To compete economically with existing sulfur processes, the sorbent durability must be increased and allow approximately for 100 sorption-regeneration cycles. At the same time, the sulfur loading in the product gas must be lowered through in-bed sulfur capture or gasification of low-sulfur coals. However, the process offers the potential advantages of increasing overall energy-recovery efficiency through the treatment of process gas with minimum prior cooling.

and a set of the set of the set

(、

· · · · · · · · · ·

* **

Limestone and dolomite have been used for desulfurization of process gases and the absorption of sulfur in the gasification reactor. In the mid-1970s, extensive fundamental research was conducted on the reaction kinetics and equilibria of these sorbents with reduced sulfur compounds.⁵ These data define the absorption and desorption reactions of sulfur compounds, which formed the basis for sulfur control in the CO, Acceptor Process. The pilot-scale tests for in-bed desulfurization of the KRW fluidized-bed gasification reactor have shown similar behavior. These materials are inexpensive and may be disposed of economically with the ash residues from the gasification process, which is an essential characteristeric for in-bed desulfurization sorbents. Limestone- or dolomite-based solid sorbent processes have the following advantages: (i) readily available, inexpensive sorbent materials; (ii) potential for once-through use of sorbent with disposal in combination with gasification ash-residues; (iii) tolerance of product-gas particulate loadings; (iv) potential for tar and ammonia cracking; (v) reasonable operating pressure drops; and (vi) easily integrated in-bed desulfurization and product-gas_desulfurization using the same sorbent material. However, the use of these materials has not been demonstrated for gasification process-gas cleanup at the commercial scale and, therefore, the following uncertainties remain: (i) sorption capacity of the sorbents at various gasification-reactor conditions and for various product-gas compositions, temperatures and pressures: (ii) disposal of solids with high concentrations of sulfides, which may oxidize to soluble or be released as sulfide gases; (iii) impact of sorbent additions on operations of the gasifier reactors; and (iv) removal of adequate product-gas nitrogen (primarily as ammonia) to meet limitations for combustion emissions.

In summary, the principal advantages of applications of solid-sorbent technologies to desulfurization of gasification product-gases are (i) reductions of gas cooling requirements and (ii) the potential to

eliminate the requirement for sulfur recovery. Reduction of gas cooling requirements will not only reduce capital investment but will also enhance significantly the overall process-energy efficiency, provided the end-use process utilizes the thermal energy of higher temperature gases. Elimination of sulfur recovery will reduce capital investment and operating costs and simplify the solids-handling and disposal operation if the sorbent can be disposed of together with the gasification ash residues.

8.5-2. Sulfur Redox Processes

Sulfur-redox processes convert sulfides to elemental sulfur through the use of oxidizing agents.⁶ In general, these processes are based on the sequential occurrence of the following three reaction steps: (i) absorption of gaseous sulfur compounds in the process solution (which is usually alkaline); (ii) oxidation of dissolved HS- to elemental sulfur by an oxidizing agent; and (iii) regeneration of the oxidizing agent.

The multiplicity of potential sulfur-oxidation states is responsible for the occurrence of extremely complex chemistry in the operation of these processes, since a wide variety of side reactions and interactions with contaminant components may occur. The operating history of sulfur-redox processes during commercial applications has been varied, but the difficulties have generally been directly related to the complexity of the gas composition being treated.⁷ Process advantages have led to their continued selection in proposed designs for gasification facilities⁸ and, therefore, further development to exploit these advantages is warranted.

Advantages of the redox processes include: (i) acid-gas removal and sulfur recovery in a single process unit, thereby eliminating one process unit; (ii) high H_2S collection efficiency, with a high selectivity for H_2S over CO_2 ; (iii) wide tolerance for inlet sulfur loading without loss of collection efficiency; and (iv) low operating and capital costs compared to use of the Claus reactor for sulfur recovery.⁹

Sulfur-redox processes depend on the successful control of sulfur-solution chemistry for reliable process design and operation. For commercially applied processes, both uncertainties of the design basis and difficulties with operational control have contributed to application problems. Uncertainties associated with sulfur-redox processes include the following: (i) little detailed information is available on process chemistry and both the equilibrium and kinetic data are insufficient to develop detailed design relationships; (ii) the complex chemistry and potential for side reactions and reactions with contaminants result in low contaminant tolerance in the inlet gas; (iii) the degradation of reagents due to incomplete regeneration and chemical and biological activity leads to higher than expected reagent use; (iv) contaminants in the inlet gas lead to decreased sulfur purity; and (v) many potential applications in the gasification industry would benefit greatly from pressurized operation, which has not yet been demonstrated. and the second s

;

(

;

ł

s r k

1.2.2.1.

.....

¥

In summary, the primary advantages of the sulfur-redox processes for gas-clean in coal-gasification are elimination of a sulfur-recovery unit, wide tolerance for varying inlet sulfur loadings, and reduced capital and operation costs compared to other sulfur-recovery processes.

References

- F. L. Robson and W. A. Blecher, "Assessment of Fuel-Gas-Cleanup Systems, Final Report," DE81025927, DOE/MC/12050-149, United Technologies Research Center, East Hartford, CT (November 1980).
- S. S. Penner et al., "Assessment of Long-Term Research Needs for Coal-Gasification Technologies," DOE/ER-78-C-01-6335, MTR-79W00160. The Mitre Corporation, McLean, VA (April 1979).
- 3. R. D. Parekh, "Handbook of Gasifiers and Gas-Treatment Systems," DE83004846, DOE/ET/10159-T24, UOP/SDC, McLean, VA (September 1982).
- Science Applications, Inc., "Coal Gas Desulfurization at High Temperatures, Status of METC Investigations," DOE/MC/16545-1666; DE85003382, Morgantown, WV (October 1984).
- G. P. Curran et al., "High Temperature Desulfurization of Low-Btu Gas," EPA 68-02-1333, 600/7-77-031, Consolidated Coal Company, Library, PA (April 1977).
- C. N. Sawyer and P. L. McCarty, <u>Chemistry for Environmental</u> <u>Engineering</u>, McGraw-Hill Book Company, New York, NY (1978).

- "Hydrogen Sulfide Removal," Chem. Eng. News 49(38), 48 September 13, 1971).
- M. S. Edwards, "H₂S Removal Processes for Low-Btu Coal Gas," ORNL/TM-6077, Oak Ridge National Laboratory, Oak Ridge, TN (January 1979).
- P. Grancher, Society Nationale Elf Aquitaine, Pau France, "Advances in Claus Technology. Part 2: Improvements in Industrial Units and Operating Methods," Hydrocarbon Processing <u>57</u>, 247 (1978).

APPENDIX: SLAG FOR IN-BED SULFUR REMOVAL*

The following sulfur-dissolution process occurs in ferroussilicate slags near 1300°C, provided the oxygen partial pressure (p_{0_2}) is less than 10^{-5} atm and SO₂ is not produced:

$$\frac{1}{2} = \frac{1}{2} = (8A-1)$$

$$\frac{1}{2} = \frac{1}{2} = \frac{1}{$$

The equilibrium constant for this process is

$$K_{p} = (p_{0_{2}}/p_{S_{2}})^{\frac{1}{2}} (p_{S} = /p_{0}^{=}),$$
 (8A-2)

and the and the and the state

(* · · · · ·

and a second second

where the ratio $p_S = /p_0$ is constant for ionized species as long as they exist. Hence,

$$K'_{p} = K_{p}(p_{0} = /p_{S}) (p_{0} / p_{S})^{\frac{1}{2}}$$
 (8A-3)

is a function of temperature only. Multiplying by (%S) dissolved and defining the sulfide capacity as

$$C_{S} \equiv K'_{p}(\%S) = K_{p}(p_{0}=/p_{S}=)(\%S) = (p_{0}_{2}/p_{S}_{2})^{\frac{1}{2}}(\%S),$$
 (8A-4)

it follows that

$$(\%S) = C_{S}(p_{S_{2}}/p_{0_{2}})^{\frac{1}{2}}$$
 (8A-5)

Thermodynamic analyses lead to the conclusion that

$$\log C_{\rm S} / 2 (1/T) = 8,190 \ {\rm K}.$$

For $10^{-5} < p_{0_2}$, atm < 10^{-3} , the sulfate or pyrosulfate may form according to the reactions

 $SO_2(g) + \frac{1}{2}O_2(g) + 0^- \longrightarrow SO_4^-$ (8A-6)

and

$$2SO_2(g) + O_2(g) + 0^{-} \longrightarrow S_2O_7^{-}$$
. (8A-7)

^{*} This section has been abstracted from a presentation made by J. F. Elliott (M.I.T.) at the Fourth Technical Meeting of the COGARN Working Group (May 23, 1986).

The sulfide capacity C_S is seen to depend on the equilibrium constant K_p , the ratio of O^{-} to S^{-} activities in the slag, and the %S dissolved. It is obtained in practice by measuring PO_2/P_{S_2} and %S. Sulfide capacities are reproduced in Fig. 8A-1 for a number basic slags as a function of mole fraction of base or lime.



Fig. 8A-1. Sulfide capacities ${\rm C}_{\rm S}$ of some simple slags.

As a practical matter, under the most favorable conditions of low oxygen and high sulfur pressures, even the most basic slags will contain only a few wt% of S. Sulfur removal from hot gases is most effective when a separate oxysulfide phase forms in addition to the slag. The oxysulfide phase may be the liquid phase in the Fe-O-S system (Fig. 8A-2), or it may be solid calcium sulfide (CaS). The equilibrium oxygen and sulfur pressures at which the liquid phase in the Fe-O-S system is stable at 1300°C is shown by the stability diagram for the phase in Fig. 8A-3. On the low sulfur-pressure side, the phase may be saturated with respect to metallic iron, FeO(s) or magnetite (Fe₃O₄). The oxygen pressures for equilibrium between FeO, CO(g) and CO₂(g) at several temperatures of interest are shown in Table 8A-1.

10

۶. در

, ,

· · · · · · · · ·

It is seen that, for coal-gasification systems, good desulfurization can be achieved with the formation of the oxysulfide or sulfide phase, but not through the action of the slag phase alone. Desulfurization in coal-combustion systems by way of the slag that may be formed may not be practical, particularly if the slag is in equilibrium with the oxygen potential of the combustion gases.



Fig. 8A-2. The 1300°C isotherm of the Fe-O-S system; "FeO" denotes the lack of stoichiometry in the phase.



Fig 8A-3. Stability diagram of the Fe-O-S system at 1300°C; "FeO" denotes the lack of stoichiometry in the mixture.

°C	°F	p ₀₂ , atm	_{₽CO} / _{₽CO2}
800	1475	$10^{-19.5}$	1.8
1000	1830	$10^{-15.5}$	2.6
1200	2160	$10^{-12.5}$	3.0
1400	2550	10^{-10}	3.3

Table 8A-1.Equilibrium oxygen partial pressures when the reaction $FeO + CO = CO_2 + Fe$ occurs, coupled with $CO + \frac{1}{2}O_2 = CO_2$.

The preceding comments indicate the importance of studying phase equilibria in coal slags and the need to perform quantitative work in this field in order to make useful predictions or correlations about the extent of sulfur dissolution in coal slags as functions of lime addition under equilibrium conditions. The extent to which equilibrium conditions are limiting practical system performance remains to be evaluated.



CHAPTER 9: ENVIRONMENTAL ISSUES*

9.1. Introduction

We present an overview of technical and regulatory issues affecting the environmental control of coal-gasification processes and discuss future regulatory directions and their implications for coal-gasification research. We review recent data characterizing emissions from various types of gasifiers and the methods presently available for the control of gaseous, liquid and solid contaminants. Key research needs are suggested which relate to meeting current and future environmental requirements at minimum cost.

`. ~.

9.2. Overview of US Regulatory Policy

9.2-1. Trends in Environmental Regulation

Concern over environmental quality in the US has been at the forefront of national attention since the early 1970s, when Congress enacted sweeping new laws related to air- and water-pollution control. Since that time, environmental regulations have continued to grow more complex and comprehensive, having profound impacts on a wide variety of industrial and energy-conversion processes.

Figure 9.2-1 graphically depicts the long-term trend in US environmental regulation over the last century.¹ It shows the total number of federal laws related to environmental protection up to the present date. The dramatic increase in the last two decades underscores the now

* This chapter has been written by Edward S. Rubin.

well-accepted fact that environmental regulations play a critical role in determining the viability of technological systems such as coal gasification. Recent trends suggest that environmental constraints are



Fig. 9.2-1. US laws on environmental protection (Ref. 1).

likely to grow more important over time and must thus be factored carefully into research development planning for advanced energy-conversion technologies. The major elements of current regulatory policy affecting coal gasification are briefly reviewed in Sec. 9.2-2, followed by a discussion of future regulatory directions and their implications.

9.2-2. Elements of Current Policy

Table 9.2-1 summarizes some of the key elements of environmental regulatory policy affecting coal-gasification plants. These regulations

fall into two general categories: (i) standards defining acceptable environmental quality and (ii) standards limiting the discharge of specific substances to the environment from specified sources. It is the latter type of standards which most directly affect the design and cost of coalgasification systems, though in many cases environmental quality standards also play a major role, particularly in plant siting.

k

i.

; '

: :

9.2-2A. Air Pollution Control

While air-pollution-control requirements have long been part of the regulatory landscape, the Federal Clean Air Act Amendments of 1970 brought air-pollution control to the forefront of national efforts to insure a clean and healthful environment. The newly established US Environmental Protection Agency (EPA) was required by the Act to promulgate primary national ambient air-quality standards (AAQS) to protect human health and secondary standards to protect human welfare. The latter category encompassed the effects of air pollution on materials, vegetation, visibility, animal life, etc. EPA's responsibility also included a mandate to insure the "non-degradation" of air whose quality was better than National standards (including pristine areas such as National parks and forests). The air pollutants initially regulated under the Clean Air Act included SO2, total suspended particulates (TSP), NO₂, CO, and photochemical oxidants. Since oxidants are produced indirectly, guidelines for non-methane HCs were also established. More recently, lead has been added to the list of criteria pollutants. Table 9.2-2 summarizes these standards.

To achieve ambient air-quality standards, state and local authorities were directed to promulgate appropriate emissions standards, subject to approval by EPA. The right was reserved to state and local authorities to implement ambient air-quality standards more stringent than the National standards and to regulate pollutants not covered by Federal standards. State emission limits for individual sources of air pollution typically specify a maximum allowable discharge rate and/or concentration of each regulated pollutant. In some cases, specific control methods for limiting pollutant discharges are specified.

The Federal role in the direct regulation of emissions is limited by the Clean Air Act to specific categories of new sources, including new

Table 9.2-1. Elements of environmental regulatory policy affecting coal-gasification plants.

Air Pollution Control

National Ambient Air Quality Standards (Primary, Secondary, Nondegradation) Federal New Source Performance Standards

National Emission Standards for Hazardous Air Pollutants

State and Local Standards (Air Quality, Emission Limits, Control Methods)

Water Pollution Control

Federal Safe Drinking Water Standards

Federal New Source Performance Standards

National Clean Water Act

Toxic and Hazardous Waste Regulations

State and Local Standards (Stream Quality, Effluent Limits, Treatment Methods)

Solid Waste Control

Federal Toxic and Hazardous Waste Regulations

State and Local Standards (Classification, Disposal Methods)

Pollutant	Primary Standards	Averaging Time	Secondary Standards		
со	9 ppm 35 ppm	8-hr ^a 1-hr ^a	None		
Lead	1.5 µg/m ³	Quarterly average	The same as the primary		
NO2	0.053 ppm	Annual (arithmetic mean)	The same as the primary		
Particulate matter ^b (TSP)	75 μg/m ³ 260 μg/m ³	Annual (geometric mean) 24-hr ^a	60 μg/m ³ c 150 μg/m ³		
Ozone	0.12 ppm	1-hr ^d	The same as the primary		
Sulfur oxides	0.03 ppm 0.14 ppm	Annual (arithmetic mean) 24-hr ^a 3-hr ^a	- - 0.5 ppm		

Table 9. 2-2. National ambient air-quality standards; codified at 40 CFR Part 50.

^aNot to be exceeded more than once per year.

^bChanges to the TSP standard were proposed in the Federal Register (March 20, 1984). The notice proposed changing the indicator from TSP to particles smaller than 10 μ m. Ranges of 24-hr standards of 150-250 μ g/m³ and annual standards of 50-65 μ g/m³ were proposed. An annual secondary TSP standard in the range of 70-90 μ g/m³ was also proposed.

^cGuide to achieving the 24-hr standard.

^dThe standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is equal to or less than 1.

automobiles and classes of new stationary sources of emissions. The latter include specified industrial processes judged by EPA to represent major potential sources of air pollution. Currently, they include approximately 60 sources, including fossil-fuel-fired steam generators, petroleum refineries, chemical plants, and coal- carbonization (coking) plants, but not coal-gasification facilities. The 1970 Clean Air Act specified that Federal New Sources Performance Standards (NSPS) for designated processes should require the use of "best adequately demonstrated technology," taking into account cost and other factors. In practice, NSPS requirements have come to represent the nominal design standard for new facilities. **** · · · ·

and the state of the second second

۰*.**

/ ^ ^ / / へんし

51 -51 -

1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.

:

By requiring that NSPS limits reflect the technological ability to reduce emissions, Congress put into place a dynamic constraint that is independent of ambient air-quality considerations, except in cases where the latter require emission controls more stringent than NSPS requirements. Table 9.2-3 illustrates the impact by showing recent changes in pollutant-emissions limits for coal-fired power plants. Standards for SO₂, NO_x and TSP all have become more stringent over time in response to technological improvements. As an indication of current trends, standards applicable to the Cool Water coal-gasification plant in California are also shown. The data suggest the potential for further tightening of Federal NSPS requirements, especially for NO_x emissions, which may be reduced by an order of magnitude with currently commercial technology.

The list of air pollutants regulated at the federal level has also been expanded over time to include chemical species designated as hazardous. Pollutants currently regulated or proposed to be regulated by National Emission Standards for Hazardous Pollutants (NESHAP) are shown in

| Pollutant | Pre-
NSPS | 1971
NSPS | 1978
NSPS | Cool Water
(1984) |
|-----------------|--------------|--------------|---------------------------------|---------------------------------|
| TSP | ~0.2 | 0.1 | 0.03 | 0.03 |
| so ₂ | None | 1.2 | ~0.1-1.2
(70-90%
removal) | 0.04-0.4
(95-97%
removal) |
| NO _x | None | 0.7 | 0.5-0.6 | 0.065 |

Table 9.2-3. Trend in air-pollution emission standards for new coal-fired power plants (lbs/10⁶ Btu).

Table 9.2-4. A much larger number of organic and inorganic chemicals have been identified as being potentially hazardous or toxic, of which about 25 are under study by EPA as part of their current commitment. New approaches involving risk assessment and risk management are being used to guide the development of regulatory priorities and standards at the Federal level.

While the potential for Federal regulation of coal-gasification plants has been extensively studied, no regulations have yet been proposed since the industry has yet to materialize. In the meanwhile, state and local regulations will determine allowable emission limits at coal-gasification facilities.² Many states are now also moving to develop toxic air programs that may have implications for coal-gasification plants in the future.

9.2.2B. Water-Pollution Control

Current regulatory policy for water pollutants bears a number of similarities to air-pollution control in that standards apply both to water quality and effluent discharges, with the federal role in the latter area limited to specified categories of new sources. In contrast to uniform National standards of acceptable air quality, water-quality standards are determined by individual states; thus, it is not at all uncommon to find different states setting different limits for a given pollutant on the same river. The Federal Water Pollution Control Act Amendments of 1972 aimed to "restore and maintain the chemical, physical, and biological integrity of the nation's waters," establishing the "national goal that the discharge of pollutants into the navigable waters be eliminated by 1985." Thus, the notion of "zero discharge" is imbedded in current Federal legislation. Furthermore, the 1972 Act established a National goal of having water quality which provides for the protection and propagation of fish, shellfish, and wildlife, while also providing for recreation in and on the water. Toward this end, states individually set their own receiving water-quality standards, subject to EPA approval. There are also general water-quality criteria designed to protect the water uses of streams. These limits typically refer to the elimination of floating solids, films, scums, bottom deposits, and objectionable odors. States also set specific limits for particular pollutants, e.g., all states typically set limits on pH, temperature, and dissolved oxygen (though, as noted earlier, the values of these limits may

differ from state to state).

Effluent discharge limitations generally reflect technological means of control and often are only loosely related (if at all) to water-quality standards. Thus, concepts such as "best practicable technology currently available" and "best available technology economically achievable" provide the guidelines for limiting specified water pollutants from new sources subject to Federal regulation and also guide the setting of many state and local standards. Federal NSPS do not currently cover coal-gasification facilities, so that waste-water effluents from such plants are subject only to state and local regulatory requirements which vary across the country.

Other elements of current regulatory policy in the water area are the US Public Health Service Drinking Water Standards. While these do not impact coal-gasification facilities directly, they do have an indirect effect in that some of these standards are used as criteria for determining the toxicity of leachable materials from solid wastes, including coal-gasification wastes. Wastes found to be hazardous require special handling.

| Promulgated | For the oming [†] |
|---------------------|----------------------------|
| Asbestos | Butadiene |
| Beryllium | Carbon tetrachloride |
| Mercury | Cadmium |
| Vinyl chloride | Chromium |
| Coke-oven emissions | Chloroform |
| Benzene | Ethylene oxide |
| Inorganic arsenic | Ethylene dichloride |
| Fugitive volatiles | Methylene chloride |
| | Perchloroethylene |
| | Trichloroethylene |

Table 9.2-4. Pollutants subject to national emission standards for hazardous air pollutants.

to when we read

11

;

[†]EPA Notice of Intent to propose standards issued in 1985; promulgation is expected in 1988.

9.2-2C. Solid Waste Control

Important Federal legislation regarding the handling and disposal of solid wastes has come along only in the last decade in the form of the 1976 Toxic Substances Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA). A principal concern of this legislation is the potential for releasing hazardous or toxic chemical substances into surface or ground water systems as a result of runoff or chemical leaching through soils. To a large extent, the focus of this concern has been wastes from various chemical and industrial processes (as opposed to those from coal-conversion processing). Nonetheless, as air and water pollution regulations have prohibited or minimized the release of coal-related pollutants to the water and air, their presence in solid wastes has grown in significance.

The designation of wastes as either hazardous or non-hazardous under RCRA is perhaps the most critical factor affecting coal-gasification processes. At the present time, EPA regulations treat high-volume wastes from coal combustion at electric power plants as a special category exempt from the procedures for determining toxicity on a case-by-case basis. Limited testing of wastes from coal-gasification plants shows characteristics similar to those from conventional coal combustion, though coal-gasification plant wastes are not currently exempt from RCRA. Wastes found to be hazardous according to EPA criteria must be handled and disposed of in special disposal sites, adding considerabley to the complexity and cost of disposal. These regulations are still developing and could affect coal-gasification facilities in the future. In addition, state and local regulations also apply, which may be more stringent than Federal regulations or guidelines for waste disposal.

9.2-3. Future Regulatory Directions

The clear trend toward increasingly stringent regulation of emissions to air, water and land has significant implications for the development of coal-gasification processes. In particular, the following regulatory directions are likely to be of special importance: (i) New Source Performance Standards for conventional pollutants (e.g., SO₂, NO₂, TSP) will continue to become more stringent as better technology becomes available to reduce emissions below currently achievable levels. (ii) Concern over hazardous and toxic substances is rapidly expanding the list of pollutants of concern to include many organic species and trace elements not heretofore regulated or measured (or, in some cases, measurable). This is a multi-media problem, affecting air pollutants, water pollutants and solid wastes. (iii) The policy of zero discharge of waste-water contaminants will continue to play an important role in the design and siting of coal-gasification facilities. Indirectly, it will also increase the severity of solid-waste disposal-problems. (iv) Regulations regarding the handling and disposal of solid wastes will continue to grow in importance. For example, regulations recently proposed by EPA include a modification of the procedure used to determine leachate toxicity, adding organics and other elements to the test criteria. The current exemption of coal ash and slag as non-hazardous under RCRA would also be removed. These changes would introduce a high degree of uncertainty that coal-gasification wastes could consistently be classified as non-hazardous.

All of these items have implications for coal-gasification research needs. Recommended research to address current environmental issues and anticipate new ones in the future are discussed at the end of this chapter, following a review of recent characterization studies and current methods of environmental control. ¢

 \mathbb{C}^{*}

4." , };

ł

;

9.3. Environmental Emissions from Coal Gasification

Table 9.3-1 summarizes some of the potential pollutants associated with coal-gasification plants. Gasification plants potentially constitute a major source of water pollutants, in addition to air pollutants and solid wastes. Because coal is chemically complex, gasification reactions are capable of directly or indirectly producing a wide range of organic and inorganic compounds whose presence may constitute an environmental problem or hazard.

9.3-1. Process Overview

To highlight the nature and sources of environmental emissions of concern, we show in Fig. 9.3-1 a typical configuration for a plant producing low- or medium-BTU gas (in this case for electric power generation).^{*} Coal may first go through a preparation or pre-treatment step, which may give rise to small quantities of particulate matter and (if mild heating is involved) sulfur dioxide emissions. This step is typically well controlled.

| Air | Water | Land |
|------------------|---------------------------------|-----------------|
| so ₂ | NH ₃ | Slags |
| NOx | ФОН | Ash slurries |
| TSP | CN | Fines |
| HCs | SCN | Dry residues |
| CO | BOD | Waste treatment |
| H ₂ S | COD | Sludges |
| COS | TOC | Spent catalyst |
| NH ₃ | TSS | |
| HCI | TDS | |
| HCN | pH | |
| Metals | H ₂ S | |
| Organics | S ₂ O ₃ = | |
| | so ₄ = | |
| | CI | |
| | F | |
| | Alkalinity | |
| | Oils/grease | |
| ←−−−−− Ha | zardous or toxic substan | ces> |

Table 9.3-1. Some potential pollutants from coal-gasification plants.

^{*} Power generation represents an environmental worst case since the coalgas products are burned, releasing pollutants into the environment. Other applications, such as chemical manufacture or high-BTU gas production, involve converting or upgrading the product into a useful form, which reduces the environmental consequences at the gasification facility.



いたいことの

÷.

The state of the second

トニト・

;

 $\sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j$

1.5

5.1.1

í.

Fig. 9.3-1. Typical environmental control and emissions for coal-gasification processes.

Emissions from the gasifier itself consist primarily of slag or ash, which is quenched or sluiced with water upon removal. After exiting the gasifier, the gas products are typically cooled by water quenching (or other form of cooling) to remove particulate matter and gas-phase condensables. This procedure gives rise to the principal wastewater stream associated with coal-gasification plants. The product gas is next routed to an acid-gas removal-system where sulfur (predominantly in the form of H_2S) is removed. If the product gas is then used for power generation, it is combusted, giving rise to conventional air-pollutant emissions (primarily SO_2 and NO_v).

Other sources of emissions are the various environmental control technologies used to treat primary waste streams. These include the wastewater-treatment system, sulfur-recovery system, cooling towers, and any flares or incinerators included in the plant design. Figure 9.3-1 shows the types of environmental emissions typically associated with these components. Thus, coal-gasification processes represent potentially significant sources of air pollutants, water pollutants and solid wastes.

9.3-2. Recent Characterization Studies

Recent characterization studies of emissions from coal-gasification facilities have been conducted by the US DoE and EPA. Most of this work was conducted in the mid-to-late 1970s and early 1980s when the potential for a significant coal-gasification industry in the US appeared real. The DoE work focused primarily on a number of pilot plants constructed in the 1970s to test several advanced gasification processes. $^{3-5}$ EPA studies focused more intensively on commercial gasification facilities in different parts of the world. A series of recently published reports by EPA summarizes the results of its multi-year testing $program^{6-8}$ and provides a comprehensive overview of environmental data for coal-gasification facilities. These summaries cover a variety of gasifier types and characterize emissions of air pollutants, water pollutants and solid wastes. Environmental characterization studies have also been carried out at the Great Plains gasification facility in North Dakota and at the Cool Water plant in California, and some information from these facilities is now becoming available. These plants are discussed later in this chapter.

9.3-2A. Air Pollutants

Tables 9.3-2 and 9.3-3 summarize features of the ten coal-gasification facilities characterized in the EPA studies. These include both air-blown and oxygen-blown gasifiers, encompassing fixed-bed, fluidized-bed, and entrained-bed designs.

The characterization of air-pollutant emissions is focused on sulfur and nitrogen species, which are the key pollutants of concern in coal gasification. Figure 9.3-2 summarizes the partitioning of sulfur among various outlet streams for each of the gasifiers tested.⁶ Most of the total sulfur in coal is converted to gaseous species, with small amounts of sulfur

exiting the gasifier in process waters and solids. Figure 9.3-3 shows the distribution of sulfur species in the vapor phase. Most of the product gas sulfur is seen to be in the form of H_2S , which accounts for 82-94% of the total vapor-phase sulfur in the eight gasification processes for which data were available. Reduced sulfur species, including carbonyl sulfide (COS), methyl mercaptan (CH₃SH), ethyl mercaptan (C₂H₅SH), and carbon disulfide (CS₂) generally were present at detectable levels where analyses were conducted. The most prevalent of these species was COS, which averaged about 10% for the processes tested.

č .

12 - 12

÷

Manual La Star .

ì

The fate of total nitrogen generally parallels the outlet sulfur distribution, with the majority of nitrogen exiting in the gas stream, as shown in Fig. 9.3-4. In these cases, however, several of the gasifiers have significant quantities of nitrogen in aqueous and by-product tar streams. Most of the vapor-phase nitrogen appears as ammonia, with the balance appearing as cyanide and thiocynate (Fig. 9.3-5). For the four low-BTU gas processes for which data were available, ammonia accounted for 81-87% of the vapor-phase nitrogen (excluding N₂). No vapor-phase volatile amines of low molecular weight organo-nitrogen species determinations were reported for these processes. For two of the gasifiers (Lurgi and Koppers-Totzek,) the low ammonia levels correspond to conditions downstream after an aqueous quench rather than upstream, as in the other cases. All of the gasification systems incorporate some type of quenching or cooling step downstream of the gasifier, in which nearly all of the nitrogen compounds are transferred to an aqueous phase.

Other potential air pollutants from coal-gasification facilities involve various fugitive emissions from cooling towers, seals, flanges, etc., and particulate emissions resulting from carryover of gasifier solids. Particulate emissions, however, are not usually significant because of the quenching and downstream processing that removes virtually all solids from the gas. To the extent particulate emissions are significant, they are most likely to be found at auxiliary facilites such as coal-fired steam plants or solid-waste incinerators. Fugitive emissions, on the other hand, have not been well characterized in past studies and represent an area where additional research is needed.

| Type of Gasifier | Site | Type of Coal | Year
of
Study | Product Gas
Heat
Content [†] |
|-----------------------------------------------------|-------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|---------------------------------------------|
| Chapman-Wilputte | Kingsport, TN | Virginia bituminous | 1978 | Low |
| Foster-Wheeler/
STOIC | Univ. of
Minnesota
(Duluth) | Bituminous coal from Pinnada
Seam | 1981 | Low |
| Koppers-Totzek | Modderfontein,
So. Africa | Bituminous, high volatile coal
from So. Africa | 1979 | Medium |
| Lurgi, dry ash | Westfield,
Scotland | Rosebud, sub-bituminous coal
from Montana; bituminous
coals from Percy, Illinois;
and Pittsburgh non-caking and
non-swelling coal from the
Federal No. 1 mine | 1973-
1974 | Medium |
| Lurgi-type, dry
ash | Kosovo,
Yugoslavia | Lignite from Kosovo mine | 1981 | Medium |
| Lurgi, tri-state
synfuels test | Sasolburg,
So. Africa | Western Kentucky coal | 1981 | Medium |
| Riley (modifica-
tion of Morgan
Gas Producer) | Worchester,
MA | North Dakota lignite | 1979 | Low |
| KRW-PDU | Madison, PA | Wyoming sub-bituminous coal,
Pittsburgh No.8 bituminous coal,
and North Dakota lignite | 1983 | Medium |
| Texaco | Ruhrkohle/
Ruhrchemie,
FRG | Illinois bituminous coal | 1980 | Medium |
| Wellman-Galusha | Glen-Gery
Brick Co.,
York, PA | Pennsylvania anthracite | 1978 | Low |
| Wellman-Galusha | Fort Snelling | North Dakota lignite
(Indianhead) | 1978 | Low |

| Table 9. 3-2. Coal and coal-gasification facility type (Net. 0 | Table | 9.3-2. | Coal and | coal-gasification | facility type | Ref. | 6). |
|----------------------------------------------------------------|-------|--------|----------|-------------------|---------------|------|-----|
|----------------------------------------------------------------|-------|--------|----------|-------------------|---------------|------|-----|

[†] Low means less than 5500 kJ/m³; medium means approximately 11,000 kJ/m³.

9.3-2B. Water Pollutants

The quantity and quality of wastewaters produced by coal-gasification facilities depend significantly upon the gasifier type, the feed-coal characteristics, and the nature of gas cleanup and ash-removal/handling systems. Wastewaters may be categorized into two gen-

| 6). | |
|-----------------|--|
| (Ref. | |
| studies | |
| EPA | |
| for | |
| facilities | |
| al-gasification | |
| б
С | |
| Comparison o | |
| 9.3-3. | |
| Table | |

| Texaco
(Ruhrchemië) | × × | × | ቤ | ्रि
भि | ω | w | 00 | ×× | * | ×× |
|----------------------------------------|----------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|-----------------------------------------------------|-------------------------------------------------------------------------|-------------------------------------------------|------------------------------------|---------------------------------------------------------------------|------------------------------------------------------------------------|-------------------------------------------------|----------------------------------------------------|
| Koppers-Totzek
• (Ptolemais) | × × | × | ¥ | त्व
मि | S | w | υο | *** | | ×× |
| Koppers-Totzek
(Modderfontein) | × × | × | ¥ | 년
[1] 1 | S | S | υο | * * * | | ×× |
| KRW
PDU | × × × | × | ቤ | β | A | ω | υo | x | x | |
| Lurgi-type
(Kosovo) | * * * | х | քւ | ¥р | Ą | S | οŭ | ×× | × | ×× |
| Foster-
Wheeler/
STOIC | × × | x | ¥ | ۲D | Ð | ч | D Q | ×× | × | ×× |
| Riley | × | х | A | ጃዞ | Д | ω | сс
Р С | × | × | × |
| Wellman-
Galusha
(Glen-Gery) | × | × | A | Χq | A | s | сс
А СС | × | ; | < × |
| Wellman-
Galusha
(Fort Snelling) | × × | × | Ą | ХD | Ð | S | A CC | × | : | ×× |
| Chapman | × | × | A | Хн | Ð | v | с
Ч | × × | × | ×× |
| ъ | COAL HANDLMG
Receive presized coal
Crush/pulverize
Screen
Thermal drying
Slurrying
Air classifying | COAL FEEDNG
Lock hoppers
Screw feed/entrainment
Slurry pumping
Barrel valve | GASIFICATION
Atmosphere (A)/pressur-
ized (P) | Moving-(M)/fluid-(F)/
entrained-bed (E)
Thin bed (T)/deep bed (D) | Slagging (S)/agglomerat-
ing (A)/dry ash (D) | Single-stage (S)/two-
stage (T) | Cocurrent (C)/
countercurrent (CC)
Air blown (A)/O2 blown (O) | GAS CLEANUP
Cyclones
ESP
Quench/scrubbing
Acid gas removal | ASH REMOVAL/HANDLING
Lockhoppers
Ash plow | Slide valve
Water quench
Conveyor/drag chain |

^aNot applicable.

1111

ł

• • •

ł







ころ いいか した かいわり あいいい

Fig. 9.3-3. Distribution of vapor-phase sulfur species (Ref. 6).



Fig. 9.3-4. Nitrogen distribution among outlet streams, excluding N_2 (Ref. 6).



the state of the second

....

, ,

1

- 11

Fig. 9.3-5. Distribution of vapor-phase nitrogen species (Ref. 6).

eral groups: those from tar-producing gasifiers and those from non-tar producing gasifiers. The former refer to fixed-bed systems which produce substantial quantities of phenolics, oils and tars, while the latter category includes ash-agglomerating, fluidized-bed, and entrained-bed gasifiers which produce little or none of these pollutants.

Coal gasification wastewaters include gas-quench condensates,

cyclone-dust quenchwaters, ash-pan waters, gas-compression and cooling condensates, acid-gas removal waters, and leachates from slag and ash-disposal facilities. Among these, the quench condensates represent the principal wastewater source in terms of pollutant strength and stream volume (Table 9.3-4). The aqueous pollutants of greatest environmental concern are ammonia, cyanide, phenols, and sulfur compounds (primarily suflides).

Characterizations of wastewater contaminants were conducted by EPA for the ten low- and medium-BTU coal gasifiers shown in Table 9.3-2.⁷ Tar producing (fixed-bed) systems are the Chapman, Wellman-Galusha, Riley, Foster Wheeler/STOIC, and Lurgi processes. Entrained-bed gasifiers are represented by the Koppers-Totzek and Texaco processes, while the KRW process development unit (PDU) represents an ash-agglomerating fluidized bed process. Waterwater data were catalogued in terms of conventional pollutants (e.g. BOD, COD, NH₃, TDS, etc.), trace elements, and organics. Wastewater sources were treated in three general categories: (i) process waters from the gasifier, particulate removal, gas cooling, and acid-gas removal operations, (ii) process waters from ash and slag handling, and (iii) leachates from gasification slag and ash.

Tables 9.3-5 to 9.3-11 summarize the EPA data on conventional pollutants, trace metals, and organics in some of the major process streams of tar- and non-tar producing coal-gasification wastewaters. These data con-

| Casifier | Coal | Wastewater
produced,
kg water/kg coal | Steam
consumed,
kg steam/kg coal | Tar/oil
produced,
kg T-O/kg coal | Phenols
produced,
kg C ₆ N ₅ OH/kg coal | |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|---------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------|---------------------------------------------------------------------|--|
| Lurgi ^a | Montana Rosebud ^b | 1.0 1.25 | | 0,04 | 0.004 | |
| | Illinois No. 6 ^b | 2.1 | 2.51 | 0.03 | 0.005 | |
| | Illinois No. 5 ^b | 1.8 | 2, 25 | 0.05 | 0.005 | |
| Pittsburgh No. 8 ^b | | 2.6 | 3.24 | 0,05 | 0,004 | |
| | Montana Rosebud ^C | 0.9 | 1.01 | 0.04 | 0.005 | |
| Texaco ^d | Illinois No. 6 ^e | 0.7-1.3 | 0.78 ^f | g | g | |
| Koppers-Totzek ^h | Illinois No. 6 ^C | 0, 9 | NA ^I | NA ⁱ g | | |
| ^a Lurgi gasifier at Westfield, Scotland.
^b Coarse graded (6-32 mm).
^c Fine graded (2-10 mm).
^d Ruhrkohle/Ruhrchemie in Oberhausen-Holten, FRG.
^e Pulverized (< 2 mm). | | | ^f Steam flow rate is taken as the sum of fresh makeup
slurry water, coal moisture, and water in additives
and flocculants.
^g Negligible.
^h TVA projections. | | | |

Table 9.3-4. Normalized production of quench liquors/gas-cooling condensates (Ref. 7).

| Gasification
system | Riley | Chapman | Wellman-
Galusha
at Fort
Snelling | Koppe | Koppers-Totzek at Modderfontein KRW-PDU | | | | | |
|------------------------------------|-------------------|---------------------|--------------------------------------------|------------------------------------|-----------------------------------------|-----------------------|-----------------------|----------------------------|--------------------|---------|
| Type of waste-
water | Ash pan | Separator
liquor | Cyclone-
dust
quench-
water | Com-
pressor
con-
densate | Com-
pressor
con-
densate | Rectisol ^b | Rectisol ^C | Sub-
bituminous
coal | Bituminous
coal | Lignite |
| pH, standard
units | 11,3 | 7.66 | 10.0 | 8.2 | 8.0 | .9.1 | \$.1 | 8.4 | 8.4 | 8.7 |
| TDS | 2,460 | 6,300 | 390 | 260 | 170 | 1,390 | 1,640 | 390 | 331 | 2, 249 |
| TSS | 32 | 144 | đ | <1 | 12 | 70 | 20 | 4,600 | 3,100 | 1,000 |
| Hardness as
CaCO ₃ | | | | 60 | 46 | 691 | 554 | | | |
| Alkalinity as
CaCO ₃ | | 2, 140 | | Z, 990 | 2,690 | 78 | 144 | 6,770 | 2, 382 | 12,067 |
| Conductivity
(umho/cm) | 2, 900 | 32, 000 | | 6,000 | 5,500 | 1,800 | 2,000 | 12,300 | 5,200 | 16,700 |
| COD | 87 | 22, 200 | 800 | 644 | 569 | 28 | 1,000 | 150 | 237 | 145 |
| TOC | 15 | ł | 185 | Ì | 1 | 1 | | 48 | 55 | 170 |
| BOD | 44 | 6,530 | 85 | | | | | | | |
| NH ₃ (total) | | 5,000 | 0.97 | 973 | 900 | 26 | 49 | 2, 430 | 965 | 4,125 |
| CN- | NDe | 1,000 | 0.36 | 7.3 | 10.5 | 2.8 | ND | 2.2 | 59 | 62 |
| SCN | <4 | 70 |] | 10.9 | 17.1 | 110 | 137 | 79 | 105 | 62 |
| H ₂ S | | < 10 | | 43.9 | 53.5 | 1.1 | 4.5 | 18 | 79 | 102 |
| s _z o ₃ | | | | 4.8 | 7.8 | 18.5 | 16.4 | 1 | | |
| 50 ⁻ 3 | | | 12 | < 1 | < 1 | < 1 | <1 | 10 | 10 | 12 |
| so ⁼ | 1,380 | 1,000 | 55 | 56 | 49 | 461 | 541 | 225 | | 65 |
| P04-3 | 0.06 | 60 | 0,1 | Z | 3 | 0.1 | 2, 8 | 3.7 | 0.6 | 1.5 |
| Chloride | 110 | 300 | 34 | 23 | 13 | 153 | 158 | 22 | 493 | 61 |
| Methanol | | | | ND | ND | <0.1 | < 0.1 | | | |
| NO ₃ | < 0.02 | | <0.5 | | | | | 1.4 | 0.9 | |
| NOZ | | | <0.01 | | | | | 1 | | |
| Fluoride | 0.71 | 200 | z | | | | [| 1.8 | 25 | 30 |
| Total sulfur | 18 | | | | | | | | | |
| NH ₃ fixed | < 30 | | | } | | | | | | |
| Carbonate | 2×10 ⁶ | | | | | | | | | |

Table 9.3-5. Conventional pollutants in coal-gasification wastewaters (Ref. 7).^a

^aUnits are mg/1 unless otherwise noted.

^d Blanks mean parameter not analyzed, ^eND - not detected. スペートス とうかいがたいたい ひしたい たいわいせん

Ľ.

2

i

*** * ***

· · · · · · · · ·

\$

^bPurified sewage used as process feedwater. ^cGooling tower makeup water used as process feedwater.

| Gasification
system | | Lurgi at Sa | usolburg | | Lurg
West | i at
field | Lurgi- | Lurgi-type at Kosovo | | |
|----------------------------------|--------------------|--------------------------|------------------------|--------------------------|----------------------------|----------------------------|-----------------|----------------------|----------------------------------------|--|
| Type of
wastewater | Raw-gas
liquor | Extracted-
gas liquor | Stripped
gas liquor | Coal-
slurry
water | Gas
liquor ^b | Gas
liquor ^c | Cyanic
water | Gas
liquor | Quenched-
ash
water ^d | |
| pH, standard
units | 9.0 | 10.4 | 6.5 | | 7.63 | 8.1 | 11.9 | 9.2 | 8.1 | |
| TDS | 1,180 ^e | 390 ^e | 420 ^e | | 1,140 | 1,940 | 590 | 2, 170 | 2,100 | |
| TSS | <1 | <1 | <1 | | f | | 140 | 150 | 8,760 | |
| Conductivity
(umho/cm) | 3,100 | 330 | 140 | 120 | | | | | | |
| COD | 12,000 | 990 | 1,400 | 170 | 5,900 | 18,600 | 205 | 18,900 | 1,460 | |
| TOC | | | | | | | | 4,970 | | |
| BOD | | | | | 4,300 | 12, 250 | | 9,030 | 90 | |
| NH ₃ (total) | 6,600 | 5,500 | 390 | 25 | | | | | | |
| CN | | 0.85 | 0.17 | < 20 | 16 | 8 | | < 1 | 0.01 | |
| SCN ⁻ | | | | 24 ^g | 210 | 60 | | <75 | 0.026 | |
| H ₂ S | 7 20 | 170 | g | | 220 | 330 | | ļ | Trace | |
| so ⁼ | 240 | 55 | 40 | |] | | | | Trace | |
| $so_4^=$ | 8.7 | 5.2 | 16.0 | | | | | | 495 | |
| PO_4^{-3} | | | | | | | | | | |
| Chloride | 1,690 | 950 | 600 | | 160 | 9 | | | 28 | |
| NO ₃ | 99 | 12 | <1 | | | | | < 1 | 4.8 | |
| NOZ | 0.15 | 0.03 | 0.04 | { | 1 | | | Trace | 0.4 | |
| Fluoride | 45 | 40 | 50 | | | | | | 0.91 | |
| Calcium | 3.2 | 1.9 | 2.9 | 770 | | | | | | |
| Magnesium | 0.51 | 0.46 | 1.0 | 91 | | | | | | |
| Sodium | 6.0 | 6.5 | 6.1 | 230 | | | | | | |
| TDS after
ignition | | | | | 20 | 30 | | | | |
| Total sulfur | | | | | 340 | 450 | 60 | 84 | | |
| Fatty acids
as acetic | | | | | 260 | 1,050 | | | | |
| NH3 - free | | | | | 4,090 | 8,930 | | 3,510 | Trace | |
| - fixed | | | | | 250 | 470 | | 250 | 1.9 | |
| Carbonate | | | | | 10,650 | 19,960 | | | | |
| Total solids | | | | | | | 730 | 2, 230 | 10,900 | |
| Total non-
volatile
solids | | | | | | | 560 | | | |
| Permanganate
number | e | | | | | | 570 | 14, 200 | 8,060 | |
| Tar & oils | | | | 1 | | | | <400 | | |

| Table 9.3-6. Conventional pollutants in Lurgi coal-gasification wastewaters (Ref | . 7). | a |
|----------------------------------------------------------------------------------|-------|---|
|----------------------------------------------------------------------------------|-------|---|

a Units are mg/l unless otherwise noted. ^bWastewater associated with Pittsburgh #8 coal. ^cWastewater associated with Montana Rosebud coal.

^dIncludes coal bunker vent-gas scrubber and ash-lock vent-gas scrubber blowdowns.

^eTDS measured at 180°C. ^fBlanks mean parameter not

analyzed.

gPossible analytical interferences.

| Gasification
system | Foster-
Wheeler/
STOIC | | Lurgi at Sa | solburg | | Lur
at I | gi-type
Kosovo | Riley | Chapman | Wellman-Galusha
at Fort Snelling |
|------------------------|------------------------------|--------------------|--------------------------|-------------------------|--------------------------|-----------------|-------------------------|------------|---------------------|-------------------------------------|
| Type of
wastewater | Ash
pan | Raw-gas
liquor | Extracted-
gas liquor | Stripped-
gas líquor | Coal-
slurry
water | Cyanic
water | Phenosolvan
effluent | Ash
pan | Separator
liquor | Cyclone-dust
quench-water |
| analysis | SSMS ^b | ICPES | ICPES | ICPES | ICPES | SSMS | SSMS | AASd | SSMS | SSMS |
| Aluminum | 30, | < 50 | <50 | < 50, | < 50 | 70 | 100 | e | ND | MC |
| Antimony | ND" | < 2, | 85, | 36 | < 2 ¹ | ND | ND | | 70 | < 60 |
| Arsenic | 30 | 1,800 ¹ | 1,700 ¹ | 1,700 ¹ | 170 | 90 | 20 | 21 | 800 | 120 |
| Bariun | 4,000 | 200 | 80 | 110 | 1,900 | 20 | 50 | 170 | 300 | 570 ⁸ |
| Beryllium | ND. | < 0.5 | <0,5 | < 0.5 | < 0.5 | ND | ND | | ND | ND |
| Boron | 400 | 32 | 26 | 28 | < 9 | 20 | 100 | | 9,000 | 9008 |
| Bromine | 100 | | • | | | 100 | 9 | | ND | 40_ |
| Cadmium | ND | < 2 | <2 | < 2 | 51 | ND | ND | <1 | 5 | < 5 ⁸ |
| Calcium | мс | 3,200 | 1,900 | 2,900 | мс | ND | 6,000 | | 2,000 | мсв |
| Cerium | ND | | | | | ND | ND | | 3 | 2 |
| Cesium | < 1 | | | l | | 4 | ND | | 1 | 4 |
| Chlorine | 700 | | | | • | 4,000 | 1,000 | мс | 200 | мс |
| Chromium | 40 | 1,500 | 2,800 | 3,900 | <1 | 9 | 5 | < 1 | ND | < 5 ⁸ |
| Cobalt | 5 | < 6 | <6 | <6 | < 5 | ≤3 | 3 | | ND | 9, |
| Copper | 20 | < 1 | 15 | 19 | < 1 | 20 | 30 | 6 | 10 | 120 |
| Fluorine | 50 | | | | | 300 | 4,000 | 530 | 2,000 | 2,000 |
| Gallium | 20 | | · | l ' | | ND | ND | | ND | 20 |
| Germanium | ND | | | | | 20 | 30 | | ND | 7 |
| Iodine | 7 | | | | | 400 | 20 | | 300 | 6 |
| Iron | 9,000 | 430 | 520 | 5,600 | мс | 4,000 | 500 | 1,900 | 1,000 | 4,9008 |
| Lanthanum | ND | .1 | -1 | . 1 | | 8 | ND | | 1 | ND |
| Lead | 10 | <2- | < 2- | 61- | 83* | 8 | 70 | 1.3 | ND | 99° |
| Lithium | 200 | <1 | 18 | 28 | 140 | 2 | 3 | | 3 | 40 |
| Magnesium | 300 | 510 | 460 | 1,000 | мс | мс | 2,000 | | 2,000 | MC |
| Manganese | <1 | <1 | <1 | <1 | <1 | 40 | 10 | 58 | ND | < 10 |
| Mercury | 4, 21 | 660- | 79* | 6. 24 | 1.9 | ND | ND | 0,5 | <0.0003 | 0.4 |
| Molybdenum | 20 | < 2 | <2 | < 2 | <2 | ND | ND | | ND | 4 |
| Nickel | 4 | < 3 | 4 | 3 | < 3 | | 80 | | | < 208 |
| Niobium | 100 | - 200 | < 700 | < 200 | | | ND | | 8 | ND |
| Phosphorus | 100 | < 200 | < 200 | < 200 | 3,200 | ND | 80 | | MC | 400 |
| Potassium | 0,000 | < 40 | < 40 | 2,400 | < 40 | 7,000 | 1,000 | | MC | MC |
| Rubidium | 30 | | ļ | | | <1 | ND | | DN
2 | 20 |
| Scandium | 10 | 600 ¹ | 2001 | - i | ,i | 52 | \$ 5 | 12 | 3 000 | |
| Silicon | 400 | 7 900 | 7 7 00 | 7 000 | | 1 000 | 30 | · · · | 2,000 | 2 000 |
| Silver | | 1,900 | 1,100 | (,800 | MC
2 | 1,000 | 1,000 | 14 | 2,000 | 2,000 |
| Sodium | 200 | 6 000 | 6 500 | 6 100 | NC | | | 1.4 | 20 | NCS |
| Strontium | MC | 14 | 0,500 | 0,100 | 1 000 | 34,000 | 20 | | | 1 1008 |
| Sulfur | >9.000 | 1 1 | | 15 | 1,900 | | MC | | ND | 1,1000 |
| Tellurium | 4 | | | 1 | MO | ND | ND | | ND | ND |
| Thallium | ND ND | < 2 ¹ | < 21 | $< 2^{i}$ | < 2i | ND | ND | | ND | ND |
| Thorium | < 10 | | | | ~0 | 40 | 10 | | | |
| Tin | ND | 1 | ł | | | ND | 20 | | 30 | 1808 |
| Titanium | 200 | <5 | < 5 | 121 | 1.800 | | 400 | 20 | | 100 ND |
| Uranium | <10 | | | | | ≤10 | ≤ 30 | | 10 | ND |
| Vanadium | 1 | <3 | <3 | 13 ¹ | 810 | | 1 | 3 | | ND 15 ⁸ |
| Ytterbium | ND | | - | | | ND | ND | | ND | 2 |
| Yttrium | 50 | < 2 | < 2 | < 2 | 190 | 30 | < 30 | | 5 | ND |
| Zinc | 40 | 8 | 11 | 29 | < 3 | 50 | 70 | 5.5 | ND | 358 |
| Zirconium | 10 | 1 | | [| | ND | ≤ 30 | - | 10 | 5 |
| | 1 | E | • | | | | | | | 1 |

.

.

^aUnits are $\mu g/l$ unless otherwise noted.

^bSSMS - spark source mass spectrometry.

^cICPES - induced coupled argon plasma-emission spectrometry.

 $^{\rm d}_{\rm AAS}$ - atomic absorption spectrophotometry.

^eBlanks mean parameter not analyzed.

^fMC - major component in the wastewater, concentration greater than 10,000 μ g/l.

^gAnalyzed by induced coupled argon plasma-emission spectrometry.

^hNot detected.

Analyzed by atomic absorption spectrophotometry.

| Gasification
system | Ko | ppers-Totzek a | t Modderfonte | in | 1 | co at
Rulu chemie | | | |
|------------------------|----------------------------|---------------------------------------|-----------------------|-----------------------|-----------------------|----------------------|-----------|----------------------|----------------------|
| Type of
wastewater | Compressor
condensate b | Compressor
condensate ^C | Rectisol ^b | Rectisol ^C | Subbituminous
coal | Bituminous
coal | Lignite | Settler
underflow | Settler
underflow |
| Method of
analysis | SSMS ^d | SSMS | SSMS | SSMS | AAS"/ICPES | AAS/ICPES | AAS/ICPES | SSMS | AAS/ICPES |
| Aluminum | 5 | 9 | 100 | 100 | ND ^g | 1,400 | 2, 400 | мсћ | мс |
| Antimony | ≤ 2 | 10 | <1 | ND | ND | ND | ND | 90 | 21 |
| Arsenic | Z | 4 | 20 | 10 | 73 | 300 | 420 | 600 | 480 |
| Barium | 100 | 40 | 200 | 200 | 1,200 | 550 | 470 | мс | 2,700 |
| Beryllium | ND | ND | ND | ND | ND | ND | 5 | 10 | 130 |
| Bismuth | 2 | ND | ND | ND | I | | | 10 | |
| Boron | <1 | < 1 | <1 | ND | 6,800 | 10,000 | мс | 700 | мс |
| Bromine | 80 | 300 | 30 | 60 | | | | 300 | |
| Calaium | 3 | NG | 1 | ND | | ND | UN
COO | 70 | 190 |
| Cerium | ND | MC | MC 1 | ND | MC | MC | 8,000 | 1 000 | mu |
| Cesium | <1 | ND | | ND | | | | 70 | |
| Chiorine | 100 | 60 | 200 | 300 | | | | мс | 1 |
| Chromium | 5 | 5 | 3 | 7 | ND | ND | ND | 4.000 | 1.200 |
| Cobalt | 3 | 1 | 1 | ≤1 | ND | ND | 12 | 400 | 260 |
| Copper | 10 | 10 | 50 | 100 | ND | 5 | ND | 700 | 7 40 |
| Dysprosium | ND | ND | ND | ND | | - | - | 50 | |
| Erbium | ND | ND | ND | ND | | 1 | | 20 | |
| Europlum | ND | ND | ND | ND | | | | 10 | |
| Fluorine | 30 | 3,000 | 400 | 3,000 | | | | мс | 1 |
| Gadolinium | ND | ND | ND | ND | | | | 30 | |
| Gailium | <1 | 3 | <1 | < 1 | | | | 2,000 | |
| Germanium | 5 | 7 | <1 | Z | | | | 3,000 | |
| Hafnium | ND | ND | ND | ND | | | | 20 | |
| Holmium | ND | ND | ND | ND | | | | 30 | |
| lodine | 500 | 8 | 8 | 9 | | (00 | | 20 | |
| Lion | 500 | 1,000 | мс | 2,000 | 1,800 | 600 | 2,300 | MC | мс |
| Lead | 20 | 1 | 20 | | ND | ND | ND | 4 000 | 1 100 |
| Lithium | 3 | 10 | 6 | 10 | טא | 100 | 44 | 70 | 3,100 |
| Lutetium | ND | ND | ND | ND | | 100 | 11 | 2 | |
| Magnesium | 1,000 | 2,000 | MC | мс | 28,000 | 7,600 | 55,000 | MC | мс |
| Manganese | 10 | 9 | 50 | 80 | ND | 610 | ND | мс | 2,500 |
| Molybdenum | 30 | 20 | 40 | 20 | ND | ND | ND | 1.000 | 1.100 |
| Neodymium | ND | ND | ND | ND | | | | 100 | |
| Nickel | 4 | 7 | 200 | 100 | ND | ND | ND | 1,000 | 1,050 |
| Niobium | Z | 5 | 2 | <1 | | | | 200 | |
| Phosphorus | 70 | 70 | 700 | 1,000 | 1,300 | ND | ND | мс | 5,800 |
| Potassium | мс | мс | 5,000 | мс | 2,700 | 4,300 | MC | мс | мс |
| Praseodymium | ND | ND | ND | ND | | | | 100 | i i |
| Rubidium | 8 | 3 | 9 | 6 | | | | 2,000 | |
| Samarium | | | UM
I | UN
S | | | | 90 | |
| Scandium | 1 000 | 51 | <1 | 1> | 20 | | | 700 | 1. (00 |
| Silicon | 300 | 100 | 1,000 | 2 000 | 38 | | ND | 1.000 | 1,000 |
| Silver | < 2 | 100 | 1,000 | 2,000 | | | ND | MC | MC |
| Sodium | 2,000 | <1.000 | >1.000 | > 2. 000 | ND | 8 600 | MC | NC | MC |
| Strontium | 70 | 30 | 300 | 500 | | | mo | 7 000 | |
| Sulfur | > 2,000 | > 3,000 | > 2,000 | > 4,000 | | | | MC | 1 |
| Tantalum | Z | ND | ND | ND | 1 | } | | 5 | |
| Tellurium | 3 | 3 | ND | ND | | 1 | | 7 | |
| Terbium | ND | ND | ND | ND | | | | i i | |
| Thallium | ND | ND | ND | ND | ND | ND | NÐ | 100 | 50 |
| Thorium | < 8 | < 3 | < 3 | <6 | | | | 200 | |
| Thulium | סא | ND | ND | ND | | | | 4 | |
| 11n
Titestur | | <1 | 4 | ND | |) | | 100 | |
| Tuanium | 30 | 200 | 100 | 200 | 46 | 18 | 110 | мс | мс |
| Lungsten | | ND | ND | ND | 1 | | | 50 | |
| Vanadium | | < 3 | 6 | | | | | 300 | |
| Viterblue | 2 | | 3 | 5 | 20 | 14 | ND | Z | 1,400 |
| Vitrium | | UN . | ND | ND | 1 | (I | | 20 | |
| Zinc | 600 | 1.000 | 1> | <1
5 000 | | I I | | 700 | |
| Zirconium | 3 | 10 | ~1 | - 5,000 | | | ND | мс | 1,700 |
| | L | 10 | ~1 | 51 | | 1 | | 1,000 | |

Table 9.3-8. Trace elements in non-tar producing coal-gasification wastewaters (Ref. 7).^a

^aUnits as $\mu g/\ell$ unless otherwise noted.

^bPurified sewage used as process feedwater.

^cCooling tower makeup water used as process feedwater.

^dSSMS - spark source mass spectrometry.

^eAAS - atomic absorption spectrophotometry.

^fICPES - induced coupled argon plasma emission spectrometry.

^gND - not detected.

 $^{\rm h}MC$ - major component in the wastewater, concentration greater than 10,000 $\mu g/\ell$.

ⁱBlanks mean parameter not analyzed.

| Gasification system | Chap | man | Foster-Wheeler/ | Riley | Lurgi-type |
|--------------------------------------|----------------------|-------------|---------------------|------------------|-----------------------------|
| Wastewater type | Separato | or liquor | Ash-fan
water | Ash-fan
water | Phenosolvan-
inlet water |
| Sample type | Average ^b | Range | Grab | Grab | Grab |
| Acid extractable compounds | | | | | |
| Phenol | 2 400 | 1900-3400 | 0.0033 | 241 | 690 |
| Methylphenols | 3,200° | 1500-4700 | NDd | ND | _ e |
| Dimethylphenols (total) ^f | 1,200 | 330-1900 | NÐ | ND | 333 |
| 2, 4-Dimethylphenol | 420 ^g | 98-820 | ND | ND | 130 |
| Trimethylphenol | 0.82 | 0.35-2.2 | ND | ND | ND |
| Indanol | 1.7 | <0.07-3.2 | ND | ND | ND |
| l-Naphthol | 5.0 | 3.3-8.5 | ND | ND | ND |
| 2-Naphtho1 | 6.7 | 5.4-9.2 | ND | ND | ND |
| Resorcinol/catechol | 30 | 3.6-65 | ND | ND | ND |
| Hydroxybenzaldehyde | 5.7 | <0.18-19 | ND | ND | ND |
| o-Cresol | - | | ND | ND | 260 |
| m-Cresol | - | | NÐ | ND | 610 |
| p-Cresol | - | | - | - | 100 |
| Total unknown phenols | - | | - | - | 698 |
| Base-neutral extractable compounds | | | | | |
| Naphthalene | 8.6 | 1.6-17 | 0.00033 | 7.4 | ND |
| Acenaphthalene | 3.6 | 1.2-<6 | ND | 2.0 | ND |
| Fluorene | 2.6 | 0.26-<6 | ND | 1.0 | ND |
| Phenanthrene/asthracene | 2.3 | 0.7-<6 | ND | 2.2 | ND |
| Fluoranthene | 5.7 | 0.3-<9 | ND | 1.7 | ND |
| Pyrene | 5.7 | 0.4-<9 | ND . | 1.7 | ND |
| Bis(2-ethylhexyl)phthalate | 12 | 1.2-32 | 0.0067 ⁿ | 11.1 | ND |
| Chrysene | 0.12 | | ND | 2.4 | ND |
| Benzo(b)fluoranthene | 0,10 | | ND | ND | ND |
| Benzo (a)pyrene | 0,12 | | ND | ND | 0.19 |
| Pyridine | 1.2 | | ND | ND | 28 |
| Ethylpyridine(s) | 18 | 1.3-61 | ND | ND | 46 |
| Quinoline | 3.1 | 0.62-5.6 | ND | ND | 5 |
| 4-Methylquinoline | 0.11 | | ND | ND | ND |
| 2 2 Dimethylaphthalene | 2.3 | 0.43-4.6 | | | |
| 2, 5-Dimethylnaphthalene | 2.3 | 0.05-<4.5 | ND | | |
| Indolo | 2,2 | <1.3-<3 | , ND | | |
| 2-Mathulindolo | 12 | 2 2 . 16 | | ND | ND |
| 3-Methylindole | 2 1 | 0 58-3 6 | | | ND |
| Diethyl phthalate | | 0.50-5.0 | ND | 19 | ND |
| Di-n-butyl phthalate | ND | | ND | 1.4 | ND |
| 2-Methylpyridine | - | | - | | 29 |
| 3- and 4-Methylpyridine(s) | - | | - | - | 13 |
| Alkylpyridine(s) | - | | - | - | 26 |
| Alkylquinoline(s) | - | | - | - | 12 |
| Benz(a)anthracene | - | | - | - | 0.92 |
| 7, 12-Dimethylbenz(a)anthracene | - | | - | - | 0.23 |
| Benzo(b)fluoranthene | - | 1 | - | - | 0.68 |
| 3-Methylcholanthrene | - | | - | - | <0.004 |
| Dibenz (a, b)anthracene | - | | - | - | 0.02 |
| 252 Group (as benzo(a)pyrene) | - | | - | - | 1.26 |
| Volatile organic compounds | | | | | |
| Benzene | 0.63 | 0.56-0.74 | - | - | 0.9 |
| Toluene | 0.42 | 0.38-0.46 | - | - | 0.5 |
| Ethylbenzene | 0,048 | 0.022-0.106 | - | - 1 | ND |
| m, p-Xylene | 0.15 | 0.124-0.172 | - | - 1 | ND |
| o-Xylene | 0,28 | 0.034-0.184 | - | - | 0.8 |

| Table 9 | . 3-9. | Organics in fixed | l-bed coal-gasification | 1 wastewaters | (Ref. 7 | /).ª |
|---------|--------|-------------------|-------------------------|---------------|---------|------|
|---------|--------|-------------------|-------------------------|---------------|---------|------|

•. •

ί.,

7. • .,

「いったいにあっ」に対し、おいていたが、 とうさい ドゥチック

; .`

. . . . 14

ĸ,

; Ł :

í ţ 1 . ŧ

> , . . .

; ; . :

2

・ジネトー

1

1

^a All data as mg/*l*. ^b Average of grab samples. ^cOne extremely high data point is not included in the average but the compound was identified 6 of

^dND means not detected. ^cDashes mean parameter not analyzed.

Includes 2, 4-DMP.

gThe portion of 2, 4-DMP from the B/N fraction was estimated from the amount found in the acid fraction. hProbable artifact of sample handling.

| | | | | · | ····· | r |
|---------------------------------------|----------------------------|-----------------|-------------------------|---------------------------------------|---------|-----------------------|
| Gasification system | Koppers-To
Modderfon | tzek at
tein | KI | Texaco at
Ruhrkohle/
Ruhrchemie | | |
| Wastewater type | Compressor
condensate | Rectiso1 | Subbitumi-
nous coal | Bituminous
coal | Lignite | Settler-
underflow |
| Sample type | grab | grab | | | | grab |
| Acid extractable compounds | | | | | | |
| Pheno1 | Trb | Tr | 0.19 ^c | - | 0.16 | 0.0026 |
| Dimethylphenols (total)d | ND ^e | ND | - | - 1 | _ | ND |
| 2. 4-Dimethylphenol | ND | ND | - | - | - | ND |
| o-Cresol | ND | ND | ND | - | ND | ND |
| m-Gresol | ND | ND | ND | - | ND | ND |
| p-Cresol | - | - | ND | - | ND | - |
| Total unknown phenols | - | - | - | - | - | - |
| Basc-neutral extractable
compounds | | | | | | |
| Naphthalene | Tr | Tr | 10.0 | 0.26 | 0.20 | ND |
| Acenaphthalene | ND | Tr | 1.0 | 0.040 | 0.060 | ND |
| Fluorene | ND | 0.001 | 1.0 | 0.10 | 0.11 | ND |
| Phenanthrene/anthracene | ND | Tr-0.0046 | 2,71 | 0.44 | 0.040 | ND |
| Fluoranthene | ND | 0.0063-0.019 | 0.94 | 0.30 | 0.001 | ND |
| Pyrene | ND | 0.025-0.097 | 0.68 | 0.36 | 0.001 | ND . |
| Bis (2-ethylhexyl) phthalate | Tr^{f} | ND | - | - | - | 0.0081 |
| Chrysene | ND | 0.034 | ND | 0.020 | ND | ND |
| Benzo(b)fluoranthene | ND | 0.002 | ND | ND | ND | ND |
| Benzo (a)pyrene | ND | ND | ND | 0.005 | ND | ND |
| Pyridine | ND | ND | ND | Tr | 0.25 | - |
| Diethyl phthalate | $\mathbf{Tr}^{\mathbf{f}}$ | Trf | _ | - | | ND |
| Di-n-butyl phthalate | 0.006f | ND | _ | - | _ | ND |
| Benz(a)anthracene | ND | 0.016-0.023 | ND | 0.010 | ND | ND |
| Benzo(b)fluoranthene | ND | 0.015 | _ | _ | - | ND |
| Dibenz (a, b)anthracene | ND | ND | - | - | - | ND |
| Volatile organic compounds | | | | | | |
| Benzene | ND | ND | 0.15-1.10 | 0.007 | 0.020 | - |
| Toluene | ND | ND | - | - | - | - |
| Ethylbenzene | ND | ND | - | - | - | _ |
| m, p-Xylene | ND | ND | - | - | _ | - |
| o-Xylene | ND | ND | - | - | - | - |
| Chloroform | Tr | Tr | - | - | l . | - |
| Total volatile organics | - | - | - | - | - | 0.03-0.05 |
| | l | L | I | 1 | 1 | I |

Table 9.3-10. Organics in non-tar-producing coal-gasification wastewaters (Ref. 7).^a

^aAll data as mg/l.

^b Tr means trace (detected but at an unquantifiable level below 0.001 mg/l).

^cDashes mean parameter not analyzed.

^dIncludes 2, 4-DMP.

^eND means not detected.

^fProbable artifact of sample handling.
| | Bioassay Test Results | | | | | |
|-----------------------------------------------------------------|-----------------------|--------------------------|---------------------------------------------------|------------------------------------------------|--|--|
| Gasifier/wastewater | AMES ^a | In-vitro
cytotoxicity | Freshwater algae ^c
EC ₅₀ | $\frac{1}{10000000000000000000000000000000000$ | | |
| Lurgi-type Kosovo/gas
liquor | positive | СНО-М | _e | - | | |
| Lurgi-type Kosovo/
pretreated gas liquor | negative | CHO-M | - | | | |
| Lurgi-type Kosovo/
ASTM slag leachate | negative | CHO-ND | - | • | | |
| Lurgi Sasolburg/
pretreated gas liquor | - | - | - | 4.5-7.5% | | |
| Lurgi Sasolburg/
bioreactor effluent | - | - | - | 38% | | |
| Riley/ash leachate | negative | CHO-L | 3% ^f | ~ | | |
| Riley/cyclone dust
leachate | negative | CHO-ND | 4% | - | | |
| Chapman/separator
liquor | negative | RAM-ND | 0.1 to 1.0% | 0.02% | | |
| Wellman-Galusha
(Fort Snelling)/
ash sluice water | negative | WI-38-M | - | - | | |
| Wellman-Galusha
(Fort Snelling)/cyclone
dust quench water | negative | WI-38-ND | - | - | | |
| Wellman-Galusha
(Glen-Gery)/ash
sluice water | negative | WI-38-ND | - | - | | |
| Wellman-Galusha
(Glen-Gery)/ash
leachate | negative | WI-38-ND | - | - | | |
| Texaco Ruhrkohle/
Ruhrchemie/settler
underflow | negative | СНО-Н | 1.4-1.7% | 1.2-1.3% | | |
| Texaco Ruhrkohle/
Ruhrchemie/ASTM
slag leachate | negative | CHO-ND | 13-19% | - | | |
| Texaco Ruhrkohle/
Ruhrchemie/ASTM
fines leachate | negative | CHO-L | 10-11% | 9.0% | | |
| Texaco Ruhrkohle/
Ruhrchemie/bioreactor
effluent | negative | CHO-ND | 20% | 9.3-13% | | |

Table 9.3-11. Summary data for wastewater bioassay tests (Ref. 7).

;

1 :-

, . . .

5.55

:

2. 2. -

ς...

1

I, $\left\{ r \right\}$

į

ţ

1

ć

^aSalmonella bacterial mutagenicity assay (S. typhimurium).

^bCHO - Chinese hamster ovary clonal toxicity assay; RAM - rabbit alveolar macrophages toxicity assay; WI-38 - human lung fibroblast cells; L - low toxicity; M - moderate toxicity; H - high toxicity; ND - no detectable toxicity.

 $^{
m cSelenastrum}$ capricornutum, ${
m EC}_{50}$ - concentration of effluent estimated to cause a 50% decrease

in biomass. dPimephales promelas, LC_{50} - concentration of effluent estimated to cause a 50% decrease in the fish population.

eDashes mean parameter not analyzed.

f Values expressed as percent concentration of sample in dilution water.

firm that quench condensates produce the most contaminated waste streams from coal gasification. These streams contain substantial amounts of COD, BOD, NH₃, SCN, CN, reduced sulfur compounds, carbonates, and dissolved solids. The fixed-bed gasifiers also contain significant quantities of dissolved organics and volatile inorganics. Trace-element compositions generally reflect the composition of the parent coal, with most of these substances reporting to the liquid or solid effluent streams from the gasifier.

The critical point affecting the research agenda for coal gasification is that wastewater treatment processes add considerable cost to the overall system, so that process improvements which reduce or eliminate these steps are highly desirable. Similarly, a better understanding of fundamental process chemistry, particularly in the context of recycle and reuse of contaminated waters, could help minimize the need for downstream treatment. We return to these points in summarizing research recommendations at the end of this chapter.

9.3-2C. Solid Wastes

The major solid-waste streams from coal-gasification processes are the ash or slag from the gasifier, plus dust collected in the cyclone separators found in some process designs. Byproduct tar and oil may also be discharged from some types of gasifiers. EPA test data on solid wastes from various gasifiers include characterization of chemical properties, physical characteristics, leaching test, and bioassay tests (Table 9.3-12). Details concerning these data are summarized in Ref. 8.

The most critical aspects of solid-waste handling and disposal concern whether or not the waste is classified as hazardous under RCRA or whether it poses any biological hazard, as indicated by bioassay tests. Results for gasifier ash, slag and cyclone dust, which originate primarily from the inorganic components of coal, have demonstrated that these materials are non-hazardous under current RCRA criteria (Table 9.3-13). This observation is consistent with the results of other testing programs carried out by the US DoE on several coal-gasification pilot plants. Available data for gasifier ashes, slags and dusts suggest similarities to ashes from conventional coal-combustion systems.⁸ The general conclusion from characterization studies to date is that disposal of gasifier and cyclone solid wastes should not require management practices substantially different from those currently used for coal-combustion solid wastes. As noted earlier, however, EPA has recently proposed modifications to the current RCRA criteria which could make the future status of coal-gasification wastes far less certain. In this context, additional testing of archived samples of gasifier ash and slag could provide an expanded data base to assess the impact of new RCRA test criteria.

EPA characterization studies also included tar- and oil-discharge streams typical of fixed-bed gasifiers. These indicated the presence of polynuclear aromatic compounds (PNAs) including benzo(a)pyrene, one of the most potentially hazardous PNAs identified in gasifier tars.⁸ In addition to toxic or carcinogenic organic compounds, these streams were found to contain many trace elements. Co-disposal of such substances with other solid wastes could affect their RCRA classification. Since these tars and oils have relatively high heating values, however, they are quite suitable (and often used) as a fuel rather than a solid waste. The environmental concerns in this case could include the ultimate fate of trace metals and the emission of trace organics from incomplete combustion.

こうさない ちゅうわがた おうざ けんしょう ふい ビュちゅう スパート・ション

i

9.3-3. Methods of Environmental Control

We present in this section a very brief overview of current and developing methods for environmental control of major contaminants at coal-gasification facilities.

9.3-3A. Air Pollutants

As previously noted, emissions of sulfur species have traditionally constituted the primary air-pollution concern at coal-gasification facilities. Current regulations also focus on emissions of particulates and nitrogen oxides, while future regulations may address hazardous or toxic species such as organics and trace metals. One of the virtues of coal gasification has been the ability to reduce atmospheric sulfur emissions to levels far below those achievable in conventional coal-combustion systems. This result is achieved because sulfur occurs primarily in the form of gaseous H_2S (rather than SO_2), thus making it amenable to removal by a variety of physico-chemical acid-gas removal-processes already commercialized in related industries such as petroleum refining. Whether the acid-gas removal-process is viewed as an environmental control technology or simply as a process component depends on the process application. For high-BTU gas production, removal of sulfur is a necessary part of the process to avoid contamination of methanation catalysts. In the production of fuel gases, however, the acid-gas removal-step is needed primarily to comply with environmental regulations on allowable SO_2 emissions once the fuel is burned. In this case, it is clearly an environmental control technology.

Conventional acid-gas removal processes operate in conjunction with a sulfur-recovery system, which typically converts H_2S and other reduced sulfur species to elemental sulfur, one of the major by-products from coal gasification. A typical sulfur-recovery system might consist of a Claus plant with a tail-gas treatment-system. For properly operating systems, atmospheric emissions would consist of some tail-gas SO_2 and/or $\rm H_2S$ in very low concentrations (several ppm). The largest source of $\rm SO_2$ from coal gasification arises from the combustion of the low- or medium-BTU coal-gas product, where the $\mathrm{H}_{2}\mathrm{S}$ not removed by the acid-gas removal-system is oxidized to SO₂ on combustion.* This combustion-gas stream is also the principal source of nitrogen oxide emissions, which are derived from fuel-bound nitrogen (principally from ammonia not dissolved in the gasifier quench stream), plus thermal NO_v produced from nitrogen and oxygen present in airblown gasifiers. Nitrogen oxide control measures thus consist of ammonia removal together with combustion controls designed to minimize the formation of thermal NO, by methods such as steam injection, burner-design modifications, and other standard methods.

^{*} This statement applies to fuel-gas applications such as electric power generation. For other applications, the largest source of SO₂ emissions is likely to be an auxiliary coal-fired boiler producing steam for process use.

| ssay T | Cytotoxicity
Rodent acute
toxicity | x
x
x | x
x | | X
X | | × | × | | |
|-------------|---------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| ioas | Mutagenicity | × | × | | | | × | | | |
| щ | Tetsw-deerT
viizixot aayla | | | | × | | | × | | |
| | Aquatic acute
toxicity | | | | | | | × | | |
| hing
sts | Lesoly (
Josrixe MT2A | | | | | | × | | | × |
| Leac | Leaching/
RCRA extract | | × | × | × | × | × | | × | × |
| sol | Specific
sere area | | | | | | × | | | • |
| risti | trotros deA | | | | | | × | | × | × |
| cter | Moisture content | | | | | | × | | | × |
| lara | Bulk density | | | | | | | × | | × |
| al Ch | Particle
Trorphology | | | × | | | | | | |
| ysic | Specific gravity | | | × | | | × | × | | × |
| ਸੂਸ | Particle-size
Dation | | | × | × | | | × | | × |
| | Radiochemistry | | × | × | × | | | × | | × |
| ries | sisylsas lsreaiM
Ass fo | | | | | | | × | × | |
| opert | \stanixorq
sisylsns stsmitlu | | × | × | × | × | × | × | | × |
| cal Pı | Organic
spunoquos | | | × | × | × | × | × | | × |
| hemic | Trace element
composition | × | × | × | × | × | × | × | | × |
| 0 | Totsl elementsl
composition | · X | × | × | × | × | × | × | | × |
| | Source tests
and evaluation
program | ıpman | llman-Galusha
rt Snelling) | llman-Galusha
en-Gery) | ey gas
ducer | ster Wheeler/
DIC | rgi-type
sovo) | zaco
hrchemie) | opers-Totzek
olemais) | M |
| | Chemical Properties Physical Characteristics Leaching Bioassay I
Tests | ProvinceProvinceTotal elementalTotal elementalTotal elementalTotal elementalTotal elementalTrace elementTrace elementalMineral analysisTrace elementalMineral analysisTrace elementalMineral analysisTrace elementalMineral analysisMineral analysisMineral analysisSpecific gravityMineral analysisMineral analysisMineral analysisSpecific gravityMatricle-sizeMutage toxicityMutage toxicity | Пока сопрозітіон В. О. Пока сопрозітіон В. О. Пока сопрозітіон В. О. Какіосінски В. С. Пока сопрозітіон В. С. Какіосінски В. С. Пока сопрозітіон В. С. Какіосінски В. С. В. С. В. С. В. Сопрозітіон В. С. В. С. В. С. | A Display="background-color-width: color-width: color | Clericity Protonicity Protonicity Mutagenicity Prot | Adventure Total elemental Adventure Total elemental Adventure Total elemental Adventure Trace Adventure Trace Adventure Trace Adventure Adventure </td <td>Mathematical and services Mathematical and services Particle Particle Particle Particle <t< td=""><td>Channel of a strate and with a</td><td>Addition Addition Addition a</td><td>Chemical and urves Source and urves a durve a durve a durve b durve b durve</td></t<></td> | Mathematical and services Mathematical and services Particle Particle Particle Particle <t< td=""><td>Channel of a strate and with a</td><td>Addition Addition Addition a</td><td>Chemical and urves Source and urves a durve a durve a durve b durve b durve</td></t<> | Channel of a strate and with a | Addition Addition Addition a | Chemical and urves Source and urves a durve a durve a durve b durve b durve |

;;

1

Table 9.3-12. Solid-waste data for source test and evaluation programs (Ref. 8).

ŝ.

14

1

\$

| | Facil | ities ^a | | BCRA | |
|------------|----------------|--------------------|--------------------------------|-------|--|
| Elements | High | Low | Range | Limit | |
| Aluminum | F | A | < BC ^b -0.15 | | |
| Antimony | - ^C | - | < 0.005-<0.050 | 1 | |
| Arsenic | D | G, H | < 0.002-0.033 | 5 | |
| Barium | K | F | 0.019-7.2 | 100 | |
| Beryllium | - | _ | <0.0005-<0.002 | | |
| Cadmium | L | D,F | <0.0005-0.1 | 1 | |
| Calcium | В | С | 0.099-MC ^d | | |
| Chromium | E | D,G | < 0.001 -0.3 | 5 | |
| Cobalt | F | A | < BC-3.3 | | |
| Copper | В | D,G | <0.001-0.1 | | |
| Iron | E | D | <0.008-10 | | |
| Lead | н | D, F, G, L | <0.002-0.025 | 5 | |
| Lithium | G | А | ND ^e -0, 29 | | |
| Magnesium | В | С | 0.036-MC | | |
| Manganese | В | E | 0,001-0,5 | | |
| Mercury | - | - | <0.0002-<0.0005 | 0.2 | |
| Molybdenum | E | А | < BC-0.1 | | |
| Nickel | B,E | А | < BC-0.04 | l | |
| Potassium | В | I | ND-MC | | |
| Selenium | А | С | < 0,001-0,01 | 1 | |
| Silicon | в | С | 0. 2-MC | | |
| Silver | K | D | < 0.0005-0.007 | 5 | |
| Sodium | D | F | 1.6-140 | | |
| Strontium | В | С | 0.06-6 | ; | |
| Titanium | A,B | G,I | < 0.005-0.1 | | |
| Vanadium | E | A | ND-0.07 | 1 | |
| Zinc | С | А | <bc-4< td=""><td></td></bc-4<> | | |

Table 9.3-13. Summary ranges of chemical concentrations of elements in RCRA EPA extracts from gasifier ashes, mg/l (Ref. 8).

^aThe code used in this table to identify source tests is as follows: A, Chapman; B, Wellman-Galusha (Fort Snelling); C, Wellman-Galusha (Glen Gery); D, Riley; E, Lurgi type (Kosovo); F, Texaco (Ruhrchemie); G, Lurgi (SASOL 1); H, IGT U-GAS; I, KRW-WY subbituminous coal; J, KRW-Pittsburgh #8; K, KRW-ND lignite; L, Foster-Wheeler/STOIC.

 $^{\rm b}$ <BC = less than or equal to blank concentration.

^cAll analyses below detection limit.

^dMC = major component.

^eND- not detected.

In view of regulatory trends, improved NO_X control methods may be needed in conjunction with hot-gas cleanup systems currently being developed for application to IGCC power generation. High-temperature pollutant control offers the significant advantage of eliminating the need to quench and subsequently treat the condensables from gasifier products. While recent DoE research on high-temperature removal of sulfur and particular matter appears to be quite promising, levels of NO_x emissions are similar to those currently required for new coal-fired power plants (i.e., about 0.6 lb/MBTU). Thus, additional efforts are warranted on high-temperature removal systems to achieve the much lower levels of NO_x emissions currently obtainable with low-temperature gas-treatment processes and commercial flue-gas treatment systems.

<u>،</u> ۰

and the second s

: .

: :

í

Other potential air pollutants from coal-gasification processes are largely fugitive in nature. Here, the need for or viability of additional control technology remains speculative and large a matter of future regulatory developments. In these cases, more complete characterizations of fugitive organic and inorganic materials are the first step required to assess the need for additional controls.

9.3-3B. Water Pollutants

Wastewater-treatment systems at coal-gasification plants are designed primarily to deal with the quench-condensate stream plus smaller streams such as those from acid-gas removal-processes, ash sluicing, etc. Several steps are common to wastewater-treatment systems. These include the stripping and recovery of the ammonia and phenols, which represent potentially useful by-products. This step is typically followed by a biological oxidation process to remove additional organics. In some instances, there may be added still another polishing operation such as filtration through activated carbon.

As noted, requirements for coal-gasification wastewater-treatment presently depend on state and local regulations. At plants subject to zerodischarge regulations, treated waters and waste sludges typically are sent to an impermeable solar evaporation pond in regions where rainfall levels are relatively low. However, this method is not viable in many parts of the country. In these cases, some allowable discharge may be permitted, depending on local circumstance; otherwise, alternative methods of disposal involving wastewater recycle must be used. No generalizations are possible at this time since US experience is extremely limited.

9.3-3C. Solid Waste

Disposal of gasification-plant solid wastes generally involves a conventional sanitary landfill with an impermeable liner to prevent leaching into groundwater. As noted earlier, waste disposal methods are determined principally by whether or not wastes are classified as hazardous by Federal or state agencies. To the extent that future research leads to innovative means of utilizing coal-gasification wastes in ways that are economically productive, the uncertainties and costs of dealing with solid-waste disposal problems may be greatly ameliorated. Additional discussions of the use and disposal of ash from gasifiers are given in Sec. 13.2.

9.4. Experience at Commercial Facilities

In recent years, two commercial facilities have come on-line in the US, which provide the most up-to-date experience in dealing with environmental problems of coal gasification. These facilities are the Great Plains coal-gasification project in North Dakota (producing SNG) and the Cool Water gasification project in California (producing electricity in an IGCC). Here, we briefly highlight some of the environmental control issues and performance data that are available from these plants.

9.4-1. The Great Plains Gasification Plant

The Great Plains facility represents the first US plan constructed to demonstrate the production of SNG at a commercial scale. Despite the financial problems surrounding operation of the plant in the current market environment, it remains a technological success insofar as production of pipeline-quality gas is concerned. Environmentally, however, Great Plains also has demonstrated the potential pitfalls of applying off-the-shelf technology to new situations. In this case, the Stretford unit employed for sulfur removal has failed to operate as anticipated, with the result that emissions have not complied with SO_X regulations.⁹ The problem is generally attributed to the presence of trace compounds in the gas stream which adversely affect Stretford process chemistry and catalyst performance. After many months of study, however, no solution has yet been found and the plant

continues to operate under a special variance from the North Dakota Pollution Control Agency.

Other environmental control systems at Great Plains appear to be performing adequately, though all details of environmental monitoring have not yet been made public. Since the Great Plains facility employs a tar-producing Lurgi gasifier, special attention has been paid to waste-water treatment and disposal. Cleaned waters from the wastewater-treatment facility are recycled as cooling-tower makeup-water since no discharge are permitted. Dewatered cooling-tower and wastewater treatment sludges are incinerated and disposed of with the solid residue by deep-well injection. Gasifier ash, however, is classified as non-hazardous and is disposed of in a conventional landfill. A detailed environmental monitoring program is being carried out as part of the current plant operation under the auspices of DoE.

9.4-2. The Cool Water Gasification Facility

The 100 MW_e Cool Water coal-gasification project produces condensates from an entrained-bed Texaco gasifier, which are treated in a sourwater stripper. The effluent is then sent to an evaporation pond along with clarified waters from the slag- and ash-handling system. Groundwater monitoring tests to date indicate no leakage around the evaporation pond or slag disposal areas.¹⁰ The gasifier slag at Cool Water has been designated as non-hazardous according to Federal and state criteria based on standard leaching tests for trace elements and organics. Typical results are shown in Table 9.4-1.

The performance of air pollution control systems at Cool Water has exceeded that needed to comply with applicable emission limits imposed by California. The principal emission sources are the stacks of the heatrecovery steam generator (HRSG) and the plant incinerator. Results of compliance testing and supplemental environmental monitoring for the steam-generator stack gases are shown in Tables 9.4-2 and 9.4-3, respectively. Emissions of SO₂, NO_x, and CO are significantly below allowable limits, with low to negligible levels of trace metals, organics, and other potentially harmful pollutants. Qualitatively similar findings result from com-

pliance and supplemental testing of the incinerator stack gases, as is shown in Tables 9.4-4 and 9.4-5.

| Ignitability
Corrosivity
Reactivity | |]
]
] | Negative
Negative
Negative | |
|-------------------------------------------|-------|---------------------------|----------------------------------|--------------------|
| RCRA EPA Param | eters | Leachate
concentration | RCRA
limit | Detection
limit |
| Arsenic, | mg/l | ND | 5.0 | (< 0.06) |
| Barium, | mg/l | 0.039 | 100.0 | |
| Cadmium, | mg/l | ND | 1.0 | (< 0.002) |
| Chromium (total), | mg/l | ND | 5.0 | (<0.005) |
| Lead, | mg/l | ND | 5,0 | (<0.08) |
| Mercury, | mg/l | ND | 0.2 | (<0.0004 |
| Selenium, | mg/l | ND | 1.0 | (<0.08) |
| Silver, | mg/f | ND | 5.0 | (<0.002) |

Table 9.4-1. Results of Cool Water solid-waste tests (Ref. 10).

(a) Gasifier slag: RCRA waste-testing results.

(b) Gasifier slag: State of California waste-leaching testing results.

| Parameter | | Leachate
concentration | California
limit | Detection
limit |
|------------------|------|---------------------------|---------------------|--------------------|
| Antimony, | mg/l | ND | 15 | (0,001) |
| Arsenic, | mg/f | ND | 5.0 | (0.003) |
| Barium, | mg/l | 25 | 100 | |
| Beryllium, | mg/f | ND | 0,75 | (0.001) |
| Cadmium, | mg/l | ND | 100 | (0.05) |
| Chromium, | mg/l | 1.6 | 560 | |
| Chromium (+6), | mg/f | ND | 5,0 | (0,005) |
| Cobalt, | mg/l | 0.14 | 80 | |
| Copper, | mg/l | 0.25 | 25 | |
| Fluoride, | mg/f | 3.8 | 180 | [|
| Lead, | mg/l | 0.36 | 5.0 | 1 |
| Mercury, | mg/L | ND | 0,2 | (0,0002) |
| Molybdenum, | mg/l | ND | 350 | (0.002) |
| Nickel (total), | mg/l | ND | 20 | (0,001) |
| Selenium, | mg/l | ND | 1.0 | (0,001) |
| Silver, | mg/l | ND | 5.0 | (0.002) |
| Thallium, | mg/l | ND | 7.0 | (0.002) |
| Vanadium, | mg/l | 1 | 24 | (0.003) |
| Zinc, | mg/l | ND | 250 | |
| LC-50 (96 hours) | mg/l | > 500 | | Lua |

ND = not detected.

 SO_2 control at Cool Water is obtained by using the Selexol acid-gas removal-process in conjunction with a Claus/Scot sulfur-recovery system. Sulfur levels in the gas are reduced by 95-97%. NO_x emissions are controlled through steam injection in the gas turbine. When normalized on coal-energy input, NO_x emissions are an order of magnitude below current New Source Performance Standards for coal-fired power plants. This level is comparable to emissions achieved by using selective catalytic reduction systems on coal-fired power plants in Japan and the FRG.

While the environmental control equipment at Cool Water has generally performed quite successfully, some aspects of the original design still remain to be demonstrated. For example, problems encountered during start-up required incinerating the off-gas stream from the waste-water treatment process rather than direct treatment in the Claus/Scot unit as designed. Similarly, some rerouting of plant wastewater and recycle streams directly to the evaporation pond was required to achieve adequate performance of the water-treatment facility. Understanding and correction of these problems is expected as plant operation continues.

ŝ

, ² 4

9.5. <u>Research Needs and Priorities</u>

We now present a summary of key recommendations related to the environmental control of coal-gasification facilities. These recommendations are framed by several general questions regarding the methods and cost of meeting current and future environmental control requirements: (i) Are adequate control technologies available to meet current environmental control requirements for surface coal-gasification facilites? Can the performance of such technology be predicted reliably to assure compliance with current requirements for air, water and solid waste emissions from commercial gasification processes? (ii) What are the anticipated trends in future environmental control requirements, and how will these affect future gasification technology in various applications? Is adequate technology and information available to handle potential future situations? (iii) What is the potential for significantly reducing the cost of environmental control through new process development and/or the development of improved control technology? What research is needed to pursue these opportunities?

Each of these issues provides a context for research recommendations. The scope of these recommendations is tailored to the mission of DoE's Surface Coal Gasification Program. Priorities are designated as either 1 (high) or 2 (lower).

9.5-1. Current Control Technology

Environmental research on coal gasification processes conducted over the past decade has been focused, to a large extent, on characterizing the chemical composition of gaseous, liquid and solid waste streams from various types of gasifiers. This procedure has aided the design of technology for air-pollution control, waste-water treatment, and solid-waste disposal, with the result that current environmental control requirements are generally met, albeit based often on empirical design criteria rather than fundamental understanding.

Recent experience also underscores the continuing need for more fundamental research on process factors related to environmnetal control. Examples from the two most recently commercialized US coal-gasification facilities serve to illustrate the general point that, while control technology is available to meet current environmental regulations, the performance of such systems cannot always be predicted reliably and, in some cases, falls short of the mark. Invariably, this problem reflects a lack of basic understanding of process and chemistry details relevant to environmental control-system design and performance. The two areas where additional research may be especially productive are in gaseous pollutant removal and water treatment/recycle systems. The following research recommendations are thus suggested with priority 2: (i) Basic research is needed to obtain better understanding of the process chemistry related to the control of gaseous pollutants. The chemistry of sulfur removal from complex gas mixtures, including the effects of trace compounds found in coal-gasification plant processes, is a particular area of concern. (ii) Fundamental research is similarly needed on gasification-process water-chemistry, particularly in the context of waste-water recycle systems (which offer the potential for waste elimination). This research should provide a basic understanding of

the reactions of species and the fate of contaminants common to coal-gasification process condensates and wastewaters.

9.5-2. Future Environmental Requirements

Our earlier discussion showed that, over the past two decades, there has been a clear and continuing trend toward more stringent environmental control requirements for energy-conversion processes of all types. In recent years, environmental requirements have become more comprehensive in scope, covering emissions to all environmental media (air, water and land). At the same time, the level of sophistication with which potential pollutants are identified, measured, and regulated has also increased. While the nature of future environmental requirements inevitably remains speculative, the following-general trends are likely to affect coal gasification processes: (i) Control of criteria air pollutants (those originally and a second sec

;

: . ; . ;

11 } }

; '...

1

| Parameter | Units | Emission
limit | 1984
Test | 1985
Test |
|---------------------|----------------------------|-------------------|--------------|--------------|
| Sulfur dioxide | lb/hr | 35 | 33.1 | 16.8 |
| Nitrogen oxides | lb/hr
ppmv @ 15% oxygen | 140
50 | 61.2
22.8 | 68.9
25 |
| Carbon monoxide | lb/hr | 77 | . 2.9 | 3.7 |
| Fluoride | lb/hr | None | 0.0053 | NR. |
| Mercury | lb/hr | None | ND | NR |
| Beryllium | lb/hr | None | ND | NR |
| Sulfuric acid mist | lb/hr | None | 2,7 | NR |
| Particulate loading | lb/hr | None | 1.23 | NR |

Table 9.4-2. EPA performance-test results for the Cool Water HRSG stack gases (Ref. 10).

^aApproval to construct/modify a stationary source: 9 December 1981, EPA Region II.

ND = not detected at the following detection limits: mercury (<0.000065 lb/hr) and beryllium (<0.00016 lb/hr).

NR = not required for the 1985 performance tests.

| Environmental parameter | Units | Mean
value | Detection
limit |
|--------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|------------------------------------------------------------------------|----------------------------------|
| Carbon monoxide
Carbon disulfide
Carbonyl sulfide
Hydrogen sulfide | bburn
bburn
bburn
bburn | l
ND
ND
ND | (<0.025)
(<0.025)
(<0.025) |
| Ammonia
Hydrogen cyanide | ppmv
ppmv | 6
0.01 | |
| C2-C6 Hydrocarbons
Benzene | ppmv
ppmv | ND
ND | (<1)
(<1) |
| Hydrogen bromide
Hydrogen chloride
Hydrogen fluoride | ppmv
ppmv | 0.33
0.73
0.21 | |
| Radon-222 | pCi/L | 0.23 | |
| Volatile trace elements detected | | | |
| Boron
Calcium
Chromium (total)
Copper
Iron
Mercury
Nickel (total)
Silicon
Zinc | ppmv
ppmv
ppmv
ppmv
ppmv
ppmv
ppmv
ppmv | 0.14
4.1
0.063
0.087
0.45
0.0067
0.32
7.6
0.49 | |
| Organic compounds detected | | None | |
| | | | |

| Table 9.4-3. | Cool Water | HRSG stack | gases: | supplemental | environmental | data | (Ref. 1 | 0). |
|--------------|------------|------------|--------|--------------|---------------|------|----------|-----|
| • • | | | | | | | v | |

ND = not detected.

Table 9.4-4. EPA performance-test results for the Cool Water incinerator-stack gases (Ref. 10).

| Parameter | Units | Emission
limits | 1984
Test | 1985
Test |
|--------------------|-------|--------------------|--------------|--------------|
| Sulfur dioxide | lb/hr | 4.4 | 3.2 | 3.4 |
| Fluoride | lb/hr | None | 0.06 | NR |
| Mercury | lb/hr | None | 0.00015 | NR |
| Beryllium | lb/hr | None | ND | NR. |
| Sulfuric acid mist | lb/hr | None | 0.0002 | NR. |

ND = not detected at a beryllium detection limit of <0.000002 lb/hr.

NR = not required for the 1985 performance test.

.

| Environmental parameter | Units | Mean
value | Detection
limit |
|----------------------------------|-------|---------------|--------------------|
| Carbon monoxide | ppmv | 26 | |
| Carbon disulfide | ppmv | ND | (<0.025) |
| Carbonyl sulfide | ppmv | ND | (<0.025) |
| Hydrogen sulfide | ppmv | ND | (<0,025) |
| Ammonia | ppmv | 18 | |
| Hydrogen cyanide | ppmv | 0.014 | |
| Nitrogen oxides | ppmv | 64 | |
| C2-C6 hydrocarbons | ppmv | ND | (<1) |
| Benzene | ppmv | ND | (<1) |
| Hydrogen bromide | ppmv | 0,26 | |
| Hydrogen chloride | ppmv | 1.5 | |
| Hydrogen fluoride | ppmv | 0.072 | |
| Radon - 222 | pCi/L | 0.56 | |
| Volatile trace elements detected | | | |
| Boron | ppmv | 0.22 | |
| Calcium | ppmv | 2.5 | |
| Chromium (total) | ppmv | 11 | 1 |
| Cobalt | ppmv | 0.051 | |
| Iron | ppmv | 7.8 | 1 |
| Magnesium | ppmv | 1.2 | |
| Manganese | ppmv | 0.34 | |
| Mercury | ppmv | 0.12 | İ |
| Nickel (total) | ppniv | 62 | 1 |
| Silicon | ppmv | 1.7 | |
| Sodium | ppmv | 0.63 | |
| Titanium | ppmv | 0.15 | 1 |
| Zinc | ppmv | 0.37 | |
| Organic compounds detected | | None | |

Table 9.4-5. Cool Water incinerator-stack gases: supplemental environmental data (Ref. 10).

0

÷,

ļ,

÷

1.

regulated by the 1970 Clean Air Act, e.g., SO_2 , particulate matter, NO_x , HCs, and photochemical oxidants) will continue to be important. Recently, the NSPS for combustion-related pollutants have tended to become more stringent as control-technology capabilities have improved. In terms of future developments, the commercialization of technology yielding much lower emissions of NO_x at coal-fired power plants than were heretofore required may compel further tightening of current NSPS requirements in the future, particularly if NO_x emissions prove to be implicated in environmental issues such as acid rain. (ii) Hazardous and toxic air pollutants are likely to become more heavily regulated in response to concerns over their health and ecological impacts. In the context of coal-gasification processes, this problem could affect emissions of heavy (trace) metals and organic compounds emitted in small quantities. (iii) Zero discharge of waste-water contaminants can be expected to continue to be the prevailing philosophy guiding regulatory requirements at the Federal, state and local levels. This requirement could have significant implications for commercial coal-gasification facilities in parts of the country where relatively simple methods such as solar evaporation ponds cannot be used. (iv) The disposal of solid as well as liquid wastes will come under increasing scrutiny to ensure that waste materials by-products and potential leachates are environmentally benign. Criteria defining hazardous and toxic substances are likely to evolve as new measurement techniques and research results become available.

Research recommendations flowing from these observations include the following with priority 1: (i) Sustained research is needed to characterize emissions of trace metals, organic compounds and other potentially hazardous or toxic substances to air, water and land emanating from coal-gasification process streams, control technologies, fugitive emission sources, and leachates. (ii) Continued research is similarly needed in the areas of solid and liquid waste management, particularly the characterization of wastes under evolving RCRA criteria, and the utilization of solid residues as by-products rather than wastes. Understanding of the fate of organic and inorganic contaminants in the environment, both near-source reactions and longe-range transport, is needed.

9.5-3. Advanced Control Technology

Environmental-control systems currently account for a significant portion of total coal-gasification process-costs, so that high priority must be assigned to novel or advanced methods for reducing these costs while maintaining environmental quality standards.

The ability to eliminate or substantially simplify environmental control processes will depend, in part, on the gasifier design and perhaps, more substantially, on process application. Thus, processes yielding gas for use at room temperature invariably produce condensates requiring some degree of waste-water treatment, in addition to gaseous pollutant removal (although gasifier types such as entrained beds produce inherently cleaner condensates than others, e.g., tar-producing fixed-bed gasifiers).

On the other hand, gasifier applications for electric power generation offer the potential for significant simplification of environmental control systems by using hot-gas cleanup. Removal of pollutants at high temperatures, followed by combustion of the gaseous products, not only yields improved process efficiency but also eliminates several unit operations required for low-temperature processing (e.g., waste-water treatment). The ongoing DoE research program on hot-gas cleanup offers an excellent opportunity for major improvements of this nature. Our priority 1 research recommendations are: (i) Current DoE research on hot-gas cleanup is important, generally well-focused, and deserving of strong continued support. Key research needs have been identified and are being pursued to develop viable means of particulate and sulfur removal at high temperature using gas treatment and/or in-bed removal processes. (ii) Additional research appears to be needed to ensure that NO_y emissions with hot-gas cleanup systems can be controlled to the same degree that is achievable with current low-temperature coal-gasification systems and combustion-gas treatment devices. Such levels are an order of magnitude lower than current NSPS requirements, but represent reasonable targets for on-going research and development.

t L

.

ŗ

ì

References

- S.B. Baruch and J.S. Feher, "Toxic Substances: Future Electric Utility Considerations," <u>Proceedings of the American Power Conference</u>, Vol.47, Illinois Institute of Technology, Chicago, IL. (1985).
- 2. E.S. Rubin and F.C. McMichael, Environ. Sci. Technol. 9, 112 (1975).
- J.P. Fillo and M.J. Massey, "Fate of Phenols During the Gasification of Coal," <u>Symposium Proceeedings Environmental Aspects of Fuel Conver-</u> <u>sion Technology IV</u>, Report No. EPA-600/7-79-217, PB880-134729, NTIS, Arlington, VA (September 1979).
- 4. R.G. Luthy, J.Water Pollution Contr. Fed. 53, 325 (1981).
- R.M. Felder and J.K. Ferrell, "Pollutants from Coal Conversion Processes," Report No. DoE/PC/30232-T8 to US DoE from North Carolina State University, Raleigh, NC (1983).

- M. Kilpatrick, "Coal Gasification Environmental Data Summary: Sulfur and Nitrogen Species, " Report No. EPA-600 /7-86-015b, US EPA, Research Triangle Park, NC (April 1986).
- F.J.Castaldi and F.D. Skinner, "Coal Gasification Environmental Data Summary: Low and Medium-BTU Wastewaters," Report No. EPA-600/7-86-015a, US EPA, Research Triangle Park, NC (April 1986).
- A.G. Eklung, "Coal Gasification Environmental Data Summary: Solid Wastes and Byproduct Tars," Report No. EPA-600/7-86-015c, US EPA, Research Traingle Park, NC (April 1986).
- 9. V.P. Sabin, "Progress Report on Great Plains Gasification Project," <u>Alternate Energy '86 Conference</u>, Council on Synthetic Fuels, Captiva Island, FL, May 1986; also, private communications with US DoE, Radian Corp., and ERT, Inc. (1986).
- R.W. Grover et al., "Preliminary Environmental Monitoring Results: Cool Water Coal Gasification Program," <u>National AICHE Meeting</u>, Boston, MA, American Institute of Chemical Engineers, NY (April 1986).

CHAPTER 10: COAL BENEFICIATION*

This chapter is an introduction to coal beneficiation. It includes a brief review of current commercial practices and several developmental coal-cleaning methods. Recent advances in coal beneficiation processes have been driven by environmental concerns and the desire to produce superclean or ultraclean coal to make coal-water slurry fuels. Coalwater slurry fuels are being developed as a potential replacement for No. 6 fuel oil in oil-fired power plants. Some of these techniques may also find applications in coal gasification.

Coal beneficiation research should focus on attaining a better understanding of coal morphology and on developing innovative coal-cleaning methods that can yield high ash and sulfur removals from coal in a cost-effective manner.

10.1. Background

Coal beneficiation is basic to coal-conversion processes because most of these technologies are designed to handle coals that have specific properties. Mined coal does not conform to these specifications. For example, Lurgi gasifiers require coal that is approximately 2 in to 1/4 in in size, while Koppers-Totzek gasifiers require coal that is 90% less than 200 mesh in size. It is evident that lower levels of impurities in the coal reduce cleanup required during conversion or post-conversion

^{*} This chapter has been prepared by Suman P.N. Singh, Chemical Technology Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831. ORNL is operated by Martin Marietta Energy Systems, Inc., under contract No. DE-AC05-840R21400 with the U.S. DoE. The author thanks R.E. Hucko (DoE, PETC) for assistance in providing recent information on developmental coal-cleaning technologies funded by PETC.

processing. Coal beneficiation has received far less attention than other cleanup technologies. As environmental laws become stricter, greater reliance is likely to be placed on coal beneficiation in order to comply with regulations.

Raw coal ranges in size from large rocks to dust. In addition to the organic coal matter, the mine product contains shale from mine partings, stray machine parts, pieces of lumber, water and ash, as well as other mineral impurities such as pyrites. The raw mine product is often referred to as run-of-mine (ROM) or as-mined coal.

Coal beneficiation is a generic term that is used to designate the various operations performed on the as-mined coal to make it more suitable for end-use application without destroying the physical identity of the coal. Coal beneficiation includes coal preparation and washing. In the past, when the primary need was for lump coal, coal beneficiation consisted of manual operations such as hand picking of coal lumps from the mine product. In recent years, the term coal beneficiation has been redefined to include the entire spectrum of operations, ranging from the relatively simple crushing and size classification operations (that are almost routinely performed on all coals used today) to rather elaborate chemical and microbial processes that are being developed to render the ROM coal more suitable for the end-use process.

The extent to which a coal is beneficiated is determined by several factors such as the ROM coal ash, sulfur, and moisture levels; end use; emissions regulations on the end-use facility; and market forces. For example, if the coal is to be burned in an existing utility boiler with soft emissions regulations, the extent of the beneficiation is likely to be minimal and may consist only of size reduction and rock removal. However, at the other extreme, if the coal is a raw material for the manufacture of a high-value product (e.g., activated carbons or carbon electrodes), the level of beneficiation may be quite extensive and a much higher coal cleaning cost is justified because of the higher value obtained for the cleaned-coal product. Beneficiating the coal has the following advantages: (i) The cleaned coal is more uniform in size, composition, calorific value, and moisture content. When the cleaned coal is consumed, it results in more reliable and uniform operation. (ii) By reducing the ash in the coal, beneficiation contributes to reduced slagging and fouling in the furnace, thus increasing boiler on-steam availability, decreasing

maintenance, and lowering overall operating costs. (iii) Reducing the sulfur level in the coal reduces sulfur oxide emissions after combustion and, thus, decreases flue gas desulfurization (FGD) requirements. This decrease may translate into reduced production costs. Sulfur oxide emissions from power plants have been implicated as one of the major precursors of acid precipitation (acid rain).¹ (iv) Removal of the associated mineral matter and sulfur from the ROM coal results in lower transportation costs for shipment of the same energy value, higher combustion efficiency, and reduced ash disposal and FGD requirements for the same furnace calorific value. (v) The moisture content of the cleaned coal may be reduced, thereby yielding improved coal handling and burning characteristics. This procedure leads to more efficient fuel use because less energy is wasted in drying the coal. (vi) Beneficiation can be used to tailor the coal to customer specifications, thus creating a higher value for the product. (vii) Beneficiation may allow the use of many high-sulfur and high-ash coals which could not otherwise be used, thereby increasing the usable energy-resource base.

1.2.1.1

Coal beneficiation also has negative aspects. The major disadvantages are as follows: (i) Beneficiating the coal results in reduced marketable coal output from the mine product because some of the coal is discarded with the refuse. (ii) Beneficiating the coal involves capital and operating costs that must be recovered and result in higher prices for the product coals. (iii) The beneficiation-plant operator is confronted with the problems and cost of disposing of the plant refuse in an environmentally acceptable manner. These problems are either absent or significantly reduced when as-mined coal is shipped directly to the consumer.

The advantages of some coal beneficiation generally outweigh the disadvantages. A study by Hoffman et al.² indicated that coal beneficiation, combined with FGD, appeared to offer the most economical means of achieving sulfur oxides emission control for coal-burning facilities at an SO₂ emissions limit of 1.2 lb/10⁶ BTU. As emissions regulations become more stringent, coal beneficiation will become more attractive. For some coals, beneficiation may eliminate the need for FGD systems.²

Coal is expected to provide an increasing share of National energy needs. According to the U.S. Bureau of Mines,³ coal use for power generation alone in the US is expected to rise from 52% in 1986 to 63% by the year 2000. Future coal-utilization plants will be required to meet increasingly stringent environmental regulations that are motivated by acid precipitation and solid-waste disposal concerns. The supply of compliancequality coal may be limited; if so, coal beneficiation will play an increasingly important role in meeting the Nation's energy needs in an environmentally acceptable manner.

Summaries of current coal beneficiation methods and recent advances in coal cleaning are given in the following sections and will provide a perspective of the technology. References 4-7 may be consulted for further details.

10.2. Current Commercial Practice

Current commercial coal preparation relies primarily on physical (mechanical) processes to beneficiate the coal. The chemical, microbial, and other novel coal beneficiation technologies of recent origin are at various levels of process development. None of the novel methods have found commercial application because their use is not yet cost-effective.

Physical beneficiation processes involve gravity separation, centrifugal action, the use of surface tension, and magnetic separation to separate lower-density coal matter (specific gravity ~ 1.2) from higherdensity impurities (specific gravity > 2.5). Physical beneficiation processes generally consist of combinations of some or all of the following unit operations:

Size reduction - This operation consists of reducing the size of the coal received from the mine (often 24 in x 0) to more manageable dimensions. Size reduction is usually accomplished by using equipment such as rotary breakers, impact mills, and single- and double-roll crushers. Sketches of some typical size-reduction equipment are shown in Fig. 10.1.

Size Classification - This operation consists of segregating the coal into various size fractions to facilitate downstream processing. Both the ROM coal and the crushed product may be classified into different size fractions. Equipment for size classification includes stationary, vibrating, and cross-flow screens and classifying cyclones. Figure 10.2 presents some sketches of typical size-classification equipment.

Cleaning - This operation, which is at the heart of many coal-beneficiation plants, primarily involves separation of the physically attached sulfur compounds and/or mineral impurities (of higher specific gravities) from the coal (of lower specific gravity). It is often accomplished by using jigs, cyclones, and concentration tables, which utilize a combination of frictional, gravitational, and centrifugal forces to effect an apparent density-differential separation between the coal and its sulfur and mineral impurities. Schematics of typical equipment used in coal-preparation plants are given in Fig. 10.3.

Another commonly used cleaning method is heavy-medium separation, in which we employ an intermediate specific-gravity suspension of fine, dense minerals (e.g., magnetite or sand) in water to effect the desired separation. In general, heavy-medium separation results in a fairly high recovery of the clean coal, although the clean coal must be separated from the dense medium before it can be either used or processed further. Because of this additional processing step, heavy-medium separation incurs higher operating costs than similar beneficiation processes using only clear water.

é i V

1.1.1.1.

; ;;

Froth flotation processes are also generally used to beneficiate very fine-size (28 mesh x 0) fractions. In froth flotation, the coal is beneficiated in a liquid medium (water) by finely dispersed air bubbles which are injected into the coal bath and float the very fine, clean-coal particles to the liquid surface, where they are mechanically skimmed. A surfactant is generally added to the coal bath in order to render the coal more hydrophobic and thereby facilitate coal flotation. Impurities associated with the coal sink to the bottom of the vessel, from which they are then removed for eventual disposal.

Drying - This unit operation involves reduction of the coal moisture-content to the desired value. Various types of equipment such as screens, filters, centrifuges, and thermal dryers are used to dry the coal, depending on the moisture content desired in the product coal. Figure 10.4 is a sketch of a fluidized-bed coal-dryer installation.



(a) Rotary breaker



(b) Single-roll crusher



(c) Hammer impact mill



•



(a) Double-deck, mechanically vibrated screen



(b) Mechanically vibrated bar grizzly

, ·

1. 200 × 202 × 50 ×



(c) Sieve bend

Fig. 10.2. Sketches of typical size-classification equipment used in coal-preparation plants.



(b) Concentrating table



Fig. 10.3. Sketches of typical cleaning equipment used in coal preparation plants.

342

Coal-preparation plants use combinations of these unit operations in treating different size fractions of the raw coal, depending on specifications of the coal to be produced. The minimal level of beneficiation consists of size reduction, some size classification, and removal of trash and some mineral matter but essentially no sulfur reduction. At the minimal level, coal yields and energy recovery range from 98 to 100% of the ROM coal. Full-scale beneficiation consists of a thorough cleaning of the as-mined coal and involves all of the specified operations. Cleaned coal yields at this level range from 50 to 80%, with energy recoveries between 75 and 95% of the as-mined coal.

Coal-beneficiation costs vary because they are project- and coal-specific. Current coal-preparation plants are largely customized for specific applications. Generally, coal-preparation costs range between \$5 and \$15 per ton of cleaned coal, depending on the level of beneficiation. ę.

è

.

;

10.3. <u>Recent Advances in Coal Cleaning</u>

Advances in coal cleaning have historically tended to be evolutionary rather than revolutionary. The energy crisis of the 1970s, together with increased environmental activism, has led to the development of several novel approaches to coal cleaning. Most of the new methods are based on chemical processes to remove more of the impurities from coal than is possible with conventional mechanical techniques. Several novel physical and some microbial methods were also examined during this period. A list of these novel technologies is presented in Table 10.1. However, because of improving market conditions for petroleum products in recent years, the national interest in developing a viable synthetic fuels industry has withered and further R & D on most of these novel technologies has essentially ceased.

The impetus for recent advances in coal-cleaning methods has come mainly from the drive to produce superclean or ultraclean coal for use in coal-water slurry (CWS) fuels and concerns that emissions from coal-fired power plants are major precursors of acid rain. CWS fuels typically contain 70 to 75 wt% coal pulverized to -200 mesh, 24 to 29 wt% water, and ~ 1 wt% chemical additives to provide storage stability and improved flow characteristics.⁸ The coal used in CWS fuel must contain only very low levels of ash (< 5%) and sulfur (< 1%). As a result, new deep-coal-

cleaning methods are being developed. Table 10.2 lists some of these. Further details on these new processes may be obtained from Refs. 9-15.

10.4. Conclusions

Coal beneficiation has not received the attention given to coal combustion, gasification, or liquefaction for the following reasons: (i) Beneficiation is often regarded as a part of the overall conversion process. (ii) Coal preparation lacks the scientific appeal of the other technologies. (iii) Because coal is a commodity, market forces dictate its production at as low a cost as possible. Since beneficiation increases the coal cost, its use is minimized as far as possible.



Fig. 10 4. Sketch of a fluidized-bed coal-dryer installation.

(iv) Past emissions regulations could generally be met by installing controls downstream of the conversion step. However, while FGD is a plausible emission-control method, it is expensive and has less-thandesired reliability. As emission regulations are tightened, coal beneficiation may be required.

| Chemical beneficiation processes |
|-----------------------------------|
| Meyers |
| Battelle hydrothermal |
| Ledgemont |
| KVB |
| PERC oxidative desulfurization |
| JPL low-temperature chlorinolysis |
| ARCO promoted oxydesulfurization |
| |
| |

Table 10.1. Novel coal-beneficiation technologies developed during the 1970s and early 1980s.

· - - · · · · ·

• • • • • • •

· · · ·

し、こんに

••••

C. e.

;;

ŝ

1

Table 10 2. Novel developmental coal-cleaning processes of recent origin.

| Technology | Developer | Reference(s) |
|------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|--------------|
| Physical Methods | | |
| Ultrasonic comminution | Energy Minerals Research Co. | 9,10 |
| Dry electrostatic separation | Advanced Energy Dynamics,
Inc. | 10 |
| Microbubble flotation | Bechtel National, Inc./
Bergbau Forschung GmbH | 10 |
| Otisca-T process | Otisca Industries Ltd. | 11 |
| Chemical Methods | | |
| Microwave treatment | General Electric Co./TRW | 10 |
| Gravimelt process | TRW | 12,13 |
| Supercritical extraction | Consolidated Natural Gas
Research Co. | 14 |
| Aqueous cupric chloride treatment | ORNL | 15 |
| Sodium hypochlorite treatment | Signal Research Co. | 15 |
| Microbial Methods | | |
| Microbial coal cleaning using <u>thiobacillus</u>
<u>ferrooxidans</u> , <u>sulfolobus</u> <u>acidocaldarius</u>
and other bacteria | Atlantic Research Corp.,
Institute of Gas Technology,
Lehigh University | 10 |

S. S. J. P. S.

70 Y 45

-21

14

15 6234

steel .

and the second

Ň

Sylve.

Several authors^{2,4,16,17} have shown that coal beneficiation, either alone or in combination with FGD, is a cost-effective sulfur oxide emissions control strategy. The authors of a recent study¹⁸ have shown that the use of specially beneficiated coal in a moving-bed gasifier leads to sharp (70 to 90%) reductions in sulfur-emission levels and tar formation and to significantly higher (~ 83%) gasification efficiency.

While R & D on chemical coal-cleaning processes has not yet led to a commercial process, R & D on physical methods is responsible for development of the Rotating Probability (RO-PRO) screens and the BATAC jig. Chemical processes that reduce coal-ash and sulfur contents to very low levels are, at present, too expensive and, therefore, R & D effort should focus on cost reductions for these technologies.

DoE research efforts should be directed toward two aspects of coal beneficiation: (i) gaining a better understanding of coal morphology and (ii) developing innovative coal-cleaning technologies through the small (e.g., 20- to 50-1b/hr) pilot-plant scale. Research on coal morphology is important in order to guide the development of more efficient coal-cleaning methods and should receive perhaps 30% of the funds allocated for coal beneficiation R & D.

References

- Interagency Task Force on Acid Precipitation, "National Acid Precipitation Assessment Program Annual Report 1984 to the President and Congress," p. 34, Washington, D.C. (1985).
- L. Hoffman, S.J. Aresco, and E.C. Holt, Jr., "Engineering/Economic Analyses of Coal Preparation with SO₂ Cleanup Process for Keeping High Sulfur Coals in the Energy Market," EPA-600/7 -78-002, U.S. Environmental Protection Agency, Washington, D.C. (1978)
- 3. N.P. Chironis, Coal Age <u>21</u>(2), 60 (1986).
- P.J. Phillips, "Coal Preparation for Combustion and Conversion, Final Report," EPRI-AF-791, EPRI, Palo Alto, CA (May 1978).
- S.P.N. Singh and G.R. Peterson, "Survey and Evaluation of Current and Potential Coal Beneficiation Processes," ORNL/TM-5953, ORNL, Oak Ridge, TN (March 1979).

- T.F. Edgar, <u>Coal Processing and Pollution Control</u>, Gulf Publishing Company, Houston, TX (1983).
- Y.A. Liu, ed., <u>Physical Cleaning of Coal:</u> Present and Developing <u>Methods</u>, Marcel Dekker, Inc., New York, NY (1982).
- 8. T. Moore, EPRI J. <u>9</u>(6), 6 (1984).
- 9. S.R. Taylor, W.B. Tarpley, Jr., and G.R. Moulder, "Ultrasonically Enhanced Size Reduction of Coal," pp. 256-68, Proceedings of the 5th International Symposium on Coal Slurry Combustion and Technology, Vol. 1, Tampa, FL (April 25-27, 1983).

÷. ,

Ç.

3

•

¥.,

.....

; ; .`

- R.E. Hucko, DoE/PETC, "Monthly Status Report January 1986," memorandum to G.E. Voelker, DoE Program Manager for Coal Preparation, Feb. 6, 1986.
- D.V. Keller, Jr., "Coal Refining by Physical Methods for the Preparation of Coal Slurries with Less than One Weigh Percent Ash," pp. 269-78 in Ref. 9.
- 12. R.A. Meyers, L.C. McClanathan, and W.D. Hart, "Development of the TRW Gravimelt Process, pp. 112-14 in Proceedings of the 2nd Annual Pittsburgh Coal Conference, Pittsburgh, PA (September 16-20, 1985).
- 13. J.F. Jones, R.A. Meyers, L.C. McClanathan, and W.D. Hart, "Applicability and Cost of Gravimelt Coal for Coal Liquid Mixtures," in Proceedings of the 3rd Annual Coal Liquid Mixtures Workshop, Technical University of Nova Scotia, Halifax, Nova Scotia, Canada (October 12-14, 1983).
- 14. G. Carli, "Coal Beneficiation by Expansion of a Supercritical Coal/Water Slurry, pp. 306-15 in Proceedings of the 7th International Symposium on Coal Slurry Fuels Preparation and Utilization, New Orleans, LA (May 21, 1985).
- 15. Y.A. Attia, ed., <u>Coal Science and Technology 9. Processing and</u> <u>Utilization of High Sulfur Coals</u>, Elsevier Science Publishers, B.V., Amsterdam, The Netherlands (1985).
- 16. J.D. Kilgroe, "Uses of Coal Cleaning for Air Quality Management," paper presented at the Second Conference on Air Quality Management in the Electric Power Industry at the University of Texas at Austin Center for Energy Studies, Austin, TX (Jan. 22-25, 1980).
- 17. M.J. Laurila, Coal Mining 22(9), 36 (1985).
- H.N. Conkle et al., "Experimental Testing of a Catalytically Treated Coal in a Moving Bed Gasifier," EPRI-AP-4506, EPRI, Palo Alto, CA (March 1986).

CHAPTER 11:

í.,

.....

.....

1.1.1

いいたいがいい

- "Emeric" Sec.

;

OPTICAL DIAGNOSTICS FOR <u>IN</u> <u>SITU</u> MEASUREMENTS IN COMBUSTION ENVIRONMENTS CONTAINING COAL PARTICLES*

Abstract - Much of the recent progress in understanding pulverized coal combustion is attributable to the use of new optical diagnostics for in situ measurements of gas temperatures, concentrations of major and trace gas species, particle-size distributions, particle-surface temperatures, and gasand particle-velocity fields. In addition, advanced methods, which are now undergoing laboratory development and validation, hold promise for measuring in situ the composition of both entrained particulates and deposits on material surfaces exposed to coal-combustion environments. There is great potential for more widespread application of these techniques in the future, particularly in laboratory bench-scale studies. We describe some of the more promising of these new optical methods. This is not intended to be a comprehensive review but rather draws heavily on many of our own experiences. The emphasis is on studies of entrained-flow environments derived from the combustion of pulverized coal. These environments are hostile with regard to in situ optical interrogation in the sense that they are characterized by high temperatures, high particulate loadings and flow turbulence, and require the use of windows that limit optical path lengths and signal-to-noise ratios.

* This chapter has been prepared by D.R. Hardesty and D.K. Ottesen (Sandia National Laboratory, Livermore, CA 94550) and was presented by the authors at a NATO Workshop on "Fundamental Physical Chemical of Pulverized Coal Combustion," Les Arcs, France (July 30, 1986). The instrumentation requirements for coal gasification are similar to those for direct coal combustion and experimental facilities are interchangeable.

After presenting an outline of diagnostics requirements, we present a framework, in terms of two principal classes of flows, for considering the relevance of various techniques in applications involving combustion flows with pulverized coals. We discuss advantages and limitations of <u>in situ</u> methods for (i) measuring gas-phase temperatures; (ii) measuring the major and minor gas species concentrations; (iii) measuring particulate properties, including sizes, temperatures, velocities, number densities, and flux; and (iv) measuring gas velocities in the presence of a broad distribution of particle sizes. Special consideration is given to our most recent work on the application of laser spark-spectroscopy for <u>in situ</u> measurement of the elemental composition of entrained particulates.

11.1. Introduction

Recent progress in understanding pulverized-coal combustion is attributable, in part, to the use of new optical diagnostics for <u>in situ</u> measurements of gas temperature, concentrations of major and trace-gas species, particle-size distribution, and gas- and particle-velocity fields. There is great potential for more widespread application of these techniques in the future, particularly in laboratory bench-scale studies. In addition, advanced methods, which are now undergoing laboratory development and validation, hold promise for <u>in situ</u> measurement of the composition of both entrained particulates and deposits on material surfaces exposed to coal-combustion environments. We emphasize the features of optical diagnostics that have the greatest potential for near-term application to detect the properties of gaseous or particulate species in small-scale pulverized-coal (PC) combustion experiments. These experiments contain many of the hostile features of practical combustors (e.g., high temperature, high particulate loadings, and flow turbulence).

11.2. <u>Diagnostics Requirements</u>^{1,2}

Perhaps the key ingredient in defining the applicability of any optical technique for PC studies is the degree of temporal and spatial resolution required. All other requirements are derived from the specific parameters to be measured and depend upon the diagnostic system itself. To order this discussion, we define two classes of PC combustion flows as shown schematically in Fig. 11.2-1. Class I includes all wall-bounded, laminar and turbulent duct flows, while Class II refers to mixing, ducted, laminar, or turbulent shear flows. Unconfined, premixed or diffusion flames are special cases of Class I or Class II, respectively. With the notable exception of suspended or electrodynamically-levitated particle experiments, these represent the two limiting cases of the myriad of possible laboratory-scale PC combustion studies. Clearly, some methods are useful in some applications but have little advantage over more conventional methods (e.g., intrusive probes for thermometry and gas or solids extractions) in others. Where the measurement needs suggest that an optical technique be applied, consideration of the key features of the two classes of flows in Fig. 11.2-1 helps to define diagnostics requirements.

11.2-1. Characteristics of Class I Flows

The important features of Class I flows include: (i) well mixed gases; (ii) temporal steadiness; (iii) negligible pressure gradients; and (iv) plug flow, where reaction zones extend along the space coordinate or are very small or near zero in extent (e.g., in the post-flame zone). Mean radial gradients in temperature, velocity, or particulate loadings are either negligible (distribution curve A) or at most are on the order of the transverse duct dimension (distribution curve B) due to, for example, a nearby bend in the duct. In some cases, smaller characteristic dimensions and steeper gradients arise due to the presence of surfaces inserted in the flow.

.

The range of gas-phase parameters for Class I flows is: temperature, 1100 to 2000 K; major species concerntrations (in mol%) from 0.03 (H_2O) to 0.8 (N_2); minor species concentrations from a few to 100 ppm for SO₃ and less than 2000 ppm for NO and SO₂. Concentrations of CO due to incomplete combustion may range from a few hundred ppm to several percent. In addition, at combustion temperatures, volatilization of some mineral species such as vanadium, sodium and potassium occurs. For typical amounts of



Fig. 11.2-1. Two principal flow regimes for PC combustion. Class I: wallbounded duct flows; Class II: mixing and ducted shear flows.
these species in the unreacted coal, the highest concentrations to be expected are on the order of 25 ppm for sodium and potassium and 1 ppm for vanadium. Concentrations of these mineral species in the tens to hundreds of ppm will occur after cooling and condensation.

As noted, an important feature of any coal-derived flow is the high loading density of entrained particulates including coal, char, free mineral matter, soot and fly ash. Mass-loading densities are typicially weighted toward the large particle sizes. Of special importance for optical measurements is the wide distribution of both size and particle number densities. Figure 11.2-2 summarizes several recent observations of the number-size distribution of particulates in a variety of typical steady combustion environments. Particle velocity is a function of the mass and size of the particle and may range from a few to a hundred m/sec. In general, particles of different sizes move at different velocities because of the slip with the gas stream.

. . .

۲ ۲

11.2-2. Diagnostics Considerations for Class I Flows

For these steady flows, requirements on temporal resolution are minimal; time-averaged measurements are adequate. An exception is the case where both the mean value and turbulent fluctuations of velocity are required, e.g., for heat-transfer estimates. Similarly, requirements on spatial resolution are generally not severe, e.g., none for flat(A) profiles or about 0.1 of the duct diameter for a skewed (B) profile. In view of these relaxed requirements on resolution, intrusive isokinetic probes (where sampling velocities match the mean gas flow velocity) may be valid diagnostic candidates. The alternative choice of an optical method would have to be based on other considerations such as the inherent errors and flow disturbances introduced by intrusive probes. For Class I flows, line-of-sight as well as spatially-resolved optical methods are generally applicable. Either may yield the desired information for a flat radial profile (A). However, most of the advance optical methods require tight focusing of laser beams, either in principle or to overcome natural signal to noise limitations. Thus, a spatially resolved measurement is obtained whether it is needed or not.



Fig. 11.2-2. Particle number densities and particle sizes for soot, PC fines and fly ash in combustion flows; see Ref. 1 for the literature citations given in the legend.

11.2-3. Characteristics of Class II Flows

The important features of CLass II flows include: (i) locally unmixed gases and particulates with potentially steep gradients in all properties; (ii) locally unsteady flow with substantial turbulent fluctuations; (iii) finite mean pressure gradients and three-dimensional flow, both in the mean and in the turbulent fluctuations; (iv) particle motion may have significant inertial components; and (v) the range of mean values for the concentrations of gaseous and particulate species is from zero to the levels indicated for Class I flows. Local zones of high temperature and high rates of chemical reaction can generate high levels of intermediate species such as the free radicals OH and C_2 . !

"I de la servicia a servicia

·: . . .

たいとれた

11.2-4. Diagnostics Considerations for Class II Flows

The unsteady, three-dimensional, steep gradient character of such flows generally precludes the application of line-of-sight optical diagnostics. The exceptions to this include visualization techniques that may be of use in whole flame observation and line-of-light indicators of gross flame behavior. The existence of regions of steep gradients and high turbulent intensities imposes severe constraints on diagnostics. High spatial resolution is required to measure local properties (on the order of 1 mm^3 for small geometries and perhaps 1 cm^3 for large flows). As indicated by the schematic of a typical local probability density function (PDF) of, e.g., gas temperature in the reacting shear layer, Class II flows have regions where fluctuations about the local mean value are bimodal; the conventional definition of the mean value may be very misleading. In such regions, high temporal resolution is required in addition to high spatial resolution. Adequate time resolution for Class I flows is likely to be on the order of 50μ sec. In other words, single-pulse measurements with pulse widths less than 50μ are dictated; the PDF must be constructed from an ensemble of such single pulse data. In some cases, such as for a singleparticle-counting diagnostic system, this process occurs naturally and the number of counts of particles in each size bin is stored. In other cases, as in any of the Raman scattering techniques, the diagnostic must be

specially configured to acquire single-pulse information. In still others, as in laser-Doppler velocimetry, an ambiguous jumble of information may be generated due to the difficulty of distinguishing true turbulent fluctuations from variations caused by the size dependence of particle velocity. Locally high concentrations of reaction intermediates (such as OH and C_2) may be exploited in some diagnostics to sense local temperature or zones of incipient soot formation. On the other hand, the presence of C_2 and other reaction-generated hydrocarbon species can have strong adverse noiseinducing consequences on laser-based-diagnostics.

In Class II flows, probe measurements of local values of gas temperature, species concentrations and particulate loadings are highly questionable from virtually every technical viewpoint. Without exception, it would be advantageous if a suitable, nonintrusive optical diagnostic with the required spatial and temporal resolution were available for measuring each important local property in Class II flows. As is discussed in the following sections, in principle, this is the case. In fact, however, there have been few validated measurements using advanced optical methods in flows where coal or coal slurry fuels have been used.

11.3. Gas-Phase Temperature Measurement

In this and in the next section, promising and principally laser-based optical methods for measuring the temperature and concentrations of major and minor gas species in Class I or II PC combustion are summarized.

11.3-1. Raman Scattering Techniques

Temperature measurement in flames using Raman spectroscopy has been an active area of research for more than a decade. For most applications of Raman scattering in combustion, temperatures are calculated from vibrational or rotational population distributions in N_2 , which is at high concentration levels in nearly all regions of air-fed flames. In addition, it has been demonstrated that the rotational and vibrational modes of N_2 are close to equilibrium with the translational mode for the great majority of

combustion situations. Raman scattering has the important advantage that the temperature can be calculated from relative scattering intensities for different transitions.

11.3-1A. Spontaneous Raman Scattering

Spontaneous Raman scattering (SRS) is a proven temperaturemeasurement technique and has been widely applied in clean flames. Incident photons (usually from a fixed-frequency laser) are scattered at frequencies which are shifted by the energy difference between two vibration-rotation levels. Temperature measurements are typically performed by using the ratios of the intensities of the Stokes (lower frequency) and anti-Stokes (higher frequency) signals or by resolving the Raman signal spectrally (using either Stokes or anti-Stokes lines) and fitting theoretical curves to the data. Application of spontaneous Raman scattering to luminous flames has been complicated by the weakness of the Raman signal relative to background emission. The presence of particles in combustion gases introduces severe problems for any SRS method. Incandescence from hot particles may swamp the weak SRS signal. In some cases, background-subtraction techniques, combined with high-power pulsed lasers and gated detection, may circumvent this continuous background problem. However, excessively high energy laser pulses heat particles above the gas temperature,³ causing additional radiation and fluorescence modulated at the laser frequency, radiation which cannot be eliminated by gated-detection and background-subtraction techniques. It appears that only one rather unique approach⁴ is suitable for making time-averaged SRS measurements in luminous, particle-laden flows. The system uses a cavity-dumped argonion laser of intermediate peak power (50-100 W) and short pulse length (20 ns), combined with a high repetition rate $(10^6 \text{ sec } -^1)$ to obtain moderate average power (0.5-1.0 W). The synchronous detection sampling gate is 25 ns. This system improves the average signal-to-background ration by a factor of 10 relative to a similar system using a 5 W cw laser. Flower⁵ validated the feasibility of making time-averaged temperature measurements in highly luminous flows by this method. Application of the technique is restricted to environments

which are steady over the time period required for the measurement (1 to 10 minutes with an optical multichannel detection system.)

11.3-1B. Stimulated Raman Scattering Techniques

Stimulated Raman scattering techniques have important advantages over spontaneous Raman techniques for probing luminous, particle-laden or turbulent flows. In the most widely developed method, coherent anti-Stokes Raman scattering (CARS), the Raman-scattered signal is emitted coherently, i.e., it has the laser-like directionality. Thus, much greater discrimination against background luminosity is possible. Further, signal levels are usually sufficiently high that temperature measurements are possible with a single laser pulse for both Class I and Class II flows. CARS requires two lasers, a pump laser and a Stokes laser. A CARS experiment is depicted schematically in Fig. 11.3-1. When the difference frequency between the pump laser ($\boldsymbol{\omega}_{p})$ and the Stokes laser ($\boldsymbol{\omega}_{s})$ corresponds to a Raman resonance (ω_s) of the probed species, a signal at the anti-Stokes frequency $2(\omega_n - \omega_s)$ is generated. The Stokes laser must be either tunable or broadband and is typically a dye laser. The response of the molecule to the pump and Stokes beams can be described in terms of the third-order resonant susceptibility. The susceptibility can be divided into a resonant part, which has a strong frequency dependance, and a nearly frequency-independent nonresonant component. The resonant and nonresonant signals interfere and the disappearance of the resonant signal into the nonresonant background determines the sensitivity limit for CARS. As will be shown, there are essentially two approaches, scanned CARS, a time-consuming method, and broadband CARS, a rapid and more promising approach for PC combustion studies. Much current research on broadband CARS is devoted to improving the accuracy and precision of single-pulse temperature measurements. The precision of the technique is presently limited by frequency noise in the broadband dye-laser spectrum.

Accurate modeling of CARS spectra is necessary to extract quantitative temperature and concentration information. Such modeling requires molecular linewidths and transition frequencies. The molecular susceptibility must be convoluted with the laser linewidth in order to com-pare theoretical and experimental spectra. The temperature is deduced by

least-squares fitting of computer-generated spectra to obtain the best match to experimental spectra. Because this least-square fitting is such a timeconsuming procedure, various fast algorithms have been developed for singlepulse broadband CARS temperature measurements.

and the second
i: -

t F

; [. [

:

<u>}</u>.

- 1.25 2.5 1.5 1.5 2.5

.

2.

11.3-1C. Application of SRS and CARS to Pulverized Coal Combustion

Although background flame emission is rarely problematical in CARS measurements, the interaction of the high-intensity laser beams used for CARS with particles in the flame causes difficulties. As has been noted, the laser radiation may heat particles to very high temperatures and cause laser-modulated particulate incandescence. Other, more subtle effects occur in particle-laden flows, particularly in the case of soot-laden environments. When soot particles are rapidly heated by laser absorption, C_2 concentrations increase considerably in the gas phase surrounding the particles. Interferences can arise in the CARS measurements as the result of laser-induced C_2 fluorescence. In flows seeded with coal slag, Beiting⁶ observed a coherent background signal in the region of the nitrogen spectrum, which interferes with CARS thermometry. The source of the background has not been fully explained.

Recently, Lucht⁷ completed the most systematic investigation to date of the applicability of CARS for gas-phase temperature and species concentration measurements in a PC combustion environment. Using a wellcontrolled, coal-seeded laminar flow reaction, CARS spectra of oxygen and nitrogen were successfully acquired and temperatures were determined from theoretical fits to nitrogen spectra. Significant spectral interferences were observed in the oxygen spectra because of laser-induced particle breakdown at high laser power. Lucht used the system shown in Fig. 11.3-1. The pump and Stokes beams were generated by a Molectron Nd:YAG laser and Quanta-Ray dye laser. The 532nm, frequency-doubled 10 Hz output of the Nd:YAG laser serves both as a CARS pump beam and as a pump for the dye laser (bandwidths are 0.1 and 0.2 cm⁻¹, respectively). The pump beam is split into two equal intensity beams; all three beams are focused on a common probe volume (4X0.2X0.2mm) by a 238-mm focal length lens. In this work, the narrowband dye-laser frequency was scanned across the Raman resonances of



Fig. 11.3-1. Schematic of experimental arrangement for scanned CARS diagnostics with a 2-channel system using in situ referenced background subtraction.⁷

oxygen or nitrogen to generate the CARS signal, which is focused on the entrance slit of a 1.5-m monochromator that is scanned synchronously with the dye laser. A photomultiplier (PM) tube detects the CARS signal, which is digitized and stored on a PDP 11/24 minicomputer. This time-consuming approach (30 minutes to acquire 600 frequency data points and 30 laser shots averaged at each point) has now been eliminated by using a broadband dye laser to obtain the entire CARS spectra in a single shot, with an optical multichannel analyzer (OMA) for detection rather than a PM tube; the time needed for data acquisition is reduced to a few seconds. The measurements were performed in a densely coal-seeded laminar flow reactor (100X25mm) enclosed with quartz windows. The laser beams traversed the 100-mm length, thus maximizing any effects such as absorption, which arise from propagation through the medium.

Typical results for oxygen and nitrogen spectra are shown in Fig. 11.3-2. With high pulse energies (26 mJ total pump and 5 mJ Stokes) signif-





Ì.

ار •

States and the states of the s

icant interference (random lines) were observed in the spectrum (fig. 11.3-2b) compared to a coal-free spectrum (Fig. 11.3-2a). These spectral interferences are most likely due to laser-induced breakdown at the surfaces of coal particles at random positions along the laser-beam paths. Two approaches, use of a longer focal length focusing lens or use of lower pulse energies, can circumvent this problem. In a large system, the sacrifice of spatial resolution with a longer lens may be acceptable. In this work, lower pulse energies (8 mJ for the pump and 1 mJ for the Stokes beams) greatly reduced the breakdown, but at the expense of diminishing the CARS signal (fig. 11.3-2c). Lucht successfully implemented a simple conditional sampling system to detect off-axis emission during breakdown and to reject those shots on which breakeown occurs. Time-gating detection electronics synchronously with the lasers discriminates against noise from particle luminosity. Since CARS signals from nitrogen are 100 times stronger than from oxygen, interferences are greatly reduced at the same laser energies. Figure 11.3-2d shows a nitrogen CARS spectrum obtained at high pulse energies with a very good theoretical fit superimposed. In any application, single-shot broadband CARS will eliminate additional systematic uncertain-ties in such slow scans if these are caused, for example, by unsteadiness in the combustion conditions and variation in window transparencies.

In summary, the applicability of Raman scattering techniques, both SRS and CARS, to PC combustion environments is determined by characteristics of the flow such as: (i) the particle size distribution and number density; (ii) the intensity, intermittency and scale of flow turbulence; (iii) the size and geometry of the flow; and (iv) the temperature, pressure and composition of the flow. Heavy loadings of luminous particles will be most detrimental to SRS because of the weakness and isotropic nature of the signal; CARS will be most strongly affected by turbulence and combustor size because of beam-overlap requirements and, of course, by beam attenuation at larger path lengths in particle-laden flows.

There is little doubt that, for a variety of Class II flows in laboratory combustors, CARS has potential for achieving local measurements of the probability density function of temperature, from which valid means and fluctuations in gas temperature may be inferred. The limits of applicability of CARS in such flows have not been thoroughly investigated. Beam

attenuation due to heavy particle loadings and beam steering due to turbulence are expected to be the major limitations on CARS applicability in Class II flows. Beam-steering (especially for long optical path lengths) will cause the three laser beams to diverge from the required common focal volume. If conditional sampling techniques can be devised to distinguish large beam-steering effects from the real temperature fluctuations due to turbulence, the main effect of beam-steering will be to decrease the data rate, a relatively minor consequence. Only for very clean Class II flows may the same be said for SRS. To date, a systematic demonstration and validation of CARS for local temperature measurements in Class II coal-fired flows has not been done; this is, in fact, one principal objective of current research at our laboratory.

2

,

÷

۱. •

1

:

· · · · · · · · ·

For Class I PC combustion flows, the prospect for successful application of CARS is good. For such flows, time averaging is acceptable because of the low level of temperature fluctuations. Application of SRS is severely limited by the background luminosity level, but time-gating and signal averaging may help.

11.3-2. Fluorescence and Absorption Techniques

Laser-induced fluorescence (LIF) and absorption methods (using laser diodes or other infrared sources) have been applied extensively to determine gas phase temperature in relatively clean and in soot-laden combustion environments. Fourier transform infrared spectroscopy (FTIR) has emerged only recently as a potentially useful technique for application to bench-scale coal-combustion studies (see Refs. 8-10). Laser fluorescence and absorption methods require many of the same ingredients as the CARS apparatus shown in Fig. 11.3-1. A laser-pumped tunable dye laser (for LIF) or FTIR source is required, with detection at 90° with respect to the incident beam for fluorescence or along the beam for absorption. In these measurements, the variable frequency light source is tuned to a real electronic transition of a molecule or atom. The species absorbs laser radiation and is excited to a higher-lying electronic state. The excited state species can decay back to the ground state by spontaneous emission (fluorescence), a process in which a photon is emitted isotropically. The fluorescence or absorption signal is proportional to the exciting state population of the mol-

ecule or atom. Unfortunately, the excited state population resulting from laser excitation depends not only on the rates of laser absorption and spontaneous emission but also on collisional transfer rates, which must be measured or estimated.

Numerous studies in clean flames have been performed in recent years using LIF (including various special derivatives, such as two-line fluorescence) from the hydroxyl (OH) radical to measure temperatures in flames. Laser-excited OH fluorescence is attractive as a temperature diagnostic because of signal-strength considerations; OH is typically present in high concentrations in flames, and several vibrational bands of the first excited electronic transition lie at the frequency-doubled wavelengths of high-efficiency rhodamine laser dyes. In addition, the frequency and radiative transition rates of OH rotational transitions are unusually well-characterized. Fluorescence from vaporized atomic species (assumed to be in equilibrium with the combustion gases) can also be used to infer gas temperature. Five methods have been outlined 12 for measuring flame temperature using atomic fluorescence. Because numerous possible seed atoms (e.g., lithium, sodium, potassium) have electronic transitions in the visible region of the spectrum, where ring dye lasers operate very efficiently, such techniques offer the possibility of temperature measurements at kHz data rates.

In a similar way, temperatures of molecular gas-phase species in flames have been determined from absorption spectra. Infrared sources are generally used for absorption measurements because all molecules, except homonuclear diatomics, have strong absorption bands in this spectral regime. As with LIF, temperatures are determined from the assumed equilibrium Boltzmann population distribution among the vibration-rotation energy levels.

11.3-2A. Application of LIF and FTIR to Pulverized Coal Combustion

In general, application of LIF or absorption techniques for gas-phase temperature measurement in pulverized coal-combustion environments will be feasible in situations where SRS is only marginally applicable. The strength of the LIF signal will depend on the type of species probed. Because transient species such as OH will be used for the LIF temperature mea-

surement in unseeded flows, LIF will be useful as a temperature diagnostic only in relatively high-temperature regions. In such regions, where transient species concentrations may be very high (typically 1000 ppm for OH), the strength of the LIF signal is likely to be orders of magnitude higher than the Raman signal. Thus, in situations where temperature and particle loadings are high and SRS cannot be used, LIF temperature measurements may be possible. LIF is an attractive alternative to CARS in some instances since less complex apparatus and data-reduction procedures are involved. Single-pulse LIF temperature measurements may be possible. LIF is an attractive alternative to CARS in some instances since less complex apparatus and data-reduction procedures are involved. Single-pulse LIF temperature measurements will require either a fast-scanning dye laser or laser excitation with two or more distinct frequencies for the so-called two-line methods. No obvious technical obstacles exist for single-pulse, two-line temperature measurements methods, although no such measurements have been reported in flames to date. Seeding the flow with species such as atomic sodium will extend the temperature range of applicability of LIF at the cost of added experimental complexity to ensure uniform seeding, but may possibly introduce some uncertainty about the effect of the seed species on local reaction processes. In many coal-derived flows, sufficient atomic absorbers may already be present. An important consideration for application of LIF in PC combustion studies is the effect of fluorescence trapping or re-absorption of fluorescence emission as it traverses the medium between the probe volume and collecting lens. In axisymmetric Class I flows, the symmetry (or lack of symmetry) of the fluorescence temperature profile should be an excellent indication of these effects. In Class II flows, it may be much more difficult to detect the influence of fluorescence trapping, and serious temperature errors could result.

キャン・センド ひ

ļ: Ņ

.

.

The feasibility of FTIR absorption thermometry in PC combustion experiments is largely the result of the fact that modern infrared sources are much brighter than the infrared emission of the hot gases in the flame. This is especially true for applications in bench-scale experiments. However, even in situations where the infrared emission from the flame is comparable to that of the infrared source, modulation of the source provides discrimination against the infrared emission of the flame, provided the combined infrared intensities do not saturate the detector.

11.4. Gas-Phase Species Concentration Measurement

In this section, we comment briefly on the prospects for application of both Raman scattering techniques and laser-induced fluorescence or absorption methods for the detection of gas-phase species concentrations in PC combustion environments.

11.4-1. Raman Scattering Techniques

Spontaneous Raman scattering (SRS) is a well-developed technique for measuring concentrations of major species in clean flows, including combustion and turbulent mixing flows. However, SRS has not been applied to measurements in environments laden with coal particles, soot or gas-phase hydrocarbons, due to interferences from particulate luminosity and broadband fluorescence from the gaseous organic species. As noted, CARS has been applied for gas thermometry in a wide variety of combustion systems, but CARS has not been as widely applied for concentration measurements. Concentrations may be calculated from CARS signals, either from the signal intensity or by using the ratio of the resonant and nonresonant CARS signals. The disadvantage of calculating concentrations from signal intensity is that the CARS signal strength is very sensitive to factors such as beam overlap and the temporal structure of the laser pulse, which can vary substantially over the course of an experiment or even from one laser pulse to the next. In principle, more precise and accurate concentration measurements are obtained by using the ratio of the resonant CARS signal from the species of interest to the frequency-independent nonresonant background. Such measurements can be performed by using polarization analysis to separate the CARS signals into resonant and nonresonant signals, separately recording the intensities of each signal, and then recording the ratio spectrum. Variations in CARS signal strengths from pulse to pulse are reflected in both the resonant and nonresonant signals, and are approximately cancelled by using signal ratios. Calculations of species concentrations from the ratios is straightforward, provided that the nonresonant susceptibility is a accurately known. Alternatively, broadband CARS spectra can be directly analyzed to obtain species concentrations when the resonant and nonresonant signal magnitudes are approximately equal.

There have been very few attempts at obtaining species concentration measurements using CARS in heavily particle-laden combustion and gasification environments. A few preliminary demonstrations have been done for Class I flows. 7,13,14 We are not aware of any, even preliminary validations of CARS for species concentration measurements in coal-fired, Class II flows. While the few results for the Class I flows have been encouraging (i.e., a CARS signal was detected and a concentration estimated), from the standpoint of proof and validation of the diagnostic technique, much remains to be done, even for well-defined high-temperature environments. In view of the aforementioned uncertainties in interpreting CARS spectra (including such phenomena as pressure narrowing), considerable fundamental diagnostics research on the method is required.

•

; ;

11.4-2. Fluorescence and Absorption Techniques

11.4-2A. Laser-Induced Fluorescence

In recent years considerable progress has been made in defining the limits of accuracy of various laser-induced fluorescence (LIF) techniques for detecting species concentrations. Species of interest in PC combustion flows, which may be measured by using LIF, can be divided into three basic categories: (i) radical species such as 0, OH, and NH which are important in reaction kinetics and pollutant formation; (ii) pollutant species such as NO, CO and SO; and (iii) metal atoms such as Na, K and V and compounds such as NaS which are important in corrosion, fouling and slagging.

The use of LIF techniques as a diagnostic for species concentrations in PC combustion has not been actively pursued. One reason for the lack of activity is that the detection of free-radical molecular species, which has been the primary objective of fluorescence investigations in combustion media to date, has not been of particular interest to coal-combustion scientists. However, recent fluorescence investigations of turbulent diffusion flames have shown that the radical pool is far from equilibrium in some portions of the flame. Consequently, accurate predictions of processes such as NO formation and CO burnout may require accurate knowledge of radical concentrations. In addition, there is indication that OH may be responsible for oxidation of coal volatiles, as well as for direct

attack on the residual char. Therefore, we expect to see more applications in PC combustion but this will be difficult when particle loadings are high.

Quantitative fluorescence diagnostics of pollutant species such as NO and CO, while certainly feasible, have not yet been demonstrated, even in laboratory flames. Qualitative fluorescence methods may be of use in locating high zones of soot and HC formation. Most HCs, including soot precursors, have strong absorption bands in the visible and near ultraviolet and produce broadband flourescence emission in the visible portion of the spectrum. Fluorescence techniques for the measurement of Na have been actively pursued for over a decade; in fact, Na has served as a model atom for the development and demonstration of numerous fluorescence techniques. LIF techniques for measurements of other metal atoms are less well-developed, but it is anticipated that techniques developed for Na will also be applicable to numerous other metal atoms. LIF diagnostics of species such as NaS are handicapped by the lack of a well-developed spectroscopic data base.

11.4-2B. FTIR Absorption Techniques

The commercialization and widespread use of FTIR spectrometers has facilitated their use for quantitative gas analyses. This progress has been aided by the availability of increasingly accurate values for infrared line strengths, as reported in the literature. Furthermore, virtually all gases (except homonuclear diatomics) have at least one strong infrared absorption band in the mid-infrared region (400-4000 cm^{-1}) that is easily accessible to most FTIR instruments. With many different species present in the sample, the mid-infrared region may become congested with many absorption lines. However, in most cases, the features caused by different species may be sorted out if the spectra are taken at sufficiently high resolution (0.5 $\rm cm^{-1}$ or better), since each species has a unique infrared absorption spectrum. Also, the task of sorting out the spectrum is much easier if only low molecular weight species (those having fewer than 5 atoms of atomic weight greater than hydrogen) are present in the sample. Clearly, lower gas concentrations can be measured if higher signal-to noise (S/N) spectra are obtained. With FTIR, a number of factors influence the maximum attainable S/N. For example, averaging many spectra together improves the S/N by a factor equal to the square root of the number of spectra averaged. The

price one pays for improved S/N is the increased time required to acquire the data.

いたたち

ι.

\$

In general, FTIR spectroscopy is an effective technique for detection of many different species simultaneously over a wide spectral bandwidth when conditions permit time-averaged measurements along a line-of-sight (e.g., in laminar or turbulent, plug-flow flames and reactors). Determination of gas-phase species concentrations using absorption spectroscopy is based on the application of the Beer-Lambert Law of absorption, which relates the intensity of the light transmitted through the sample to the incident light intensity, transition line strength, transition line-shape function, concentration of the absorbing species, and path length of the light through the sample.

Recently, two groups $^{8-10}$ have explored the use of FTIR for gas-phase species concentration measurements in PC combustion studies. Solomon's work is reviewed elsewhere.¹¹ Ottesen's recent work at Sandia⁸ has been of the nature of technique demonstration and validation. In this work, he has extended FTIR measurements into the high-resolution domain in order to assess the sensitivity of the technique for the determination of the concentration and rotational temperature of various molecules in a PC combustion environment. Infrared absorption measurements were made with uniformly-sized coal particles entrained in a laminar flow reactor.

Past attempts to make high resolution absorption measurements have been plagued by the infrared emission of hot coal particles passing through the detector field-of-view. Solomon¹⁰ has attempted to make use of these emissions by inverting the order of the combustion reactor-interferometer apparatus and by extracting the average emittance of the hot particulate ensemble for a given measurement time. These particulate emission signals, however, act as an additional noise source for absorption measurements and are mitigated only somewhat by laborious time-averaging. This problem has prevented the measurement of spectra at a resolution greater than 0.5 cm⁻¹. However, this particle-generated noise occurs at Fourier frequencies lower than the pertinent bandwidth containing infrared spectral information. By electronically filtering the detector output, Ottesen successfully reduced this particulate noise and obtained the first reported measurements of pulverized coal combustion products at a spectral resolution of 0.08 cm⁻¹.

Although these measurements are more time consuming than those at

lower resolution, they allow a more accurate determination of both the molecular rotational temperature and concentration. This advantage results principally from the lessened interferences of nearby absorption lines from other species (mainly water vapor molecules) and higher excited state transitions. These measurements also showed that the measured linewidths of CO and CO₂ transitions are considerably greater than the reported values of 0.04 $\rm cm^{-1}$ at temperatures around 1300 K. Measured widths at half maximum are 0.105 cm^{-1} , and it is postulated that the additional width is caused by collisional broadening due to the large quantity of water present (15 mol%). A portion of the CO P-branch rotation-vibration band produced during the combustion of a pulverized western Kentucky bituminous coal is shown in Fig. 11.4-1. The CO rotational temperature determined from the relative intensities of the absorption lines was 1218±28 K and is in good agreement with a temperature of 1247 \pm 22 K derived from the CO $_2$ v $_3$, R-branch rotationvibration during the same experimental measurement. Reduction of the noise caused by the particulate emission increased the sensitivity for many small infrared-active molecules (CO, CH_A , NO, HCN, H_2S) to about 100 ppm for a 10 cm path length at combustion temperatures in the presence in coal particles. Current efforts at detecting minor products of combustion in situ have been hampered by the serious overlap of water-absorption lines with Nand S-containing species of interest.

11.5. Particle Size, Number Density and Temperature Measurements

Among the spectrum of diagnostic requirements for examining PC combustion, perhaps the most serious is the need for <u>in situ</u> techniques for real-time detection of the loading and size distribution of entrained particulate matter, including solid coal, char, fly ash, soot particles and liquid droplets or slurry mixtures. In fundamental bench-scale studies of the reactivity of condensed-phase fuels, there is need to obtain simultaneous information on the size, temperature and residence time of reacting particles larger than 10 μ m. <u>In situ</u> optical sizing techniques offer great promise to meet many of these measurement needs. Detailed chemical analysis will probably continue to require extractive sampling; a novel and promising <u>in situ</u> optical method called laser-sparked spectroscopy is discussed in the final section.



Fig. 11.4-1. The CO P-branch spectrum obtained by FTIR spectroscopy in a coal-seeded laminar flow reactor; rotational T = 1218 K.⁸

Optical methods can be characterized as imaging or light scatter-In the case of imaging methods, individual particles are resolved ing. while in the latter they are not. As indicated in Fig. 11.5-1, both methods can be further subdivided into ensemble or single-particle techniques. In all cases, the analysis of particle size relies on the assumption of independent light scattering, which should be valid down to particle separations on the order of four times the particle diameter and number densities up to $10^{10}/d^3$ per cm³, where d is the particle size in μ m. Because of the need for spatial resolution, real time analysis, and mass resolution (mass is concentrated in the upper end of the size distribution), the emphasis here is on the features of two of the most successful single particle counting (SPC) methods; one is a light scattering method and the other an imaging technique.

11.5-1. Single Particle Counter, SPC (Scattering) Instruments

11.5-1A. User Requirements

Hardesty¹ has summarized typical user requirements for application of SPC instruments to PC combustion environments. For many applications, both number and mass-loading densities are of interest. The latter can be inferred from SPC measurements of the former if the material density of the particulates is known. The sizing range required for most studies probably has a lower bound of 0.1 μ m, although soot formation and ash-condensation effects would require monitoring down to 0.01 μ m. However, in all likelihood, the practical limit of SPC in high number density flows is about 0.1 μ m. Minimum sensitivity to particle refractive index (m = n₁ + in₂) and particle-shape variations is desirable in coal-fired flows, where particle properties range from irregularly fractured carbon particles (n₂ ~ 0.5) to fused silica fly ash (n₂ ~ 0.001). For comparison, liquid fuel droplets are in general transparent (n₂ ~ 0) and spherical. If particle properties and shapes are known and invariant, these restrictions on instrument design become less stringent.

11.5-1B. Design Constraints

While many discussions refer to particle measurements as particle sizing, the correct reference is to particle size-distribution measurements. Measurements of particle size alone, without accurate counting of the number in each size class, is insufficient to characterize mean diameters (number, area, mass) or their integrated values. Many discussions have emphasized accurate size characterization with only limited discussion of proper number counting. In practice, accuracy of frequency-distribution measurements and derived averages are equally dependent on sizing <u>and</u> number counting accuracy.

The fundamental relations which constrain the design of SPC diagnostics based on Mie scattering are well known. Of particular concern here are the theoretical results which lead to the variety of <u>in situ</u> SPC diagnostics. First, a monotonic dependency of the scattered light amplitude on the particle size is required, with little dependence on the particle index of refraction or shape. Second, confining all measurements to the forward diffraction lobe for particles larger than about 0.1 μ m is the most advantageous. Consistent with these considerations, Fig. 11.5-2 shows a schematic

diagram of a typical SPC instrument with symbols indicating the primary instrument design variables. A laser of wavelength λ and beam f-number f_b is focused through a window of thickness and

ż



Fig. 11.5-1. Ensemble and single particle optical particlemeasurement techniques.



Fig. 11.5-2. Schematic diagram of a typical SPC device employing near-forward Mie scattering.

angle X to a beam waist W_0 . Scattered light from particles of velocity U_y is collected by a lens of open aperture $(\theta_1 - \theta_0)$ or f-number F_c at an angle θ and focused onto a detector slit assembly of width W_s . The available working space between the two lenses is denoted by L. The sample volume from which scattered light is detected is determined by the intersection of the beam focus and the image of the slit. The single-particle signatures at the detector are processed by a minicomputer to provide amplitude-frequency distributions.

Given this general configuration, there are two basic methods of relating particle size to a scattering signal. One approach 15 is based on absolute scattering and requires accurate knowledge of the distribution of laser intensity in the sample volume. The second approach¹⁶ uses the ratio of two independent absolute scattering signals from the same particle. Although ratio methods characterize particle size independently of the illumination intensity, the absolute magnitude of each ratio signal still depends on the local illumination intensity and the absolute response function. In Fig. 11.5-3, a theoretical comparison is shown of the typical absolute scattering response functions for the two classes of SPC methods. In the top half of the figure, the dashed curves refer to the angle-ratio method with different scattering angle pairs, and the solid curve characterizes a typical visibility-response curve with fringe spacing. In general, all such response curves are multivalued, which places undesirable limits on the dynamic range (in particle size) or requires multiple angle ratios to determine the correct particle size. The lower half of Fig. 11.5-3 shows typical absolute scattering response curves for both absolute and ratio scattering methods.

In our original analyses of both types of scattering methods, we considered in detail the basic relations among the elements of the typical SPC optical system, the particles being measured, and various instrument or hardware aspects. These include: (i) the dynamic range; (ii) the sample volume size; (iii) the particle number density; (iv) resolution and accuracy; (v) laser intensity in the focal volume; (vi) windows; (vii) beam steering; and (viii) electronics. The key points are as follows: (i) Enlarging the collection solid angle reduces the dynamic range. The required dynamic range in the signal for a factor of 10 in particle size approaches 10^4 . (ii) All SPC methods require knowledge of the absolute scattering response

function and the distribution of laser intensity in the sample volume. Particles of the same size, which pass through different regions of the focal volume, give rise to different scattering signatures. (iii) The maximum particle number density in the flow that can be accommodated, without having two or more particles in the sample volume simultaneously, is given by (N < 4P/V), where P is the probability of having two or more simultaneous scattering events in the sample volume V. The requirement for a small volume dictates a small beam waist W_{o} , which produces a non-uniform laser-intensity distribution in the sample volume. (iv) A 95% confidence level in the particle-count rate requires more than 1000 counts. All SPC instruments require time to acquire sufficient counts in each size bin to meet the accuracy requirement; the time required is a function of the particle loading density and will range from a few seconds to minutes for very lightly loaded flows. Thus, although data are being sensed in a single pulse mode for each particle, the measurement of a size distribution is inherently time-averaged. (v) There are simple interrelationships among the laser wavelength, the focal length of the focusing lens, the beam waist size, the depth of field, the size of the largest sensible particle and the maximum number density of the smallest particles that can be sensed.¹ In practice, these factors dictate that at least two laser beams are required to measure particles from the submicron to 100 µm range: one tightly focused to measure the small, higher number density particles and the second with a larger focus to measure the larger

; ·

;

particles. (vi) Most PC combustion experiments require windows for optical access. Displacement of the focal volume along the incident laser direction is proportional to the thickness and index of refraction of the window material; lateral displacement will occur if the beam is not perpendicular to the window. The incident beam must be monitored to account for beam attenuation due to window fouling. (vii) Beam steering, primarily due to gradients in the index of refraction of the combustion gases which are transverse to the laser and scattered beams, can be appreciable and unsteady but may be compensated for by enlarging the entrance slit of the detector. (viii) Because of the large dynamic range required of the detection and amplification circuit, logarithmic circuits or staged amplifiers are required with at least a 10 MHx frequency response.



Fig. 11.5-3. Comparison of response functions² for the ratio and absolute SPC scattering methods.

11.5-1C. SPC Intensity Deconvolution Method

The only SPC optical method that has been used reliably for measuring particles over the size range 0.1-100 μ m, at number densities from $10_2/\text{cm}^3$ at the large sizes to $10^7/\text{cm}^3$ at the small sizes, is a dual-beam absolute intensity deconvolution (SPC/ID) method.¹⁷ A key feature of this method is the use of dual beams to achieve the required small sample-volume size to accommodate the increased particle loadings at the small end of the particle-size distribution. The system uses near-forward scatter, as in

Fig. 11.5-2, with $\theta_i < 6^\circ$ to minimize refractive-index and particle-shape sensitivities. The choice of inner angle light collection, θ_i , depends on the size range of interest. The response functions for $\theta_i = 0.6^\circ$ are the solid curves in Fig. 11.5-3. Because of the variation of the laser beam intensities in the sample volume, the scattered signal is particle-trajectory dependent. A numerical inversion scheme and calibration procedure allows unfolding of the distribution of signal amplitudes and yields and indicated size distribution, which eliminates the dependence on trajectory. The scattered light from particles passing through each of the two sample volumes is collected by a single lens and divided by a beam splitter and focused onto the large and small slits, respectively.

Extensive calibration and validation experiments have been conducted by Holve.¹⁵ Figure 11.5-4 illustrates recent results obtained for the evolution of particle-size distribution in a laminar flow-reactor study of the combustion of pulverized coal and coal-water slurries.¹⁸



Fig. 11.5-4. Evolution of a bituminous coal-water slurry particle-size distribution as a function of residence time in a laminar flow reactor, obtained by using the SPC/ID system.¹⁸

11.5-2. Imaging Methods for Single-Particle Counting

All imaging methods permit, in principle, some degree of particle size-distribution measurement capability. With reference to Fig. 11.5-1, there are three basic types of systems: photographic, holographic, and image-plane coded-aperture methods. Unlike scattering techniques, all are applicable only to particles larger than the diffraction limit of <u>in situ</u> optical systems, typically 5 to 10 μ m. The first two have been extensively reviewed and will not be discussed here. The third method is relatively new. Among the three candidates, it is uniquely amenable to straightforward, real-time, spatially-resolved measurements under certain coal combustion conditions. Under the right conditions, however, it appears to be an extremely powerful method, e.g., for basic studies of the reactivity of pulverized coals, with clear advantages over scattering methods.

11.5-2A. <u>Image-Plane Coded-Aperture Single-Particle Methods</u>

Several image-plane coded-aperture systems for application to measurements of both luminous and nonluminous particles during PC combustion have recently been developed at Sandia.¹⁹ These systems have been evaluated in detail for application to flows where the particle loading density of particles larger than about 10 μm does not exceed $10^4/cm^3$. In contrast to the light-scattering methods, the image plane methods permit direct and simultaneous measurement of the size and velocity of particles. In addition, if the particles are sufficiently hot, their temperature can also be measured. In contrast to light-scattering methods, the image plane technique permits more direct discrimination against background noise because of the presence of smaller (unsized) particles in the focal volume. In other words, if it is sufficient for a particular application to measure information only on particles larger than say 10 μm and if these occur at number densities no greater than about $10^4/\text{cm}^3$, then the usual higher number densities of smaller particles may not prove limiting since reflecting or emitted, not diffracted, light is employed.

11.5-2B. The Multiple-Slit Method

In this method,¹⁹ the signal that contains the particle-size information is generated by imaging the particle onto a physical mask containing a grid of three slits and detecting the transmitted light. Particles may be illuminated or, in the case of hot or reacting particles, direct emission from the particles may be used to obtain size and velocity information. In general, deconvolution is required to extract information from any image-plane coded-aperture system. It is possible, however, to design the aperture so that the particle size can be retrieved by using only two values in the output waveform. Such an aperture is shown in Fig. 11.5-5. It is composed of two slits for encoding the particle-size

1)) 21

:::



Fig. 11.5-5. Aperture mask used in the image-plane codedaperture (SPC) method.¹⁹

information. A third slit is used in the implementation of a laser trigger to eliminate edge-effect errors and to distinguish further and minimize the size of the focal volume. The large aperture is made bigger than the largest particle to be measured; the small aperture smaller than the smallest. As the image of the particle scans across the mask, the ratio of the signals from detectors behind the apertures is proportional to the diameter of the particle. In addition to size information, the velocity of the particle can be obtained by measuring the transit time of the particle between the two apertures. Since size and velocity of a particle may be measured simultaneously, velocity-size correlations are readily derived. The method

is reasonable insensitive to particle shape. For irregular particles, the dimension measured is approximately equal to the particle length in the direction normal to the slits. While the system is insensitive to the particle index of refraction, the particle must be a diffuse surface in order to be sized correctly. This condition is particularly important when coherent illumination is used. In general, white light illumination yields better signals for non-ideal particles. It may be possible to size specular particles by back lighting and operating the system in a schlieren mode.

11.5-2C. Particle-Sizing Pyrometry Based on the Multiple-Slit Method

While none of the image-plane techniques can measure particles smaller than ~10 μ m, they do yield an important bonus capability in situations where the particles are sufficiently hot such that their incandescence can be used to obtain size information. Under these conditions, by virtue of its simplicity and ease of implementation in bench scale PC combustion environments, the multiple-slit technique is particularly amenable to integration with a multi-wave-length optical pyrometer system. The integrated system, shown in Fig. 11.5-6, has been developed for the simultaneous detection of particle size, particle velocity, and particle temperature.¹⁹ In addition, by measuring the absolute magnitude of emitted radiation, once the particle size and temperature have been determined, its emissivity may be estimated. Analysis of the particle size is done by using the ratio of the single particle signatures from the large and small slits. The particle temperature follows from the ratio of the signals from the large slit at two discrete wavelengths (assuming that the particle emits as a gray body). By the use of reflecting optics and extension of the detection system into the near infrared, the lower limits in terms of particle size and temperature may be significantly extended. Particle velocity is determined by timing the signals from the two slits.

The ability of the method to detect simultaneously the size, temperature and velocity of reacting particles is proving invaluable in recent studies of PC combustion. The system is now being routinely applied by Mitchell²⁰ to measure these properties for a variety of coals, chars and other reactive solids (and thereby to determine directly global particle reactivities) in a laboratory flow reactor.

11.5-3. Ensemble Methods for Analysis of Particulates

Our discussion has emphasized single-particle counting methods because: (i) these are generally applicable to Class I and Class II flows; (ii) they yield a direct measure of the particle size and number density; (iii) they provide a measure of the flux of particles through the focal volume (by virtue of the fact that the transit time of each particle is sensed). Ensemble methods are inherently line-of-sight measurement, with the exception of diffusion-broadening spectroscopy for local measurement of the total volume of submicron particles in the focal volume of the incident laser beam. As is shown in Fig. 11.5-1, ensemble methods fall into two classes: those that work in the Rayleigh limit of small particles (generally less than a few tenths of a μ m) and those that work in the Mie Regime (generally larger than 2 μ m).

1.



Fig. 11.5-6. An integrated single-particle imaging system for simultaneous particle sizing and temperature and velocity measurement.¹⁹

11.5-3A. Ensemble Methods for Large Particles

To measure the mean size of particles larger than $1 \mu m$, two commercial instruments are available, the Malvern instrument²¹ and the Leeds and Northrup instrument.²² Both devices operate on the principle of detecting Mie scattering from an ensemble of particles or droplets in a relatively large sample volume defined by the width of the duct and the cross section of an incident expanded laser beam. The use of these instruments and their inherent limitations with regard to determining particle-size distributions have been discussed elsewhere.¹ In general, the ensemble methods inherently yield less information than single-particle methods. In addition to the lack of spatial resolution in the ensemble methods, they provide no measure of velocity or of particle flux. However, if the phenomenon being observed is inherently unsteady, an ensemble device must be used since all SPC instruments average over relatively long times.

11.5-3B. Ensemble Methods for Measuring Particles < 0.1 μm in Size

High number densities of fine mineral matter particles, less than 0.1 µm in size, are common in most PC combustion environments (Fig. 11.2-2). These arise both from the liberation of solid mineral matter during combustion and as a result of condensation of vaporized inorganic species in the combustion and post-flame zones. In addition, high number densities of fine soot particles can be expected in regions where temperatures are high and fuel-rich conditions predominate. Of the various possible methods for obtaining information on particles less than 0.1 µm in size, only laser-Doppler-broadening spectroscopy (also called diffusion-broadening spectroscopy, DBS) permits the kind of spatial resolution required in Class II flows. The DBS technique is unfortunately applicable only to low velocity laminar flows, where particle diffusion velocities due to Brownian motion dominate particle transport through the laser focal volume. The method is extremely useful in bench-scale measurements in laminar flames and flow reactors.²³ It would appear, however, that there are no near-term candidate methods for obtaining spatially resolved sub-0.1 µm particle size measurements in highly structured Class II flows.

For Class I flows, where a flat (A) profile of local particle loading density is ensured, the conventional line-of-sight absorption method may be combined with a scattering technique to infer the total particle volume loading. The method relies on the classical assumptions and results of Rayleigh and Mie scattering and light extinction. In the Rayleigh limit, the method applies for particles which are small compared to the wavelength of light (for visible light, strictly for particles smaller than about $0.05 \ \mu$ m). In this regime, it can be shown that the ratio of the intensities of light scattered at 90° with respect to the incident beam direction to the transmitted light is a strong function of the volume fraction of particles. For larger particles, in the size range of the 0.05 to 0.1 μ m, Mie scattering can be used to advantage.

ŀ,

ł

15

...

í ; ;

•

11.6. Velocity Measurements in Particle-Laden Flows

As described earlier, in all single-particle counting diagnostic methods, the velocity of particles passing through the sample volume is measured. The measurement is essentially one of transit-timing. More precisely, only the magnitude of the component of the particle velocity projected into the plane perpendicular to the axis of the collection optics is sensed. A true velocity is measured only for well-ordered flows for which the axis of the collection optics can be arranged to be perpendicular to the flow direction. The inversion of the image-plane aperture method has also been used to measure transit times directly; two laser beams are focused in close proximity within the combustion zone and the time for a particle to transit the intervening distance is measured.

Clearly, transit-timing methods are, in principle, applicable to Class I flows. For more complex flows and in most cases where turbulent-intensity information is sought, the method of choice for direct velocity measurement is laser-Doppler velocimetry (LDV). The method is not new; fundamental descriptions of the technique are numerous. In most cases, however, the emphasis in previous work has been on the measurement of gas velocity and turbulent fluctuations associated with the gases. Small particles of uniform size and sphericity in the 1 μ m size range are typically used to minimize slip between the gas and the particles. Here, we comment briefly on some of the special considerations which pertain to velocity mea-

surements using LDV in coal-derived flows. In this discussion, basic familiarity with the conventional LDV method is assumed.

11.6-1. Application of Laser Doppler Velocimetry to Coal-Derived Flows

Despite the ready availability of commercial LDV systems, interpretation of LDV data from particle-laden, coal-derived flows is anything but a simple matter. Care is required. The two features of such flows which have the greatest impact on straightforward interpretation of LDV signatures are: (i) the need to operate with long focal-length optics in large coal-combustion geometries and (ii) the presence of high number-densities of irregular particles over (typically) a very wide size range. For most bench-scale experiments, the latter effect will dominate.

11.6-1A. The Effect of Long Focal-Length Optics

Large combustion-zone dimensions produce long optical path lengths, which require long focal-length optics. As the focal length of the incident lens(es) increases, the length of the sample or probe volume increases in the direction of the input laser beams. Consequently, off-axis (as opposed to backscatter) collection is desirable. For example, for a 50-mm beam spacing with a 120-mm (4.7-inch) focal-length lens, the probe volume length is 0.35 mm; with a 600 mm (2 feet) focal length lens, the probe volume enlarges to 8 mm. This loss of spatial resolution must be considered. While this degree of resolution may be acceptable, the probability of multiple particles in the probe volume poses problems. Another immediate effect is the decrease in efficiency of backscatter due to the decreased solid collection angle.

Multiple particles of the same size and presumably at the same velocity have the effect of degrading S/N. A higher pedestal in the LDV signature occurs due to the increased scattered light intensity, but less modulation occurs since the scattered light from different particles will be somewhat out of phase. If multiple particles of different velocities (sizes) are present simultaneously, the velocity differences will appear as random modulation of the Doppler signal.

The presence of particles in the line of sight between the detec-

tor and the probe volume can introduce problems with both signal level and noise. The problems are accentuated with longer focal-length systems. Light scattered from a large particle and crossing one of the two laser beams or which passes through the probe volume may undergo secondary scattering by particles along the (increased) line of sight. Finally, the possibility of beam refraction or steering is increased with the longer lever arms involved. Uncrossing of the incident beams causes signal dropout, and relative motion between the two beams introduction a bias error in both the mean velocity and the turbulence intensity.

ĩ

.

). 14

> , , , ,

> > ,) , i i i . . .

. . .

11.6-1B. The Effect of Different Particle Sizes

There are several additional adverse consequences of increasing particle number densities and of an increasing range of particle sizes in the flow. First, the dynamic range of the photodetector is limited. When the detection threshold is set to follow the weak signal from a small particle, the detector may be saturated by the signal from a large particle. A solution may be to use two detectors, which are set at different levels to monitor velocities of small and large particles independently. Secondly, the quality of the Doppler signal in terms of the modulation depth will most likely vary greatly. There is, in principle, an optimum ratio of particle size to fringe spacing; the result is that particles at the small and large ends of the size spectrum may be difficult to detect above the increased noise level. Finally, the single largest cause of low S/N in an LDV system is glare, usually from surfaces and windows. For example, large particles which cross the incident laser beams create glare directly or as the result of scattering off surfaces or other particles.

In summary, the necessity for careful analysis cannot be over-emphasized. Laser-Doppler velocimeter systems, whether packaged or home-grown, will invariably produce Doppler signals. Whether these mean a great deal, especially from a PC combustion flow, is another matter.

11.7. <u>Particulate Composition Measurement by Laser-Spark Spectroscopy</u> (LASS)

One of the most challenging areas for coal-combustion diagnostics

is that of determining the composition of entrained coal, char, and mineral matter particles in the combustion zone. At present, the only means for accomplishing this measurement is to extract a sample by insertion of a generally bulky, water-cooled quench probe and to subject the sample to a battery of off-line analytical techniques. In a new diagnostic research effort, Ottesen²⁴ is extending earlier work in our laboratory²⁵ on a technique called laser-spark spectroscopy (also referred to as laser-induced breakdown spectroscopy²⁶) to obtain in situ measurements of the elemental composition of particles in PC combustion environments. Although the techniques is about 6 years old, Ottesen's results are sufficiently encouraging to warrant an extended comment in this review.

A schematic diagram of the experimental apparatus²⁴ is shown in Fig. 11.7-1. The measurement sequence for single particle uses two cw lasers to provide particle-size measurements and to trigger the laser-breakdown process. A He-Ne laser beam is focused to a 50 μ m waist



Fig. 11.7-1. Schematic diagram of Sandia laser-spark spectroscopy diagnostic system. 24

size, and the 90° Mie scattering by individual particles passing through this focal volume is used as a trigger pulse. A co-linear, Ar-ion laser beam with a waist size of 250 μ m is also scattered by particles passing through the focal volume, and the intensity of the near-forward scattered light is used as a measure of mean particle size. These measurements are calibrated by using precision pinholes and uniform liquid droplets; the particle-sizing method is discussed elsewhere.²⁷ Incorporating particle-size information into the present emission measurements will help to remove data scatter caused by differences in particle size. It will also be useful in observing systematic trends in mineral composition during combustion as a function of particle size and may permit an absolute elemental mass measurement for each particle.

Immediately following the measurements of particle size, the He-Ne laser trigger pulse is used to initiate the laser spark sequence. A Q-switched Nd:YAG laser, with a maximum pulse energy of 170 mJ and a pulse width of 7 nsec at the frequency-doubled wavelength of 5320 A, is used to vaporize part or all of the coal particle. This rapid deposition of energy breaks down the molecular structures in the coal particle and ionizes the resulting atomic species forming a high temperature plasma.²⁶ The intense emissions lines from the plasma are viewed with a 0.5-m Spex monochromator, equipped with an optical multichannel analyzer capable of time resolution to 0.1 µm following the laser pulse. Ottesen's results confirm the expectation that the emission spectrum is extremely complex immediately following the formation of the plasma.²⁵ This problem is due to the presence of highly ionized species and results in a poorly characterized spectrum. By delaying the starting time of the observation, we find that a well-defined line spectrum. dominated by neutral and singly-ionized atoms, occurs approximately 2 µsec after the pulse. The results discussed here were obtained during a 2 to 4 usec window following this initial delay.

A central concern during the development of any new diagnostic technique is the issue of calibration. To date, a piezo-electric droplet generator has been used to produce uniform diameter liquid droplets, which contain a known concentration of material. For example, breakdown spectra were obtained of uniform droplets generated from dilute aqueous solutions of NaCl. Excellent straight line plots of the sodium 5890 A emission line vs salt concentration were obtained. The reproducibility of the observed emis-

sion intensities is of the order of \pm 10-20% for salt solutions of 0.05 to 0.5wt% and droplet sizes on the order of 70 µm; this fact is illustrated in Fig. 11.7-2. The dependence of emission intensity on laser energy is not straightforward. Although the Na emission increases monotonically with laser energy, no clear functional dependence is observed. It is speculated that this result is mainly caused by a complex increase of plasma temperature with incresing laser energy and the incomplete vaporization of the 70 µm droplets, even at the maximum laser energy. ²⁶ This view has not been verified.

In addition to such calibration studies, preliminary investigations of LASS applied to raw coal particles have been completed. Samples of a high-volatility bituminous coal, Kentucky No. 11, with an ASTM ash content of 10%, were used in the particle-size range of +30/-50 µm. A spectrochemical analysis of a bulk sample yielded the following observed mineral species; >1000 ppm, A1, Fe, Ca, Si; 100-1000 ppm, K, Mg, Na, Ti; <100 ppm, Mn, Cr. To date, emission lines using LASS have been recorded for all of these species except Mn and Cr. Representative spectra for four single particles are shown in Fig. 11.7-3. Additional species identified in the spectra include C, N, O and CN. CN is observed as a recombination product of carbon atoms from the organic matrix with nitrogen (the entrainment gas). Nitrogen and oxygen emissions are also observed, although quantitative analysis is not possible for these species since they originate primarily from the entrainment gas and the ambient laboratory atmosphere.

Detection of Na is best done by using the well known emission lines near 5890 A. Figure 11.7-4a shows four successive single-particle emission spectra. These spectra are representative of a much larger data set and were taken sequentially in approximately 8 sec real time. The small variation in line intensity in Fig. 11.7-4a is typical of the 80 particles which were measured. If these differences in observed intensity are caused primarily by variations in particle size, then one inference from these preliminary data might be that the sodium content is rather evenly distributed in these unreacted coal particles. A similar study for potassium content yielded much larger differences in emission-line intensities (Fig. 11.7-4a).

Also of great interest is the correlation of different emission-line intensities in a given spectroscopic region for a set of single particle spectra. This experiment has been done for two iron lines


The second conclusions and receiving write with cost is a .

aties of the contract the pyrolysic conditions may be encoursed and (2601 A and 2634 A), as is shown in Fig. 11.7-3a; the results are plotted in To a first approximation, Fig. 11.7-5a for 80 successive particles. To a this COLL: IN procedure should yield a straight line with a slope equal to the ratio of - 16 00 10 C 11111 the line strengths for these two iron transitions. This result is clearly observed for these preliminary data; some of the observed scatter may be aci LC arlith counted for by variations in plasma temperature (caused by differences in particle size and shape, the absorption of laser energy, and self-absorption of emission lines). Since these transitions do not originate from the same energy levels, changes in plasma temperature will affect their observed intensity ratios. The intensity of the stronger iron transition (2601 A) is correlated with the intensity of a carbon transition at 2475 A (as is shown in Fig. 11.7-3a) for the same set of 80 particles. These results are shown in Fig. 11.7-5b. The large scatter in the data points illustrates the great variability in Fe distribution in the raw coal particles, possibly caused by various iron-containing mineral inclusions. A much more consistent set of points is observed, however, for particles with Fe transitions of less than

2-2







Fig. 11.7-4. Spark emission spectra obtained after laser breakdown of four single coal particles; (a) sodium; (b) potassium.²⁴

391



Fig. 11.7-5. Correlation of spark-emission intensities on a particle-byparticle basis in a series of 80 single particles; (a) for two Fe emission lines; (b) for a single Fe and a single C emission line,²⁴

200 counts intensity. These points lie near the baseline of Fig. 11.7-5b and may be due to iron bound in the organic matrix of the coal, which would be much more homogeneously distributed than the mineral inclusions.

Although these early studies have shown several very interesting and exciting qualitative results, much work remains to be done in developing LASS as a diagnostic technique and in quantifying the limits of its accuracy under a variety conditions. Current efforts at our laboratory are being directed to the quantification of these emission spectra in the areas of particle size and plasma temperature measurement and emission-intensity calibration.

Laser-spark spectroscopy may also be used to sample the gas phase in a combustion environment, including very small particles which may not produce a measurable Mie-scattering trigger-signal. While some adjustment in laser energy may be required to compensate for the reduced breakdown threshold of the gas or fine aerosol,²⁶ in principle, one needs merely to sample the spark-emission spectra conditionally and to distinguish among those obtained with and without a sensible Mie signal in the particle detection channel. These complementary data are potentially valuable in determining the composition of soot, mineral matter fumes, and condensing in combustion environments.

393
