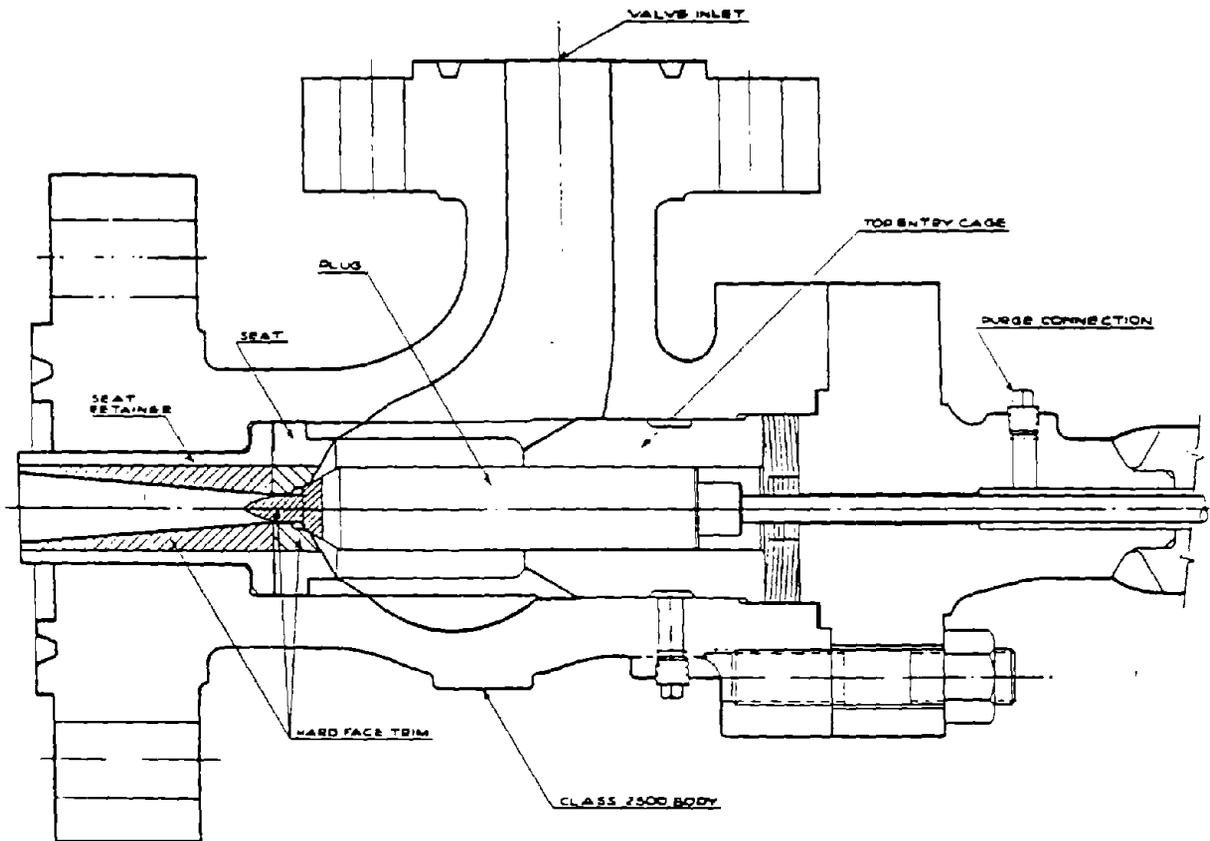


Figure 7. Slurry-Letdown Valve [24]

The poor performance of the two coating types suggests that they may not perform satisfactorily in letdown service. The consolidated diamond powder and the CVD SiC, though performing well in testing, are not readily available in sizes and shapes appropriate for valve trim applications [27].

Three-phase erosion testing conducted by the Albany Research Center resulted in the recommendation of ceramics, coatings, cermets, and bulk metals for valve trim materials. The test phases included sandblast-type impingement of media on the material under various conditions. The materials which experienced the least erosion were:

Hot pressed  $TiB_2$  from the Oak Ridge National Laboratory in Oak Ridge, Tennessee. This material provides the best erosion resistance in bulk.

Electrodeposited  $TiB_2$  from United Technologies and Avondale Research Center, Bureau of Mines.

Borided tungsten carbide with cobalt binder; Kennametal Corporation provided the Co-WC and Materials Development Corporation of Medford, Maine, borofused the coating.

Silica and silicon nitride bonded silicon carbide from the Ferro Corporation.

Controlled nucleation thermal-deposited (CNTD)  $TiB_2$ , CVD  $TiB_2$ , and CVD silicon carbide from the San Fernando Laboratories [19].

A 1979 DOE report entitled "Performance of Valve Materials Under Erosive Conditions" also suggested the use of tungsten carbide for valve trims in pressure letdown applications [28]. Bituminous Coal Research, Inc., has found it effective and economical to purchase standard tungsten carbide machine tool parts to modify the valve trim of pressure control valves. The parts are machined in-house, saving the time and money required for procuring special order trim [25].

An additional problem associated with letdown valves is erosion of the piping immediately downstream of the valve. SRC has attempted to solve this problem by using a tungsten carbide tube (choke) at the outlet of the valve orifice. This tube acts as a deceleration chamber by conducting the high speed stream beyond the valve body into an enlarged pipe [13].

The problem of erosion of the receiver piping at the outlet of the letdown valves was reduced by developing a receiver vessel consisting of a nozzle and a refractory lined pipe (Figure 8). The vessel is designed to minimize erosion by reducing the velocity of the process flow through the pipe [24].

### c. Block Valves

Block valves are used in coal conversion processes to isolate control valves, pumps, sampling lines, instrumentation, and bypass lines. Problems associated with these valves include: erosion of valve seals and internals, valve seat scoring and abrasion, build-up of solids between seating surfaces and in the valve cavity, and solidification of liquids in dead spaces in the valve body.

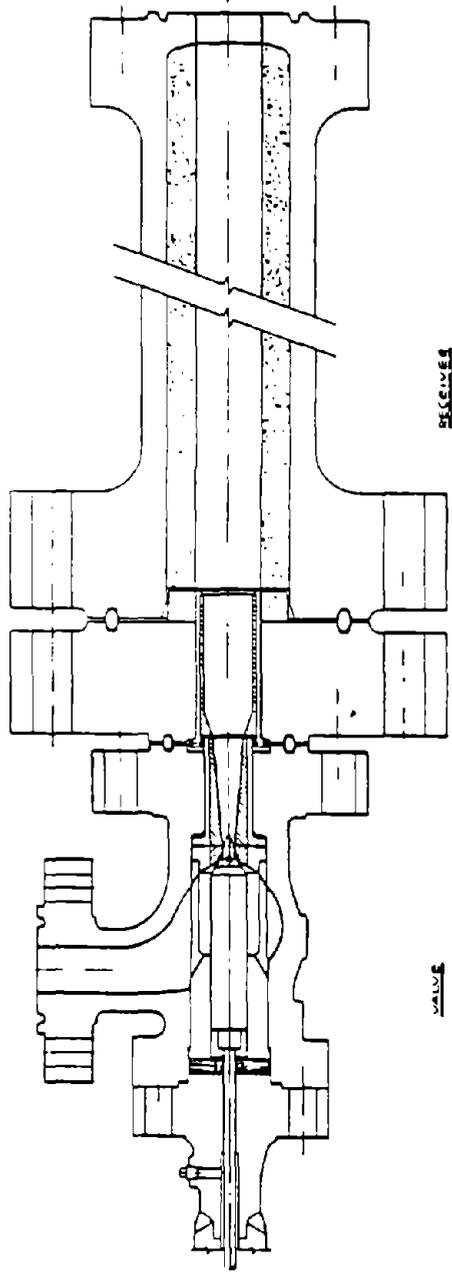


Figure 8. Slurry-Letdown Valve and Receiver [24]

The erosion of valve internals results in leakage at valve seats, gates, plugs, or balls. Build-up of solids hampers the motion of these internals and also results in process leak-by [29]. Several design features can minimize erosion in block valves used to isolate slurry flows: valve seats should be situated out of the process flow path in order to reduce erosion by the impact of the solids; the valve body should be streamlined and of a full port design to minimize erosion from process flow velocity changes; finally, the valve body cavity should be isolated from the slurry flow so that the accumulation of solids is minimized [29].

A comparison made between six different types of block valves, based on the desirable features mentioned above, is shown in Table 6. The three valve types which rank highest in this comparison are conduit-type gate valves (Figure 9), metal-seated ball valves, and tapered plug-valves (Figure 10). The soft-seated ball valve is not considered to be as effective because the elastomer seating material is not reliable at temperatures exceeding 450° F (230° C) [29].

Two recommended modifications for improved performance are the use of hard-faced seating surfaces and the installation of flushing systems to prevent the build-up of solids in the body cavity and on the seating surfaces [29].

Ball valves meet many of the requirements for on-off service in coal conversion processes. The advantages include low leakage, quick opening, low pressure drop, and relatively small size and weight. Problems with ball valves are encountered when handling slurries and solids. In these cases, erosion of seating surfaces often results from valve throttling. Abrasion of the valve body and the ball may also result from trapped residue between the two surfaces [19].

## 2. PUMPS

Problems encountered with slurry pumps include plugging, failure of mechanical seals, and erosion of pump internals. Seals usually fail due to both scoring by fine coal particles and to stress cracking from inadequate seal cooling. The pump internals fail from the erosion of impellers, wear rings, case inlets, pump heads, and casings [27].

Problems associated with piston and plunger pumps used for high temperature coal slurry service include packing deterioration and failure of the flushing system. Mechanical seals currently being investigated for use in this service are double seals, tandem seals, bellow seals, special flush systems, and the use of Acme<sup>R</sup> thread on the inner seal sleeve to expel solids. Bellow seals were found to have pressure limitations in certain services [30].

The preheater charge pumps used at a SRC plant are plunger-type pressure pumps with a flushed stuffing box and a free floating ball check. It has been found that ball check valves work well when handling flows from the discharge of the pumps; swing check valves did not perform satisfactorily for slurry flow [13].

High-pressure, high flow rate centrifugal pumps used to feed coal and oil slurries to a reactor or gasifier must be made of materials capable of handling

Table 6  
Comparison of Valve Designs [29]

Valve Type	Full-Port Design	Streamlined Flow Path	Seats Out of Flow	Erosion-Resistant Seat Material	Body Cavity Not Exposed to Solids
Conduit-Type Gate Valve	X	X	X	X	X
Metal-Seated Ball Valve	X	X	X	X	X
Tapered-Plug Valve		X	X	X	X
Soft-Sealed Ball Valve $T \leq 450 \text{ }^\circ\text{F}$	X	X	X		X
Wedge-Type Gate Valve	X			X	
Ram-Type Valve	X				

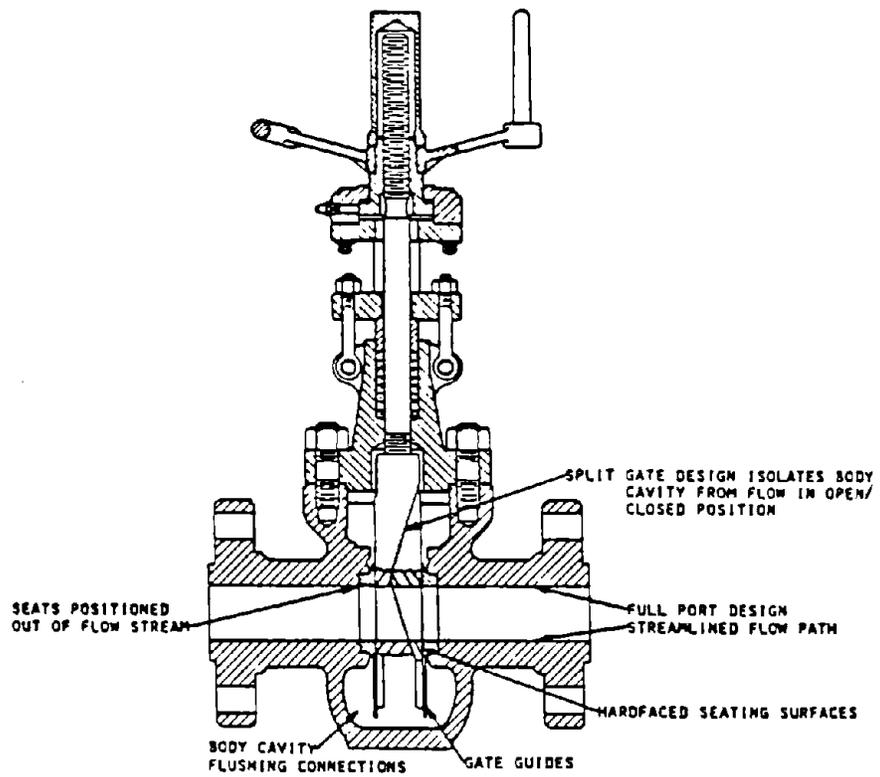


Figure 9. Through-Conduit Gate Valve [29]

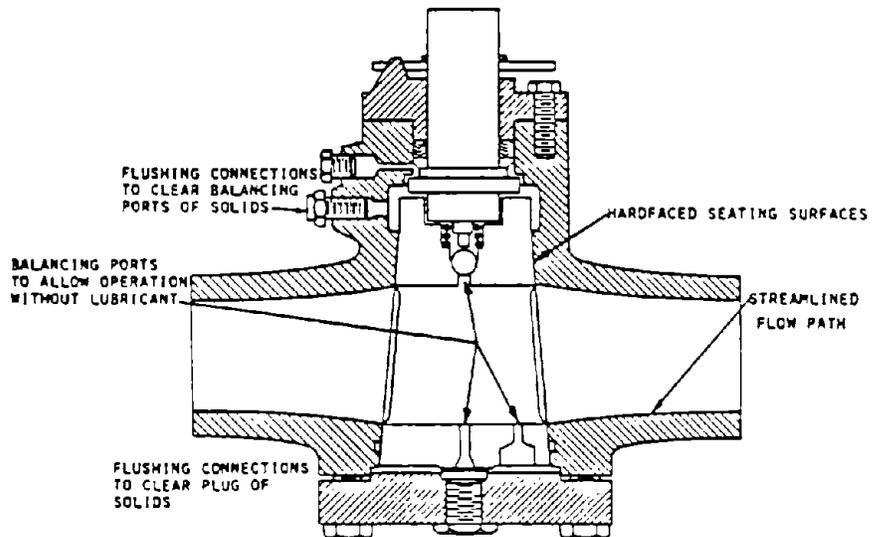


Figure 10. Tapered-Plug Valve [29]

large quantities of this erosive and corrosive mixture at temperatures as high as 750° F (400° C) and pressures up to 4,000 psia [28]. The impeller size can be increased to reduce pump wear by allowing the pump to operate at lower rotational speeds. Shaft wear can be reduced also by using lubricating oils. Mobiloid<sup>R</sup> oil was used at the SRC plant for this purpose [13].

Hard facing or abrasion-resistant alloys must be used in the body of coal slurry pumps, since failure of the cast iron casings would result in major leaks of flammable hydrocarbon solvent. They should be non-porous, smooth finished, high density, thermally stable, strong, and resistant to corrosion and erosion. These facing materials can be applied by plasma spraying, chemical or physical vapor deposition, and diamond dust coating [31].

New pumps received by the SRC plant are flame-sprayed with tungsten carbide. As the coatings wear, the parts are sent out to be recoated to proper specifications. Pump wear plates are removed frequently, and worn areas are replaced with a flame sprayed coating of tungsten carbide. A low-cobalt binder is used to resist erosion and reaction with ammonia [13].

Tests of pump materials were conducted at Battelle Columbus Laboratories to determine the best materials for use in coal slurry pumping service. Test conditions were designed to simulate flow of coal slurry through a turbine-type pump. Kennametal<sup>R</sup> sintered tungsten carbide grade K703 and borided steel were the first and second best performing materials, respectively, showing low erosion rates at both low and high flow velocities [27]. K703 is resistant to erosive wear, thermal shock, and oxidation at extreme temperatures [28]. The borided steel is more easily cast, and is, therefore, applicable for the fabrication of pump parts. In the same test, plasma sprayed tungsten carbide performed well at low flow velocity, but was easily penetrated at the high velocity. CVD titanium carbide experienced similar wear. Cast stainless steel was the least acceptable of all materials tested [27].

A DOE report, "Performance of Slurry Feed Pumps Improved" [28], noted Kennametal<sup>R</sup> K703 as having the slowest erosive rate of the materials tested. The use of sintered tungsten carbide inserts in high wear areas, such as the volute cutwater, the impeller blade edges, and the wear rings was also suggested.

Pumps with coated internal parts often experience chipping, flaking, and spalling. This is usually caused by nonuniform coating thickness and poor bonding with metal substrate. Poor bonding results when the coating has a different coefficient of thermal expansion than the substrate. Tungsten carbide, PTI-54, and Stellite<sup>R</sup> 6 have coefficients which differ significantly (as much as 34%) from that of the carbon steel or 13 percent chromium substrate, whereas Triboloy<sup>R</sup> 800 coating has a coefficient of thermal expansion which is comparable to these substrate materials [27].

### 3. THERMOWELLS

Temperature measurement in reactor vessels is often a problem in coal conversion. Thermocouples are available that can measure the high temperatures, typically 3000° F (1650° C), but it is difficult to design thermowells that are also capable of withstanding the high pressure erosive and corrosive

environment in the vessel and still provide adequate temperature indication. High temperature operations require a rapid response because of the need to closely monitor temperature fluctuations but heavy-duty thermowells inhibit the response to temperature changes [32].

One facility has designed and installed thermocouples capable of operating at temperatures as high as 2500° F (1370° C). These thermocouples (type K) are sheathed in stainless steel and encased in schedule 40 steel pipes, which are extended vertically into the bed [32].

Plant tests have been made using ceramic coated stainless steel and various alloys for thermowells; however, none of these have lasted more than 24 hours. The National Bureau of Standards, in response to a request from one facility, is working to develop new and better materials for this service. Solutions being investigated include new materials of construction and the use of non-intrusive indicators [18].

#### 4. FLANGES

The major problem associated with flanges in coal conversion plants is failure of the gasket material. Flanges used at the SRC plant are raised-face, ring-joint type with Flexitalic<sup>R</sup> gaskets. To prevent leakage at this gasket, care must be taken to avoid scoring the face during maintenance. SRC plant personnel believe use of Grayloc<sup>R</sup> (Gray Tool Company) flanges are the easiest to assemble and maintain in their particular process [13].

#### IV. WORK PRACTICES

Coal conversion processes should be conducted in closed systems using engineering controls to contain process constituents within the system. In a properly maintained system, worker exposure to process materials will occur primarily at entry and exit points within the system, during upset conditions, during activities that circumvent the closed system, or during maintenance and repair.

Supplementary engineering controls, such as local exhaust ventilation, have also been used at some facilities to control emissions at entry and exit points [13,14,15]. As a universal adjunct to these engineering measures, work practices (including good maintenance procedures, housekeeping, and isolation or certain hazardous areas or operations) are also important measures in controlling hazards.

Exposure to process constituents may be through inhalation, skin contact, or indirectly, through the use of contaminated clothing, personal protective equipment, tools, and equipment. The principal objective of good work practices examined at coal conversion plants is to minimize exposures to any constituent encountered during upset conditions or during the performance of activities which circumvent the closed-system. Those activities identified by plant management and safety personnel as requiring special work practices are maintenance activities, process stream sampling, and emergency situations.

Work practices have been developed to control exposures to compounds which are considered to present the greatest hazard. These compounds include PAHs, aromatic amines, hydrogen sulfide, and carbon monoxide. PAHs are important because a number of compounds in this group [e.g., benzo(a)pyrene (BaP) and 7,12-dimethylbenz(a)anthracene (DMBA)] have carcinogenic properties. Industrial hygiene surveys of gasification and liquefaction facilities confirmed the presence of such PAHs on work surfaces, tools, and clothing [34,35,36,37].

Hydrogen sulfide is considered a hazard because of its presence in coal conversion process streams. Hydrogen sulfide can be an acute lethal hazard in enclosed areas, such as within a vessel, or in emergency situations involving major process leaks. Carbon monoxide, a major component of the low- or medium-BTU product gas, can also be an acute lethal hazard under similar circumstances in gasification facilities.

##### A. MAINTENANCE PROCEDURES

Maintenance activities involve breaking process lines, repairing and removing process equipment, and entering vessels. Industrial hygiene surveys of eight liquefaction and gasification facilities have shown that workers engaged in these activities have the highest exposures of all workers sampled [34,35,36,37,38,39,40,54].

Many practices developed for these activities by the liquefaction and gasification facilities are related to the preparation of the equipment and worksite for maintenance work. These procedures are designed to minimize worker contact with process materials, especially the coal liquids and tars, and to avoid

hazardous conditions related to toxic gases, such as hydrogen sulfide. The key elements of these work practice procedures are: 1) isolation of the system and equipment, 2) draining and flushing the system of process material, and 3) cleaning the work area. Observations made at 19 facilities have indicated that these three elements are contained in the safety manuals of only two facilities [15,41]. Other facilities reportedly follow these procedures but did not have written procedures available at the time of the survey.

In the facilities surveyed, the plant operators generally perform the pre-maintenance activities of equipment isolation, draining, and cleaning because they are more familiar with the process design and the use of equipment than the maintenance crew. Protection of the operators is accomplished by the development of safe work procedures for these three key elements, by the use of a permit system to monitor these procedures, and by the use of personal protective equipment and clothing. These three elements are discussed in the following paragraphs.

### 1. Equipment Isolation

In the isolation step, the flow of process material into the equipment to be repaired is stopped by blanking-off all process lines entering and leaving the segment. This is accomplished by the use of valves, caps, or plugs. The simplest technique (valving) is to close the valves on all lines entering and leaving the segment being repaired. This is also the least reliable method of isolation because of the possibility of valve failure, or of a valve being opened inadvertently by another employee. However, valving is the most common technique being used in the 19 gasification and liquefaction facilities surveyed. Two of the facilities do use caps and plugs, whenever feasible, during maintenance and repair on equipment and vessels.

At facilities where valving is used to isolate equipment, reliability has been improved by added refinements. The survey team has observed the use of double block valve systems at two liquefaction facilities. The additional valve serves as a safeguard in the event that the primary shut-off valve failed to seal properly. Mechanical lockouts, such as individual personal locks or chains applied to the valve handle, were used in the other facilities; one plant used a combination of chains and lockouts [41].

Caps and plugs are more reliable because they ensure a complete physical separation of the vessel or equipment from the rest of the process. At two facilities where this technique is used [15,41], valves upstream and downstream of the vessel or equipment are closed. If the system is pressurized, bleed valves are opened to reduce the pressure to atmospheric levels before the lines are broken to apply the caps and plugs.

### 2. Draining

Draining procedures at the surveyed facilities use valves or spigots to empty vessels and equipment, and union pipe joints for line segments. Once the equipment is isolated, properly located spigots can provide a safe and controlled method of draining materials. Hot equipment is normally cooled to ambient temperatures before undertaking maintenance; however, in a production

unit this practice may not always be followed due to production concerns. To reduce the potential for skin contact or inhalation of process material during maintenance work, pipe unions or flanges are slowly opened to drain the line of process material. Drained solid or liquid materials are routed to receptacles, such as covered containers, or to drains for disposal, while vapors and gases are vented. Local exhaust supplied by flexible ducts may be used to remove vapors or gases which may be released. Once drained, the pipe segment and union are removed and the line is capped or plugged. Vessels are purged to remove residual vapors and gas.

Additional health and safety problems are present in draining isolated systems which are under high pressure. Elevated pressure problems are handled in the surveyed facilities by requiring workers to open bleed valves slowly to prevent an explosive ejection of the process material. This system was observed at two gasification facilities [41,42] where emissions were vented by piping to areas removed from the workers.

### 3. Cleaning

Cleaning operations are used to remove surface contamination, primarily coal tars, from the inside and outside work surfaces. Steam cleaning is the most common method and is used in both liquefaction and gasification facilities in which coal tars are formed as a by product of the process. Two gasification facilities did not include cleaning operations as a part of the maintenance procedures because of negligible tar formation in the gasification process [7,42].

Hydroblasting and industrial-strength caustic detergents were used in combination with steam cleaning at two of the liquefaction facilities [15,16]. Observations at these facilities indicated that the use of detergents increased the efficiency of the cleaning operation.

### 4. Vessel Entry

The liquefaction and gasification facilities surveyed have vessel entry procedures which are patterned after NIOSH recommendations [55]. These procedures follow the cleaning step and involve:

- purging the vessel with air
- checking combustible gas and oxygen levels
- checking concentration of toxic gases likely to be present
- employing the buddy system in which a person fully equipped with the necessary protective clothing and equipment is stationed outside the vessel to provide assistance in an emergency to the worker inside
- providing lifelines and necessary protective equipment to the worker entering the vessel.

At one gasification facility, air purging is preceded by a nitrogen flush. This procedure is considered effective in removing contaminants which may react with oxygen [41].

## B. HOUSEKEEPING

### 1. General Practices

Many approaches are used in liquefaction and gasification facilities to handle housekeeping duties. Clean-up activities are most commonly conducted on an as-needed basis. In some facilities, spills are cleaned as soon as possible by the people responsible for the spill. At one liquefaction facility, strict adherence to this policy, especially the "as-soon-as-possible" requirement, resulted in the cleanest liquefaction facility work environment visited. This approach can have the advantage of promoting a personal sense of ownership in a clean workplace among the workers. Another effective approach is the use of specifically assigned personnel to clean all spills as they occur [10].

Some facilities provide time in the daily schedule for operators on each shift to clean their assigned area at the end of the shift; this makes possible the daily cleaning of all areas. In other cases, plant size makes it impractical to clean all process areas in a single day [15,16]. At these facilities, one process area is cleaned each day by assigning personnel from the maintenance labor force. However, this procedure allows tars time to solidify, requiring a more rigorous cleaning procedure to clean-up the area. Clean-up can be facilitated by the application of an epoxy coating which minimizes the absorption of contaminants by the concrete flooring [4].

A less desirable method is to conduct clean-up on an as-time-permits basis [13, 14]. This requires clean-up to be performed by the operators. Where operators may have other assigned duties that take precedence over clean-up, cleaning the facility becomes irregular. Facilities surveyed that used this approach had the greatest amount of tar in the workplace. Thus, the priority given by the supervisors to a clean work environment can have a major effect on the quality of the housekeeping. Some gasification facilities need no special procedures for the clean-up of spills because tars are not a by product of their process. These facilities, because of the reduced housekeeping requirements, can be cleaned by the operators at each shutdown period [7,42,43,44].

Contaminated surfaces and tools must be thoroughly cleaned. To insure proper decontamination, the tools and surfaces can be inspected under ultraviolet light for residual contamination, such as PAHs, and be re-cleaned if necessary.

### 2. Clean-up Procedures

In general, more rigorous clean-up procedures are employed in liquefaction facilities than in gasification facilities [13,14,15,16,17]. All liquefaction facilities visited during this study use steam cleaning to remove the tar deposits, although the method of application varied. Where spills are handled on an individual basis, an absorbent such as vermiculite can be spread immediately on the spill [17]. After the tar is absorbed, the vermiculite is placed in a closed container for disposal and the area is steam cleaned. This procedure has proven to be most effective in keeping the work area free of tar deposits. High levels of tar may remain deposited where spills are simply flushed with water (the run-off is directed to a waste water treatment site) and the area is steam cleaned later, when time permits [14].

A pneumatic hammer may be used to loosen tar heavy deposits before steam cleaning [13]. However, it was observed that hydroblasting in combination with detergent cleaning was more effective for removal of tar deposits [15,16].

Steam cleaning is the most rigorous clean-up method used for the removal of tar deposits at the gasification facilities surveyed. At the two facilities in which tar formation is a problem [4,41], it was used, primarily, for removing old tar deposits rather than recent tar spills. Fresh tar spills can be cleaned by the use of a clay absorbent followed by scrubbing with soap and water. This is especially effective where an epoxy floor finish has been applied, because the finish reduces tar absorption by the concrete flooring. The substitution of chlorinated hydrocarbon solvents for detergent and water proved to be more effective in cleaning tar spills when a floor finish has not been applied. Other effective solvents are perchloroethylene, tetrahydrofuran, and methylene-based paint strippers [6,9,10]. Care must be exercised to assure that excess exposure to these materials is prevented. In gasification facilities which do not produce tars, detergent and water is effective for most cleaning operations [42].

### C. ISOLATION OF WORK AREAS

#### 1. Restricted Areas

##### a. Barricades

The most commonly observed method used to restrict personnel movement into specified areas is barricading. Entry is regulated on the basis of the individual's training in recognizing and handling existing and potential hazards within the area, and on the need to be in that area. In temporary situations, where process upsets or the performance of specific activities such as repair can create a hazardous condition, colored barrier tapes are often used as a temporary barrier to keep untrained personnel out of the area [3,10,14,15,16,42].

Permanent barriers can be erected at unit operations experiencing ongoing problems. At two facilities, the sour water/sour gas system and the gasifier areas were barricaded with chains and barrier tape [16,41]. Brightly-colored (black and yellow) tapes delineate the boundaries of the hazardous areas. The tapes were replaced on a periodic basis.

The barrier system should be appropriate for the potential hazard. For example, two facilities fabricated partitions of either steel or cinder block to barricade hazardous areas [9,45]. These partitions provided protection against high pressure leaks and possibly some protection against explosions. At one site, the bench-scale liquefaction operation was completely enclosed in a small room and entry was prohibited during operations [9]. The process was monitored using remote sensors. In a pilot plant operation, selected pieces of equipment considered to be potentially hazardous during operations, e.g., the high-pressure separator, were isolated behind steel walls [45]. In addition, the back wall was constructed as a "blow-out" panel. The use of partitions is the most effective form of barricade observed during the survey, because they prevent unauthorized entry and provide some protection against sprays of hot materials and/or explosions.

b. Limited Access

An alternative to erecting physical barriers is to limit access by prohibiting workers from entering hazardous areas [3,9]. For example, at one facility the ignition and coal feed system were considered especially hazardous because of fire incidents. At this plant, no one was permitted to enter the area during the ignition of the coal burner, which was accomplished by remote control. During operation, the coal feed area was open only to workers having specific assignments in the area. A variation on this method is to declare an entire area off-limits, with entry permitted only for limited duties.

The more effective systems prohibit unnecessary entry into the process area when equipment is operating [42]. The effectiveness of this system is enhanced by warning devices. At one facility, a sign was posted listing the precautions that must be followed to enter the area safely, and a flashing red light signified that the gasifier was in operation. These warning devices reinforce the workers' training, reminding them of the safety requirements enforced during the operation of the gasifier.

Another method of controlling access is to designate a facility as a limited access area [3,4,15,16,42,43,44]. In one plant, visitors entering the facility are assumed to be untrained and unfamiliar with the plant safety measures. A sign in/sign out system is used to monitor them while they are in the facility. Visitors to this facility must sign a log book noting the times of arrival and departure. While in the facility, visitors are provided with company escorts who are familiar with plant safety procedures. This policy provides an effective means of tracking visitors and their location in the facility, and ensures that visitors are not endangered by, unknowingly, violating safety procedures. An even more stringent policy would require all visitors planning to enter the main process area to take a brief training course outlining the basic safety program [15,16].

Limited access policies can also be provided for workers. For example, at three facilities only a fraction of the people employed at the plant work in the gasification facility [4,43,44]. Because there is some exchange of personnel between this and other plant facilities, these plants have developed a certification system to track the training status of the workers in various health and safety concerns, e.g., respirator training. Company employees entering the gasification facility must have their certification cards reviewed by the supervisor in charge. If they do not have the necessary training, they are refused entry [43,44] or are provided an escort [4].

Process areas containing one or more specific contaminants may be classified as regulated areas [9,10]. Traffic between regulated and unregulated areas is kept to a minimum to reduce the chance of contaminating unregulated areas. For example, at facilities where coal tar is the contaminant, the objective is to contain the coal tar within the contaminated process areas. The movement of personnel into and out of the regulated area is carefully controlled; tools, clothing, protective equipment, and other potentially contaminated items must be left in the regulated areas before employees may proceed to unregulated areas which are free of coal tar contamination. This is accomplished by the use of clean/dirty room systems described in section VII, B. At one of these facilities, periodic inspections of the unregulated areas are made using ultraviolet light to check the effectiveness of the regulated area policy [9].

## V. PERSONAL PROTECTION

All facilities surveyed have minimum personal protective equipment requirements for all personnel entering the process area when the equipment is operating. These are dictated by the activity being performed. The supervisor, following guidelines developed by the facility Safety Office, has the responsibility of ensuring that the proper clothing and devices are used for the planned activity. At some facilities the protective clothing and device requirements are listed on the work permit and are reviewed by the Safety Office before work may begin [43,44].

Special personal protective measures are associated with activities where there is potential for worker contact with coal-derived liquids, or for worker exposure to acutely toxic levels in the work environment. These activities include maintenance and modification of equipment, vessel entry, process stream sampling, draining vessel condensate, and emergency responses.

At these facilities maintenance and modification activities are delegated to the maintenance department, and sampling and draining activities are assigned to the operators. Both production and maintenance workers have duties which may require vessel entry.

### A. PROTECTIVE CLOTHING

Table 7 lists the minimal protective clothing requirements for the facilities surveyed. The basic requirements for protective equipment are long-sleeve cotton coveralls, hard hats, impervious gloves, and face shields [3,6,10,13,14,17,43,44]. The simplest provision is the use of hard hats (mainly a safety device) in process areas [43,44]. At these facilities, a job review is performed by the worker's immediate supervisor (following guidelines set by the Safety Office) to determine the need for additional protective clothing. This approach provides flexibility in handling tasks that present unique safety or health problems.

Long-sleeve cotton coveralls is the most common protective clothing requirement [4,6,10,13,14,15,16,42]. Cotton coveralls appear to provide adequate whole body skin protection unless an area is rubbed or abraded, e.g., knees, elbows, buttocks, or is saturated with liquid. Dry cleaning appears to be the method of choice for removing coal tar products from clothes.

Flame-retardant coveralls provide an added safety feature [15,16]. Disposable coveralls, long-sleeve uniforms [3,9,17], and lab coats [3,9,17,41,44] are also used although they do not have the durability of the cotton coveralls. Lab coats are typically used in benchscale operations. Neoprene rain coats, to provide added protection and reduce contamination of uniforms, may be used [3,17]. Safety shoes, cotton gloves, and shoe covers also are specified, in some cases [7,9,10,13,15,16]. At all operating facilities, protective clothing and equipment requirements for specific hazardous activities are more stringent than the minimum requirements that are described in Table 7 for entry into the general process area.

TABLE 7

## Minimal Protective Clothing Entry Requirement for Process Area

PLANT REFER- ENCE	PROTECTIVE CLOTHING AND EQUIPMENT								
	Hardhats	Coveralls	Uniform	Lab Coat	Rain Coat	Safety Shoes	Safety Glasses	Gloves	Shoe Covers
<u>GASIFICATION</u>									
3	x	-	-	-	-	-	-	-	-
4	x	x	-	-	-	-	x	-	-
5	x	-	x	x	-	x	x	-	-
6	x	x	-	-	-	-	x	-	-
7	x	-	-	-	-	x	x	-	-
9	x	-	-	-	-	-	-	-	-
10	x	x	-	-	-	x	-	x	x
41	x	-	-	-	-	-	x	-	-
42	x	-	-	-	-	-	-	-	-
43	x	x	-	-	-	-	x	-	-
<u>LIQUEFACTION</u>									
13	x	x	-	-	-	-	-	x	-
14	x	x	-	-	-	-	x	-	-
15	x	x	-	-	-	x	x	-	-
16	x	x	-	-	-	x	x	-	-
17	x	-	x	-	x	-	-	-	-

The most common type of impervious glove is made of neoprene [3,8,13,14,17,41,43,44]. Other gloves are made of polyvinyl chloride, polyvinyl acetate, and butyl rubber [9,10,15]. In one case, it was found that neoprene was permeated and destroyed by the coal liquids, while polyvinyl chloride was not affected [15]. Polyvinyl acetate gloves cannot be used with water because the material is water soluble. The order of preference for glove material selection, based on the Lawrence Livermore Laboratory study [49] is nitrile, Buna-N, or neoprene. Viton was not studied but is expected to perform well due to its composition and performance with similar chemicals.

Safety glasses or goggles are used with face shields to provide additional eye and face protection [3,6,10,17,43,44]. Other facilities have elected to use hoods or full-facemask respirators in place of face shields to provide this protection [15,16,41,46].

Provisions to supplement the basic protective clothing requirements have been adopted [10,15,16,41]. Boots or shoe covers are required to minimize contamination of shoes, because leather is slowly permeated by coal tars and cannot be easily decontaminated [10,16,41]. One liquefaction facility requires the use of polyvinyl chloride slicker suits, impervious to tars, as well as rubber boots or disposable shoe covers [15].

At two gasification facilities, coal tars are not considered a problem. In these cases there is no need for impervious gloves and outer clothing [7,42].

#### 1. Process Stream Sampling

Engineering control, such as use of the sample bomb, has been used to minimize worker exposure during process stream sampling. Such controls are generally installed at sample ports through which high pressure or high temperature samples are collected. Where such controls are present the use of protective clothing and equipment serves as a backup in the event of a malfunction in the controls; in the absence of engineering controls protective clothing and equipment are the primary source of protection from exposure.

The type of protective clothing and equipment used is dependent upon the location and nature of the sample being taken. Respirators may also be used to provide maximum protection. Coveralls with long-sleeves or similar apparel are used in all cases to minimize the risk of skin exposure. Rain gear of neoprene or polyvinyl chloride are used in sampling hot process materials to protect the worker from spills or splashes [13,14,15,16,17]. Aluminized coats are worn to provide added protection against radiant heat, where operating temperatures are as high as 3000° F (1649° C) [43,44].

Cotton gloves are used in the collection of coal dust samples [3,13,14,15,17,42,43,44]. Neoprene, polyvinyl chloride, and polyvinyl acetate gloves are commonly used in sampling activities involving coal-derived liquids and gas samples [6,7,9,10,13,14,16,41]. Asbestos or leather gloves may be used to collect high temperature samples [17,43,44].

Most facilities required that face protection, coveralls, and gloves be used while collecting process samples. Facilities not requiring face protection

have installed either engineering controls, such as gas sample bombs, or automated sampling devices [7,42]. The most common type of protection is the face shield [3,6,9,10,13,14,15,16,17,43,44]. The use of face shields may be optional [9]. Safety goggles may be used in combination with face shields in sampling systems under pressure or at high temperatures [3,13,14,17, 43,44]. At one facility, a hood is used in sampling pressurized systems, while at other facilities hoods are used in all sampling activities [10,17,41]. Hoods are the most effective of the options available for protecting the face and eyes. Helmet liners have been used with face shields to protect the neck and head of the worker, but this has been discontinued due to worker discomfort [10].

## B. RESPIRATORS

At most facilities, respirators are used to control inhalation exposures to process materials in activities where this hazard exists. Respirator programs at these facilities are patterned after OSHA requirements and in the case of two facilities after the American National Standard Institute's 288.2-1969 respirator code [43,44]. The programs cover worker training in the use and maintenance of respirators, and conditions under which they are required. Six types of respirators used at coal conversion facilities are listed in Table 8. Data in the table indicate that respirator protection is primarily to control exposure to coal dust, hydrogen sulfide, and carbon monoxide. The relatively nonvolatile coal liquids are not considered to present an inhalation exposure hazard at most facilities. Only two facilities have provisions for controlling inhalation exposures to coal liquids, vapors, or aerosols [6, 10]. Air-purifying respirators equipped with organic cartridges are available for this purpose.

Air-purifying respirators are used primarily in activities where low levels of hydrogen sulfide may be present. Self-contained breathing apparatus (SCBA) and supplied-air respirators are used where high levels of hydrogen sulfide and carbon monoxide, including levels immediately dangerous to life and health may be present. At one facility gas masks equipped with Type N canisters are used for intermediate carbon monoxide exposure levels (between 50 to 500 ppm) [6].

SCBAs are used primarily in emergency or unpredictably dangerous situations. At ten facilities, these respirators are placed at strategic locations within the plant so that they are accessible in emergencies [3,4,6,15,16,41,42,43,44, 46]. One facility keeps the SCBAs in the control room [14]. Escape respirators with 5 to 10 minute air packs are placed at strategic points within the structure or carried by the individual to provide a source of readily available air for evacuation from acutely hazardous areas [3,4,10,16].

The Safety Officer has responsibility for inspecting and maintaining all respirators at most facilities and is assisted by supervisors who periodically inspect respirators in storage. However, at all facilities, the worker is responsible for inspecting respirators prior to use.

TABLE 8

## Types of Respirators Used in Coal Conversion Facilities

RESPIRATOR	PLANT REFERENCE	USE
Single use dust respirator	13, 42, 43, 44	Coal dust - primarily in coal preparation area for sampling or manual loading using front-end loader
Disposable dust respirator	3, 4, 6, 13, 43, 44	Coal dust - primarily in coal preparation area for sampling or manual loading using front-end loader
Half-mask air-purifying respirator	3, 6, 7, 10, 13, 16, 42, 43, 44	Low concentrations of hydrogen sulfide
Full-facemask air-purifying respirator	6, 14, 15, 16, 17, 43, 44	Low concentrations of hydrogen sulfide
Self-contained breathing apparatus	3, 4, 6, 14, 15, 16, 41, 42, 43, 44, 46	Emergency use, high levels of hydrogen sulfide or carbon monoxide
Supplied-air with full-facemask	3, 4, 14, 16, 41, 42, 43, 44, 46	High levels of hydrogen sulfide, carbon monoxide, and vessel entry
Escape respirators	3, 4, 10, 14, 16	Escape

## C. MISCELLANEOUS

Barrier creams have been tested at three facilities for their effectiveness in minimizing skin contact with coal tars [9,10,17]. At two facilities they were considered to be ineffective and in one case promoted carelessness in worker hygiene [9,10]. At a third facility, however, barrier creams were used as a substitute for gloves [17]. The cream is applied at the beginning and in the middle of the shift.

Noise problems were associated with coal handling activities, especially at grinding operations, in several facilities [4,10,43,44]. In these cases, the use of company provided ear muffs or ear plugs was at the discretion of the worker.

## VI ENVIRONMENTAL MONITORING

Most of the operating facilities have conducted some monitoring of hazardous agents within their process areas (Table 9). The present section summarizes the types of environmental or workplace monitoring that was used by the coal conversion facilities studied. Chemical agents sampled include Coal Tar Pitch Volatiles (CTPV), hydrogen sulfide, and carbon monoxide. CTPV are monitored because the method is relatively simple, and is considered a relevant federal health standard which may be an indicator of PAH risk. Three facilities plan to implement PAH sampling. Continuous monitoring programs are in effect at 9 facilities for carbon monoxide or hydrogen sulfide. Audible and/or visual alarms are set at 50 PPM and 10 PPM for carbon monoxide and hydrogen sulfide, respectively. Audible alarms are generally located in the process area; however, one facility has the alarm situated in the control board operator area. Visual alarm backups to the audible alarm are present at 2 facilities. The visual alarms have been useful because the audible alarms are hard to hear over the background noise.

Liquefaction facilities usually do not consider carbon monoxide to be an acute health problem because it is not a major constituent of the product stream. However, continuous monitoring for hydrogen sulfide should be performed at these facilities because it is a significant byproduct of liquefaction.

### A. AREA SAMPLING AND PERSONAL MONITORING PROGRAMS

Only four of the facilities listed in Table 9 have developed and used a comprehensive survey program [6,13,15,43]. These four survey programs were oriented toward research and were designed to identify the types and levels of contaminants or contaminant classes that are present in the plant work environment and worker exposure levels. Important elements of these programs were:

- Baseline sampling for known or suspected hazardous agents as identified by a literature review.

- A sampling schedule detailing the types of samples being taken and the frequency of sampling. These programs are long-term to account for time, weather variabilities, and different operational conditions.

- Flexibility in the sampling schedule to cover unusual occurrences such as upset conditions and process alterations.

- Identification of worker categories and area sample sites.

At two facilities this program will be followed for the duration of the research project [6,13].

Two facilities are in the initial stages of developing such a comprehensive survey program [4,41]. Each plant is conducting baseline sampling to identify the types of contaminants present and the usual ambient levels. This data will be used to develop the survey program. Three gasification facilities used a more limited survey program, concentrating on grab sampling techniques

TABLE 9

## Hazardous Agents Monitored by Thirteen Plants

AGENT	PLANT REFERENCE												
	3	4	6	7	9	10	13	14	15	17	41	42	43
Benzene Solubles	-	X	X	-	0	-	X	-	X	0	X	0	X
Benzene	0	-	X	-	-	-	X	-	X	0	X	0	X
Toluene	-	-	X	-	-	-	X	-	X	-	-	-	X
Xylene	-	-	-	-	-	-	X	-	X	-	-	-	X
Hexane	-	-	-	-	-	-	X	-	-	-	-	-	-
PAHs	-	-	X	-	-	-	X	-	-	-	-	0	X
Phenols	-	X	X	-	-	-	X	-	X	0	-	0	-
Hydrocarbons	-	-	-	-	X	-	-	-	-	-	-	-	-
Methane	-	-	-	-	X	-	-	-	-	-	-	-	-
Hydrogen Sulfide	X	-	-	-	X	C	X	X	X	-	C	X	c
Carbon Monoxide	CX	C	C	C	CX	C	X	C	-	-	C	X	X
Nitrogen Dioxide	-	-	-	-	-	-	-	-	-	-	-	-	X
Sulfur Dioxide	X	-	-	-	X	-	X	-	-	-	-	-	X
Ammonia	-	-	-	-	X	-	-	-	-	-	-	X	-
Combustible Gas	-	-	-	-	-	-	-	-	-	-	C	X	-
Total Particulates	0	-	X	-	-	-	X	-	X	-	X	0	X
Respirable Dust	-	-	-	-	-	-	-	-	-	-	-	0	-
Metal	0	-	-	0	-	-	-	-	-	-	-	0	-
Noise	0	-	X	-	0	X	X	X	X	-	X	-	-
Thermal Stress	-	-	X	-	-	-	-	-	-	-	X	0	X
Ionizing Radiation	-	-	-	-	0	-	X	-	-	-	-	-	-

X Periodic scheduled sampling

- No sampling

0 Sampling Completed, no further sampling planned.

C Continuous Monitoring

for gases found in the product gas stream (Table 9) [3,9,42]. Grab sampling was conducted on a set sampling schedule with fixed area sampling sites at only one facility [42]. At two other facilities the location and timing of samples depended on the judgment of the monitoring staff or on worker complaints [3,9]. This program did not provide proper evaluation of all potential contaminant classes that may have been present in the work environment. \* The other facility had an adequate baseline program, but did not provide followup monitoring in locations where the survey had found high levels of certain potentially hazardous chemicals [42].

Four facilities were developing monitoring programs; however, they were not implemented at the time of the survey [7,10,14,17]. The ongoing sampling activities were inadequate for evaluating worker exposures at these facilities.

#### B. MONITORING RESULTS REPORTED BY FACILITIES

Area sampling was performed by 14 facilities. Sample sites were either especially selected for each survey or were fixed sites. The specially selected sampling sites were based on the plant status at the time of sampling and on the contaminant being sampled. The fixed sites were chosen to give the best cross representation of the process area over the duration of the sampling program. Workers were selected for personal sampling on the basis of job class and probable exposure; they included field operators, maintenance workers, and laboratory technicians. Field operators spend most of their time in the process area monitoring equipment and, in some cases, performing maintenance activities. Maintenance workers may be exposed during the repair of process piping and equipment. Laboratory technicians are exposed to process materials while handling and analyzing process stream samples.

The sampling and analytical methods used at the 14 facilities follow NIOSH recommended procedures, where these procedures are appropriate [77]. The monitored agents and the appropriate NIOSH sampling/analytical methods are listed in Table 10. Additional details are available in the reports of the industrial hygiene studies [1,2].

Because of limited sampling, results are not adequate to evaluate conditions in most facilities, with two exceptions. At those facilities where a good data base has been developed, it was found that measured levels of the PAH contaminants monitored were in the parts-per-billion range (micrograms per cubic meter) [6,13]. The limited results from other facilities were in the same concentration range [3,4,6,7,9,14,17,42,43]. It should be noted that sampling and analytical methods for PAH compounds are experimental and not necessarily comparable, and that monitoring was most likely to have been performed during "ideal" process conditions. Thus, the exposure concentrations reported may not accurately define the actual or normal exposures, in all cases.

#### C. NIOSH-SPONSORED INDUSTRIAL HYGIENE SURVEY

Industrial hygiene surveys were conducted at five coal liquefaction and three coal gasification facilities under contracts sponsored by the Environmental Investigations Branch, Division of Respiratory Disease Studies, NIOSH [1,2].

TABLE 10

## Sampling and Analytical Methods for Hazardous Agent Monitoring

Agent	Sampling Method	Analytical Method
Benzene solubles (Coal tar pitch volatiles)	Fiberglass filter	Soxhlet extraction, gravimetric
	Fiberglass filter/silver membrane filter	Gravimetric P & CAM #
Benzene, toluene, xylene hexane	Charcoal tube	Gas chromatography P & CAM #127
Naphthalene	Charcoal tube	Gas chromatography P & CAM #
Benzo(a)pyrene, PNAs	Fiberglass filter or Fiberglass/silver membrane	Liquid chromatography P & CAM #251
Phenolics	Silica gel	Gas chromatography P & CAM #S167
	Midget impinger	Spectrophotometry P & CAM #
Hydrogen sulfide	Midget impinger	Spectrophotometry P & CAM #126
	Detector tube	---
	Continuous monitoring	---
Sulfur dioxide	Midget impinger	Spectrophotometry P & CAM #160
	Detector tube	---
Carbon monoxide	Direct-reading meter	---
	Detector tube	---
	Continuous monitoring	---
Hydrocarbon, methane, carbon dioxide, nitro- gen dioxide, ammonia	Detector tube	---
Oxygen	Direct-reading meter	---
Combustible gas	Direct-reading meter	---
	Continuous monitoring	---
Total particulate	Fiberglass filter	Gravimetric
	Polyvinyl chloride filter	Gravimetric
Respirable dust	Cyclone/Polyvinyl chloride filter	Gravimetric
Metals	Cellulose acetate filter	Atomic absorption P & CAM #
Noise	Sound level meter	---
	Dosimeter	---
Heat stress	WBGT	---
Ionizing radiation	Geiger counter	---
	Film badge	---

The coal liquefaction studies included donor solvent, catalytic hydrogenation, and noncatalytic hydrogenation processes. Three coal gasification facilities representing the three generic type processes (fixed-bed, fluidized-bed, and entrained-bed) were studied. Sampling and analysis methods used were usually NIOSH P & CAM methods [77]; PAHs were determined by methods developed by Dynamac Corp [78]. Direct reading instruments and detector tubes were also used.

Walk-through surveys, with limited sampling, were usually performed prior to the comprehensive surveys to screen for the following classes of compounds:

- Polynuclear aromatic hydrocarbons
- Aromatic amines
- Phenolics (aromatic alcohols)
- Simple aromatics (benzene, toluene, and xylene)
- Major aliphatic groups such as C<sub>1</sub>-C<sub>10</sub> hydrocarbons, ketones, thiols, and halogenated organics
- Trace metals (arsenic, beryllium, nickel, and cadmium)
- Toxic gases (CO, H<sub>2</sub>S, NO<sub>x</sub>, SO<sub>2</sub>).

Based on these screening results and on economic considerations, classes of compounds not observed or observed in low concentrations during the limited walk-through surveys were deleted from comprehensive surveys. Some surveys also had to be performed during less than ideal weather conditions; thus, some sampling methods have capture efficiencies that are in question. Therefore, the maximum exposure values presented in this series of studies may not be representative of actual or worst case conditions.

General observations of the industrial hygiene exposures in both coal gasification and liquefaction facilities are:

The simple aromatic compounds detected were usually less than 0.5 ppm for both area and personal sampling.

Aromatic amine concentrations did not exceed 0.5 ug/m<sup>3</sup> for either area or personal samples (the capture media was in question [3]).

Aromatic alcohols were essentially non-detectable in all samples.

PAH concentrations were highest in two generic type liquefaction facilities, Tables 11 and 12.

Generally, the maintenance workers and process operators who were required to open process streams received the highest airborne PAH exposures. The same trend was apparently evident for dermal exposure to tars and oils containing PAH. Personal exposures at several plants were higher than area samples. This is usually attributed to tasks requiring process stream opening or repair of piping/equipment.

The majority of airborne PAHs were 2-3 ring membered compounds. Wipe samples taken on tools, gloves, clothes, and environmental surfaces indicate that potential skin exposure is to compounds predominantly in the 4-5 ring class; some samples containing up to 7 ring PAHs. However, skin wipe samples were not taken.

TABLE 11

Eight Coal Conversion Facilities Ranked by  
Geometric Mean PAH Area Concentration

Plant	Number of Samples	Geometric Mean ( $\mu\text{g}/\text{m}^2$ )	95% Confidence Limit ( $\mu\text{g}/\text{m}^2$ )	
			Lower	Upper
Donor solvent liquefaction	34	133.8	65.8	271.2
Donor solvent liquefaction	12	50.6	38.9	65.8
Catalytic hydrogenation-liquefaction	27	34.8	19.7	61.2
Fixed-bed gasification	19	26.8	18.3	39.1
Noncatalytic hydrogenation-liquefaction	8	21.4	4.7	96.5
Noncatalytic hydrogenation-liquefaction	13	3.9	1.3	10.9
Fluidized-bed gasification	17	2.0	0.9	4.1
Entrained-bed gasification	13	0.2	0.1	0.5

TABLE 12

Eight Coal Conversion Facilities Ranked by  
Geometric Mean PAH Concentration for Field Operators

Plant	Number of Samples	Geometric Mean ( $\mu\text{g}/\text{m}^2$ )	95% Confidence Limit ( $\mu\text{g}/\text{m}^2$ )	
			Lower	Upper
Donor solvent liquefaction	17	96.9	52.7	178.2
Noncatalytic hydrogenation-liquefaction	13	35.8	17.6	73.0
Fixed-bed gasification	4	19.3	9.7	38.4
Catalytic hydrogenation-liquefaction	9	16.7	4.8	72.7
Fluidized-bed gasification	12	4.6	1.5	14.2
Noncatalytic hydrogenation-liquefaction	4	3.1	<0.2 <sup>a</sup>	257.8
Entrained-bed gasification	8	2.6	0.9	8.1
Donor solvent liquefaction	12	<0.2 <sup>a</sup>	<0.2 <sup>a</sup>	0.2

<sup>a</sup>Lowest limit of detection

## VII. WORKER TRAINING AND PERSONAL HYGIENE

Because the coal conversion industry is basically in the pilot plant stage, hazards are not yet well defined. Education and training can play an important role in worker protection by increasing worker awareness of the potential hazards. The presence of PAHs in the workplace enhances the importance of personal hygiene in this industry.

### A. TRAINING AND EDUCATION

In the development of a total health and safety program, most of the facilities in this study have not fully utilized worker training and education. In general, training activities at coal conversion plants need more emphasis on the potential hazards associated with liquefaction and gasification plants, in order to create an awareness of these hazards among those who work with them.

Four facilities have no formal training program for new hires or transfers. The worker is expected to learn the established work practices and what protective clothing and devices are available by reviewing the plant safety manual and other safety publications. This informal approach is contrary to good occupational health and safety practice, especially for potentially hazardous processes such as pilot scale coal conversion units. Two facilities have sought to supplement worker initiative by reviewing and highlighting selected work practices and protective clothing and equipment requirements at monthly safety meetings.

One of the gasification facilities holds formal 2-hour sessions for all new employees at the facility [3]. At these sessions, hazards within the facility are identified and safe work practices necessary to avert these hazards are demonstrated. This formal session ensures that the plant safety manual is reviewed; however, the plant has no provisions, such as administering written tests on the material, to determine if the new hires understand these requirements.

At three facilities, more effective training programs provide for informal, on-the-job training by having the new hire work with experienced personnel [4,14,42]. This step is formalized at four other facilities as a requirement in the plant operating manual [13,15,41,43]. Two other facilities have set a minimal training period [10,17]. At one facility it is 90 days for new hires and as-long-as-necessary for movement to a higher job level. The other facility provides a 3-day training session: the first day is spent familiarizing the new worker with the plant layout, the second day is set aside for a dry run while the plant is shutdown, and on the third day the worker practices with the plant in operation. This procedure is successful for a pilot plant, but would obviously need to be modified for a commercial unit.

Some form of respirator training is available at all operating facilities. The basic elements of these training programs include the types of respirators available, care and maintenance of respirators, how to wear respirators, and when respirators are required.

These basic programs have been supplemented with other provisions to increase the effectiveness of the program at a few facilities. Seven provide time for training sessions and safety meetings to demonstrate how to use and care for respirators and for hands-on practice with these respirators [4,6,13,14,15,41,43]. Qualitative fit-testing is a part of the training session of seven facilities [4,6,10,13,15,41,43]. Only one facility performs quantitative fit-testing, and this is only conducted every 3 years [42].

Respirator training is repeated annually at eight facilities for all employees who may use respirators [4,6,10,13,15,41,42,43]. Three of these facilities include certification as a part of the training program to provide a means of monitoring the training status of the worker [4,41,43]. Other facilities provide respirator retraining as a part of their safety meetings, but not on a fixed schedule [3,7,9,14,17].

Training programs at seven facilities [3,13,15,17,41,42,43] include hazard identification, first aid, and familiarization with plant health and safety protocols. Three facilities require that an examination be taken at the end of the educational program to determine worker comprehension of the lessons [13,15,41]. Continuing education is provided by periodic safety meetings held at these facilities.

#### B. PERSONAL HYGIENE

Basic personal hygiene practices specified at all facilities are:

- donning clean work clothing each shift.
- washing with soap and water before eating or using lavatory facilities,
- banning of food and drink in the process area, and
- prohibiting smoking and tobacco chewing in process areas, except for designated sections.

These provisions are designed, primarily, to contain coal-derived liquids within the process area, and to prevent ingestion and skin contact with these substances. These requirements are not mandatory at two facilities but are recommended by management, and workers at these facilities have generally followed these recommendations [4,6]. One facility recommends, but does not require, showering at the end of each shift [3].

The requirements for a change of clothing vary among the facilities. A single locker is provided at five facilities [3,6,7,9,43], and three facilities [4,17,42] provide each worker with two lockers to separate work apparel and equipment from street clothing.

At five other facilities a clean room/dirty room system has been adopted [10,13,14,15,16]. In this system, there is a physical separation (generally a shower facility) between the clean and dirty areas. Figure 11 illustrates a typical design used at a liquefaction facility [13]. In this system, a worker enters the clean room at the start of the shift, places his street clothes in the locker, and dons a clean set of work clothing. He then proceeds to the dirty area, picks up the necessary gear, including safety hat, safety glasses,

---Route to Work Station  
—Route from Work Station

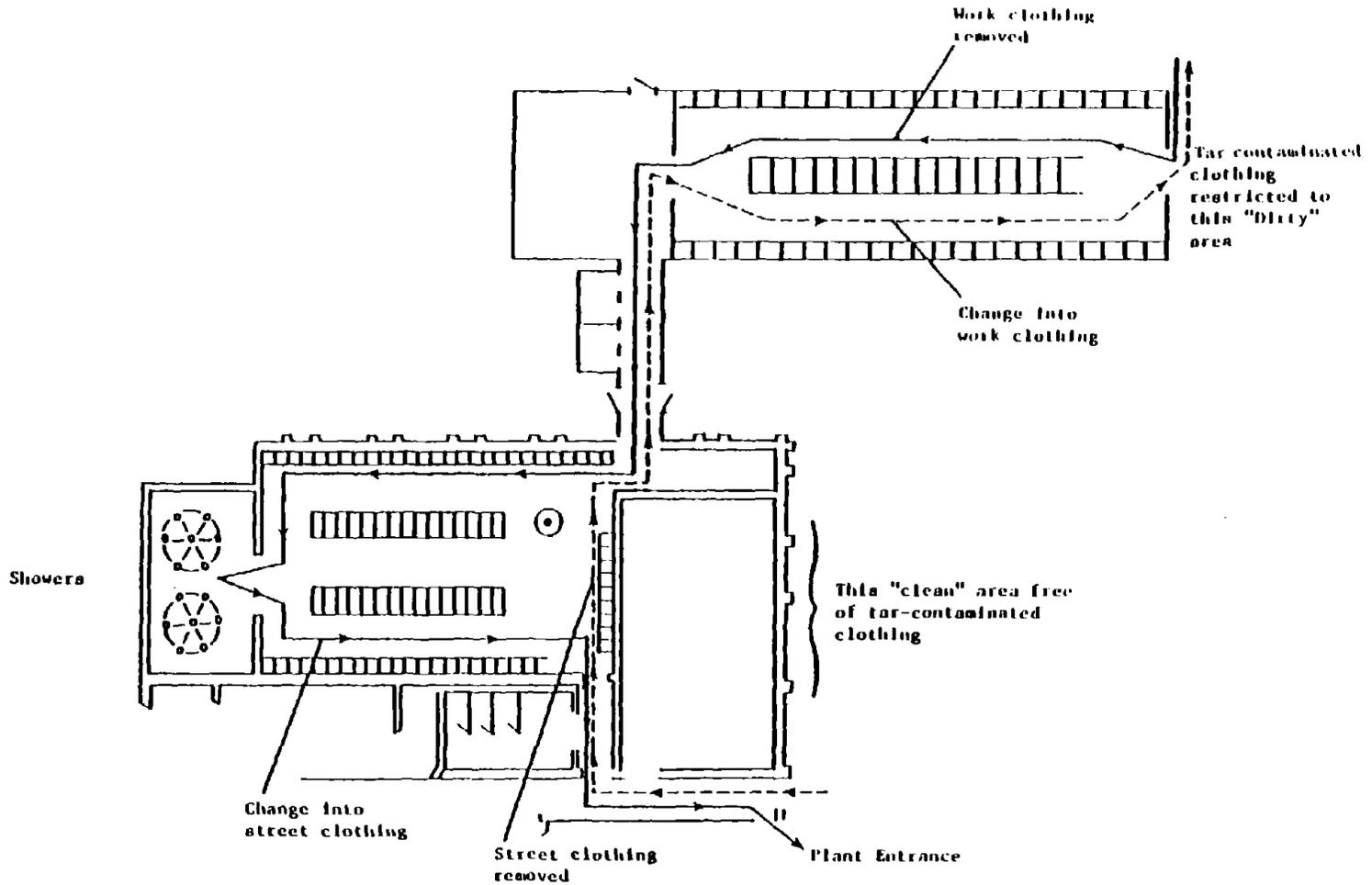


Figure 11. Locker/Change House

and work shoes, before entering the work area. At the end of the shift, the worker enters the dirty room, removes his protective gear and work uniform, places them in appropriate receptacles, showers, then proceeds to the clean room to don his street clothing. Work gear and protective equipment are kept in a locker. This system is effective in containing coal-derived liquids within the process area.

Nine facilities require a change of clothing each shift [4,7,10,13,14,15,16,17,42]. Of these, eight have a two-locker or a clean/dirty room setup. These nine facilities also provide the uniforms or coveralls and laundry service. The five other operating facilities do not require a change of clothing and do not provide work uniforms [3,6,9,41,43]. One of these facilities is a bench scale operation in which the process area is segregated into clean and regulated areas; the regulated areas contain coal-derived liquids [9]. Workers in the regulated areas must wear lab coats and these are removed prior to leaving the regulated areas. The plant believes that this system eliminates the need for a daily change of clothing. At another facility, workers use disposable coveralls in lieu of requiring a daily change of clothing [41].

Another provision observed at two facilities is to check for residual coal-tar contamination after showering by means of an ultraviolet light [9,13]. One plant has portable and wall-mounted units available which the worker can use to check for body contamination [13]. At the other facility, wall-mounted units are used only for inspection of the hands [9].

## VIII. MEDICAL SURVEILLANCE

Medical surveillance protects the health of employees by detecting incipient health problems. In addition, surveillance provides long-term health information on all workers which can be used to identify plant hazards requiring process or work practice modifications. The data and program should be reviewed by occupational health physicians annually for the several years, and at least every five years thereafter. Most occupational health programs include a pre-employment physical, annual checkups, and a termination physical. These vary from plant to plant and thus cannot be rigorously compared. However, some form of physical examination including blood tests and urinalyses is certainly necessary to assure the detection of health changes in workers.

Medical programs actually used in liquefaction and gasification facilities are summarized in Table 13. The only surveillance tool common to all facilities was the routine physical examination. At one facility, an annual examination was given only to people over the age of 45; younger personnel received an examination every two years. Preemployment physical examinations were given at 10 of the 14 facilities; termination physical examinations, at only one facility. One facility considered coal conversion unit employees to be temporary and corporate policy did not provide this service for temporary hires.

The absence of pre-employment, regular follow-up, and termination physical examinations may be attributed, in part, to the lack of autonomy of these coal conversion facilities. They are generally part of larger plants or companies, and workers are mainly transfers from other sectors of the organization or on a temporary basis. Under these circumstances pre-employment and termination physical examinations are likely to be handled at the overall plant level and not as part of the coal conversion facility program. These factors do not, however, justify an inadequate medical monitoring program. Coal conversion plant medical programs should be designed so that physical examinations and other medical services can specifically address the needs of the employees, based on the suspected toxic effects associated with these facilities.

Blood and urine samples were tested in almost half of the facilities, all of which are associated with liquefaction plants and gasification facilities that are tar producers. The most common services were x-rays, electrocardiograms, pulmonary function tests, audiograms, and blood chemistry tests. Pulmonary function tests were also used to determine the physical fitness of workers with respect to their ability to use respirators. Some facilities conducted medical history, work histories, and eye examinations.

Specialized medical tests to monitor the potential carcinogenic effects of coal-derived liquids were skin examinations and sputum and urine cytology. Skin examinations are the most commonly used tests because of the ease of the examination and because of the link between PAHs and skin cancer. In a skin examination, all blemishes, acne, and lesions are noted and recorded in the workers' medical files. Three facilities supplement this examination by color photographs. Examinations are annual, but three plants also have quarterly examinations by the plant nurse. Sputum and urine cytology are not as common because of the controversy associated with the interpretation of results. One facility has discontinued the tests because of this uncertainty.

TABLE 13.

## Comparison of Plant Medical Programs

PLANT	PROGRAM ELEMENTS				
	Annual Physical	Preemployment Physical	Termination Physical	Blood Count	Urinalysis
Noncatalytic Hydrogenation I	x	x	-	x	x
II	x	x	-	x	x
Donor Solvent I	x	x	-	-	-
II	x	x	-	x	x
Catalytic Hydrogenation	x	-	-	-	-
Fixed-Bed Gasification I	x	x	-	x	x
II	x	x	-	-	x
III	x	x	-	x	x
Entrained-Bed Gasification I	x	-	-	-	-
II	x	x	-	-	-
III	x	x	x	-	-
Fluidized-Bed Gasification	x	-	-	-	x
Molten-Salt Gasification	x	-	-	x	-
Lignite Liquefaction	x	x	-	x	x

## IX. RECOMMENDATIONS

An objective of occupational safety and health programs is to prevent or minimize worker exposures to hazardous conditions and toxic physical and chemical agents. Meeting this objective in the fledgling coal gasification and liquefaction industry poses a particular problem due to a number of technological uncertainties. Information gathered during this study of pilot and demonstration plants indicates that, due to the operating conditions and the materials handled, coal liquefaction and gasification facilities require frequent preventive and corrective maintenance. Both equipment malfunctions and human error cause gaseous discharges and liquid and solid particulate leaks and spills. Therefore, as the industry moves through the demonstration stage and into commercial status, it is essential that information on hazard control technologies be available for the formulation of occupational safety and health programs for this technology.

The earlier sections of this report summarize the approaches and solutions that have been developed to address problems encountered at a number of coal conversion process facilities. Recommendations for the prevention or reduction of worker exposure are presented in the present section according to the following classifications:

- Design and layout of process and equipment
- Selection of process equipment
- Materials of construction
- Operating and maintenance procedures
- Instrumentation
- Administrative measures
- Implementation of health and safety programs
- Research needs.

### A. DESIGN AND LAYOUT OF PROCESS AND EQUIPMENT

Frequently, modification of the design of the process or a particular piece of equipment can reduce or eliminate exposure from leaks and other uncontrolled discharges or reduce maintenance requirements. Some potential opportunities at the design stage include:

Plant layout should provide easy access to equipment with high maintenance requirements, such as slurry pumps, to reduce the time spent in the area by maintenance personnel. Where possible, such equipment should be located in areas having low levels of hazardous materials so that maintenance workers are not exposed to toxic substances from other sources. Spare pieces of critical equipment may be installed in parallel to provide continued production during preventative maintenance or repair.

Equipment should be designed to minimize noise; where high noise levels are expected, acoustical enclosures, isolation, or insulation should be considered during the design stage.

Vessels and lines should be designed to prevent accumulations of solids or liquids which will require manual clean-out. For example, cone or dished bottom vessels with drains located at the lowest point can often be drained or flushed to remove solids without worker entry.

Plant drainage systems (chemical sewers) should be designed as closed systems. They should be provided with clean-outs and with piping which leads waste discharges directly into the drain.

Process units open to the atmosphere (such as belt coolers or slurry tanks) should be enclosed and ventilated, if necessary, to carry dust, fumes, and gases to scrubbers and/or flares.

Gasifiers not requiring pokeholes are preferred. Alternatively, a means for effectively controlling the pokehole exhaust during the period it is open, such as steam venturis, should be incorporated.

Solvent deashing may be substituted for filtration or other mechanical separation techniques, eliminating some of the problems associated with filtering the liquefied coal/solids slurry, such as the exposure to filter aid materials during maintenance.

Flanges in pipes and vessels carrying high temperature gases should be welded, where possible, to prevent leaks due to warping.

## B. EQUIPMENT SELECTION

Considerations relevant to equipment selection include the following:

Sealless (canned) or diaphragm pumps may be substituted for standard pumps to eliminate leaking seals. Alternatively, a pressurized seal oil system may be effective in preventing leaks from mechanical seals.

Lines carrying heavy liquids or corrosive gases may be heated to reduce maintenance due to solidification and plugging or corrosion. Steam or thermal liquid tracing is preferable to electrical tracing to prevent possible overheating and fires.

Equipment selection criteria should include consideration of the potential for igniting flammable liquids and vapors.

## C. MATERIALS OF CONSTRUCTION

Materials of construction must be selected with care to provide low maintenance operation for extended periods of service. The highly corrosive and erosive nature of the products of coal conversion processes, especially at the

high temperatures and pressures and multi-phase flow characteristic of these technologies, cause rapid breakdown of commonly used materials. A great deal of research has been performed in this area [19,21-24, 26-31,33], but more is needed. Pumps, lockhoppers, seals, letdown valves, and piping are among the elements that are prone to failure under these conditions. At the time of the present study, proven materials did not exist for these types of components to support a commercial coal conversion industry which would operate with a frequency of maintenance which is typical of conventional petrochemical plants. This may be a limitation to the commercial viability of coal conversion technology. Much more work will be required to provide adequate materials of construction for coal conversion plants based on existing pilot processes.

#### D. PROCEDURES

The expected high frequency of leaks and repairs in coal conversion plants requires a strict adherence to established procedures to avoid situations which may result in unnecessary worker exposure to hazards. These include procedures for operation, maintenance, startup and shutdown, spill clean-up, equipment inspection and installation, and others. Plant operating procedures and maintenance schedules should be documented and adhered to; deviations from these procedures should be made only with appropriate supervisory or management approval.

Procedures should be developed to minimize potential hazards during plant startup, operation, shutdown, and during non-operating periods. Specific procedures such as the need for inert atmospheres, the need for flushing specific vessels and lines with solvents at shutdown, or the avoidance of coke formation during both operation and shutdown are important both in reducing maintenance and in avoiding the formation of potentially explosive atmospheres.

Certain pieces of equipment which are normally not used, but are needed during emergencies, should be inspected on a regular schedule. Examples are: pressure and temperature limiting controllers, failsafe devices, emergency fire fighting equipment, pressure relief valves, and gas sensing alarm systems.

Standard procedures for installing equipment are necessary. Pipe flanges, manway and vessel port covers, pumps, valves, and mechanical seals must be installed correctly and without damage to the sealing surfaces in order to produce effective seals.

Housekeeping procedures should address spill clean-up methods and responsibilities, decontamination of equipment prior to maintenance, worker protection through use of protective clothing and respirators, and separate clean and dirty change rooms. The use of steam cleaning or hydroblasting in combination with a detergent may be improved by prior application of an epoxy or other impervious coating on concrete flooring.

Craft-crossover, which permits operators to perform minor maintenance (such as adjusting leaking flanges and packing glands) immediately, may reduce the emission times. A sense of individual responsibility by line supervisors and production workers to the maintenance of a clean and safe workplace is an important and desirable factor.

#### E. INSTRUMENTATION

Instrumentation that is relevant to occupational safety and health includes devices to monitor the working environment, alarms, analytical instruments to measure chemical and physical parameters, and, to a lesser extent, some process control instrumentation. Several specific good practices for this equipment are as follows:

Several liquefaction pilot plants have area and personal hydrogen sulfide monitors which sound audible alarms located in areas subject to hydrogen sulfide emissions. Such monitors should be used routinely in high hazard areas with hydrogen sulfide. Similar systems to monitor other acutely toxic or dangerous species (such as carbon monoxide, hydrogen cyanide, and potentially explosive hydrocarbon/air mixtures) from both gasification and liquefaction processes should be considered. Generic monitoring for PAHs, such as through UV fluorescence or indicator gas techniques, should be pursued.

Nuclear, magnetic, ultrasonic, or other devices which do not directly contact the process materials should be considered for the measurement of process parameters, such as liquid levels, coal levels, gas and liquid flow rates, etc.

For those analyses which must be conducted in a laboratory, taps leading to sealed containers for sample collection should be used in order to minimize or eliminate discharge of coal-derived materials to the work environment and exposure of personnel to these materials.

Junction boxes of electronic instruments and other electrical equipment should be protected from corrosive atmospheres and should be designed for use in explosive atmospheres.

Instrument piping should be protected from plugging with particulates or other solids by purging with a suitable gas or liquid at appropriate times (such as prior to shut down). Also, good design, combined with proper preventive maintenance, can help avoid plugging.

#### F. ADMINISTRATIVE MEASURES

Management is responsible for the implementation of programs to assure the protection of worker health and safety and must comply with local, state, and federal regulations. Employers also must inform employees of potential hazards. Employees and employers share the responsibility for carrying out the programs adopted by the organization. Health and safety programs cannot succeed without cooperation between management and employees. Involving the

workers actively in planning and carrying out the program will encourage participation in the program. Workers are frequently an excellent source of information on hazards and potential corrective measures.

Specific recommendations to address these concerns include the following:

Management should demonstrate its support of the health and safety programs by exemplary behavior and by participating in program meetings and committees.

Direct worker participation in these programs should be encouraged by electing worker representatives to health and safety committees and policy setting groups.

Development of procedures for dealing with emergencies such as explosions and fires, burns, falls, and electrical shock should be included in the health and safety programs.

A job analysis should be conducted by the safety office on all activities being performed by the field operators, maintenance workers, and laboratory technicians. Work hazards should be identified and correct work practices should be developed to reduce the associated danger. Protective clothing and equipment requirements can then be developed to supplement the work practices. Excessive reliance on protective clothing and equipment instead of engineering measures and work practices should be avoided, especially in production or regular maintenance activities.

The work practice procedures and personal protective equipment requirements should be included in the safety and operation manuals.

Workers should be made aware of the interaction between personal lifestyle factors (such as smoking, stress, and exercise) and occupational effects in the promotion of an overall sense of personal health.

A good training and education program is needed in all coal conversion facilities. The program should include:

- hands-on training in the duties of the job in the presence of an experienced worker,

- informing the employee of the hazards of both the job and the plant as a whole,

- providing instruction on the type of protective clothing and equipment available, its use, care, and location,

- hands-on training in the use of protective equipment, especially respirators, and

- training in emergency procedures and the use of fire equipment.

These items should be continuously reinforced for all workers with special emphasis for new employees. When changes in operating parameters are made, the program should be appropriately modified.

## G. HEALTH AND SAFETY MONITORING PROGRAMS

Well designed health and safety environmental and medical monitoring programs are needed to assure adequate surveillance both of worker exposures and of the responses to these exposures. These programs include baseline monitoring, parameters to be measured, sample site selection, selection of workers, sampling schedule, and record keeping.

When environmental monitoring is done to determine the compounds present in the work area, it must be as representative as possible. While it is rarely technically or economically feasible to monitor every compound present, the selection of indicative compounds to be monitored must be broad enough to give a valid estimation of the hazards. Sampling site selection is also an important determinant of the reliability of the monitoring and must represent the actual workplace exposure. The selected sites should be chosen both with respect to the potential hazards and to the frequency of personnel being present. Similarly, the selection of workers participating in the personal monitoring program must give an accurate picture of worker population exposure. Sampling schedules need to be developed to provide the necessary degree of confidence with a reasonable expenditure of resources.

Baseline monitoring should include benzene solubles, PAHs, aromatic amines, phenolics, simple aromatics such as benzene and toluene, trace metals such as arsenic and nickel, respirable coal dust, hydrogen sulfide, carbon monoxide, sulfur dioxide, and nitrogen oxides.

Sampling sites should be selected to give representative contaminant levels for the entire facility; appropriate sites should be determined separately for each contaminant.

Special sampling should be conducted to characterize nonroutine situations such as process upsets, maintenance functions, and start-up or shutdown operations.

If exposures of individual workers are not routinely monitored, a job analysis may be used to select worker categories for the monitoring programs. Selection criteria should provide a cross section of exposure for each worker category in order to determine the time-weighted-average exposure for the group. Appropriate workers should also be selected to characterize nonroutine activities such as process stream sampling and maintenance of online equipment.

A sampling schedule for worker groups and area samples should include not only normal plant operations, but also process modifications as they occur.

Medical surveillance programs must provide adequate data to identify and evaluate changes in worker health brought about by exposure to materials in the workplace.

Medical surveillance programs should be as complete as possible and specifically designed for the selected worker groups. Competent medical advice should be obtained to ensure that appropriate measurements are included.

## H. RESEARCH NEEDS

Development of materials of construction which will provide for reliable service under the conditions encountered in coal conversion processes. \*

Research in this area is needed for the development of improved flange gasket materials, pump and agitator shafts and parts, totally enclosed equipment such as pumps, and loading or unloading systems which prevent the escape of material to the surroundings.

Instrumentation is needed which will measure process parameters reliably and without requiring intrusion of the closed system. Automatic inline sampling and analysis of gas streams by gas chromatography is used industrially. Development of equipment to perform these and other analytical techniques for coal conversion processes should be undertaken. Liquefaction pilot plants have experienced difficulties with inline probes for measurement of slurry viscosity and density. Currently, measurements require that samples be obtained and analyzed in the laboratory; closed loop sampling is an area for potential improvement. A means of determining the bed and ash height in gasifiers should be developed to eliminate the need for manually operated pokeholes.

Development of workplace detection, monitoring, and warning systems for PAHs both in the workplace atmosphere and surfaces, and on the workers skin.

Workplace concentrations of carbon monoxide, hydrogen sulfide, and several other gases are already routinely monitored in several coal conversion facilities. Continuous monitoring systems at potential emission sources of PAHs and/or other hazardous or indicator compounds could provide early warnings of releases of these materials. This could serve the dual purposes of reducing or eliminating the dependence on personal monitoring and of providing for the indication and location of minor leaks before they became major emissions.

Methods to monitor processing equipment in order to predict imminent equipment failure.

The abrasive nature of many of the process streams and the extremely high temperature and pressure encountered in coal conversion facilities present situations in which frequent equipment failure may occur. Strategically placed devices to periodically or continuously measure parameters such as pipe wall thickness could provide advance warning of failure such as pipe rupture and could thus prevent serious spills. Similarly, determining the amount of erosion in vessels and stills could indicate when repairs were needed without requiring shutdown for inspection. A means of determining the performance of flange gasketing material and pump and agitator seals could permit maintenance before serious leaks occurred. It would be desirable to develop non-intrusive and non-destructive measurement techniques for these purposes.

## Validation of optimum spill clean-up and decontamination procedures.

Spills and leaks are inevitable in any industrial facility. Viscous, tarry, semisolid, and solid residues are produced in many liquefaction and gasification facilities. These materials often contain toxic and/or carcinogenic compounds. Mechanical equipment and/or chemicals for cleaning up spills need to be developed to minimize exposures to these process materials. Standard procedures for decontaminating the area of the spill after clean-up, and equipment to carry out the decontamination should be developed. These procedures and/or equipment would also reduce secondary emissions into the workplace environment, thereby reducing worker exposure to toxic and/or carcinogenic materials.

Provision for long term epidemiological studies of coal conversion industry workers, including exposure measurements, identification of the population at risk, maintenance of exposure/employment records, and establishment of a registry of exposed workers.

Studies of worker health are being conducted at many of the existing facilities. These studies vary in their scope and objectives. A comprehensive study of workers in several different types of facilities, for example, liquefaction, fixed bed gasification, and fluid bed gasification, should be undertaken. This program should have as its objective the determination of long-term exposure to low levels of coal derived materials and attempt to relate any observed changes in worker health to specific constituents and levels of exposure. A comparison with a control group of workers in non-coal related occupations should be a part of this study.

Process or equipment changes to reduce or eliminate the production of toxic components.

One area which is frequently overlooked in industrial health research is the modification of the process, operating conditions, or equipment to suppress or eliminate the formation of hazardous materials. For example, in low temperature gasifiers, the tar is sometimes removed by a water quench and drummed for disposal. A process modification to collect the tar and continuously recycle it to the hot zone of the gasifier would eliminate handling and disposal. This technique would reduce potential worker exposure and also would permit recovery of the fuel value of the tar.

Another area for research is in catalysis. It may be possible to develop liquefaction catalysts which would selectively breakdown PAHs into simpler, less toxic compounds. Substitution of other catalysts in place of nickel and cobalt catalysts in gasification would eliminate the possibility of forming the carbonyl compounds of these two metals. As with other process changes, this would require both an analysis of the effects of proposed modification on capital and operating costs and an investigation of the potential health hazards of the substituted materials.

Development of information which will enable designers to anticipate and include appropriate hazard control measurements at the design stage in future full scale coal conversion plants.

In designing coal conversion units, architectural and engineering firms must comply with federal, state, and local regulations and construction codes. However, there is little in the open literature to guide them in the selection of equipment or other measures needed to protect worker health and safety. There is a great need for the development of a data base for empirical hazard control technology applications.

Standards or guidelines for allowable exposure levels for materials such as feedstocks, output streams, and process intermediates are needed. In addition, fundamental studies such as the relationship of environmental contamination with emission source parameters should be encouraged in order to develop predictive design methods to model expected emissions and exposures.

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## XI GLOSSARY

ACID GAS REMOVAL	The process of selectively removing hydrogen sulfide and carbon dioxide from a process stream.
ADMINISTRATIVE CONTROL	A method of controlling occupational exposures to hazardous agents by adjustment of work schedules and assignments to limit the amount of time employees may work in an area of potential exposure.
AMINE	Any of a class of organic compounds derived from ammonia by replacement of hydrogen by one or more univalent hydrocarbon radicals.
ANTHRACITE	"Hard" coal containing 86 - 98% fixed carbon and small percentages of volatile material, sulfur, and ash.
ASH	Inorganic matter contained in coal; the residue from the combustion of coal.
BITUMINOUS COAL	A broad class of coals containing 46 - 86% fixed carbon and 20 to 40 percent volatile matter.
BLOWDOWN	Periodic or continuous removal of water containing suspended solids and dissolved matter from a boiler or cooling tower to prevent accumulation of solids.
CERMET	A composite material made by mixing, pressing, and sintering metal with ceramic, e.g., chromium-alumina carbide, silicon-silicon carbide.
CHAR	The solid residue remaining after the removal of moisture and volatile matter from coal.
CLAUS PROCESS	An industrial method of obtaining elemental sulfur through the partial oxidation of gaseous hydrogen sulfide in air to yield sulfur and water.
COAL TAR	A gummy, black substance produced as a by-product of distillation of bituminous coal.
COKE	A strong cohesive, porous residue consisting of carbon and mineral matter formed when bituminous coal is heated in the absence or in a limited supply of air. Coke may also be formed by thermal decomposition of petroleum residues.
CSF	Consol Synthetic Fuel. A coal noncatalytic process used to liquify coal via extraction, using a recycled, hydrogenated donor solvent.

GLOSSARY (Continued)

DEA	Diethanolamine - Chemical absorbent used in an aqueous solution to remove acid gases from gas streams.
DESULFURIZATION	The removal of sulfur from hydrocarbon substances by chemical reactions and/or extraction .
EBULLATED BED	A fluidized bed in which an excess of gas is blown through the fluidized phase such that the system takes on the appearance of a boiling liquid.
EDS	Exxon Donor Solvent. A coal liquefaction process by which a separately hydrogenated solvent is recycled to exchange hydrogen with the coal for the hydrogenation step.
ENTRAINED BED	A bed in which solid particles are suspended in a moving fluid and are continuously carried over in the effluent stream.
FIXED BED	A bed in which the individual particles or granules of a solid (catalyst, absorbant) remain stationary in a chemical reactor.
FLUIDIZED BED	A bed of suitably sized solid particles through which a fluid or gas rises at a velocity high enough to buoy the particles and suspend them in the flowing fluid.
GAS LIQUOR	see Sour Water
GASIFICATION OF COAL	The conversion of coal into a gaseous fuel form by various high temperature and pressure chemical reactions with steam.
H-COAL	A catalytic hydroliquefaction process that converts high-sulfur coal to liquid fuels in an ebullation bed reactor.
HIGH-BTU GAS	A fuel gas having a heating value of about 1000 Btu per standard cubic foot.
HYDROGASIFICATION	Gasification that involves the direct reaction of fuels with hydrogen to optimize formation of methane.
HYDROGEN DONOR SOLVENT	Solvent, such as anthracene oil, tetralin, decalin, etc., which transfers hydrogen to coal constituents causing depolymerization and consequent conversion to liquid products of lower boiling range which are then dissolved by the solvent.

GLOSSARY (Continued)

LIGNITE	Brownish-black coal containing 65 - 72% carbon on a mineral-matter-free basis, with a rank between peat and sub-bituminous coal.
LIMITED ACCESS	An administrative control used to restrict a certain category of persons from a particular area. For example, visitors may be barred from an area or they must be accompanied by a trained worker.
LIQUEFACTION OF COAL	Conversion of coal to liquid hydrocarbons by reaction with hydrogen to form low molecular weight compounds.
LOCKHOPPER	A mechanical device that permits the introduction of a solid into an environment of different pressure.
LOW-BTU GAS	A fuel gas which contains nitrogen and has a heating value of up to 350 Btu per standard cubic foot.
MEA	Monoethanolamine - A chemical absorbent used to remove acid gases (see DEA).
MEDIUM-BTU GAS	A fuel gas having a heating value between about 350 and 1000 Btu per standard cubic foot.
MILL	General term applied to size reduction equipment used to grind and/or pulverize a material.
MOVING BED	A body of solids in which the particles or granules of a solid remain in mutual contact, but in which the entire bed moves in piston-like fashion.
PAH	See Polynuclear Aromatic Hydrocarbon
PEAT	An early stage of coal in which the remains of plants and ferns that have been preserved may be clearly seen. It contains a very high percentage of water.
POKEHOLE	An opening in the cover of a gasifier through which steel rods are inserted to determine the depth of the fire and ash beds.
POLYNUCLEAR AROMATIC HYDROCARBON (PAH)	Hydrocarbon compounds having a structure consisting of two or more benzene rings joined together.
PULVERIZE	Term applied to size-reduction operations where the product is generally finer than miners 150 mesh.
REGULATED AREA	Any area under the control of the employer where entry and exit is either restricted or controlled.

## GLOSSARY (Continued)

SHIFT CONVERSION	A process for the production of gas with a desired carbon monoxide content from crude gases derived from coal gasification. Carbon-monoxide-rich gas is catalytically reacted with steam to produce hydrogen and carbon dioxide; the latter is subsequently removed in a scrubber employing a suitable sorbent.
SNG	See Synthetic Natural Gas.
SOLVENT REFINED COAL (SRC)	A coal extract derived by solvent extraction. (see SRC-I and SRC-II).
SOUR GAS	A gas containing hydrogen sulfide.
SOUR WATER	The aqueous streams condensed from the coal conversion and processing areas containing hydrogen sulfide and other contaminants.
SRC-I	A solvent refined coal liquefaction process in which the primary product is a low ash, low sulfur, brittle solid fuel.
SRC-II	A modification of the SRC-I coal liquefaction process in which a low ash, low sulfur liquid fuel is produced by using slurry recycle and increased reaction severity.
SUB-BITUMINOUS COAL	Coal of intermediate rank (between lignite and bituminous); weathering and nonagglomerating coal having calorific values in the range of 8,300 to 13,000 Btu, calculated on a moist, mineral-matter-free basis.
SUBSTITUTE NATURAL GAS	See Synthetic Natural Gas
SYNTHESIS GAS	A mixture of hydrogen and carbon monoxide which can be reacted to yield a hydrocarbon.
SYNTHETIC NATURAL GAS	Substitute natural gas; a manufactured gaseous fuel generally produced from naphtha or coal that contains 95 to 98% methane and has an energy content of 980 to 1,035 Btu/scf (about the same as that of natural gas).
TAIL GAS	A gas issuing from a gas-treatment unit which may be recycled to the process or exhausted.
TAR	A dark brown or black, viscous, combustible liquid formed by the destructive distillation of coal.
WATER GAS SHIFT	The reaction between water vapor and carbon monoxide to produce hydrogen and carbon dioxide or the reverse.

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