

COAL GASIFICATION:

DIRECT APPLICATIONS AND SYNTHESSES OF CHEMICALS AND FUELS[†]

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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 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 likely to grow more important over time and must thus be factored carefully into

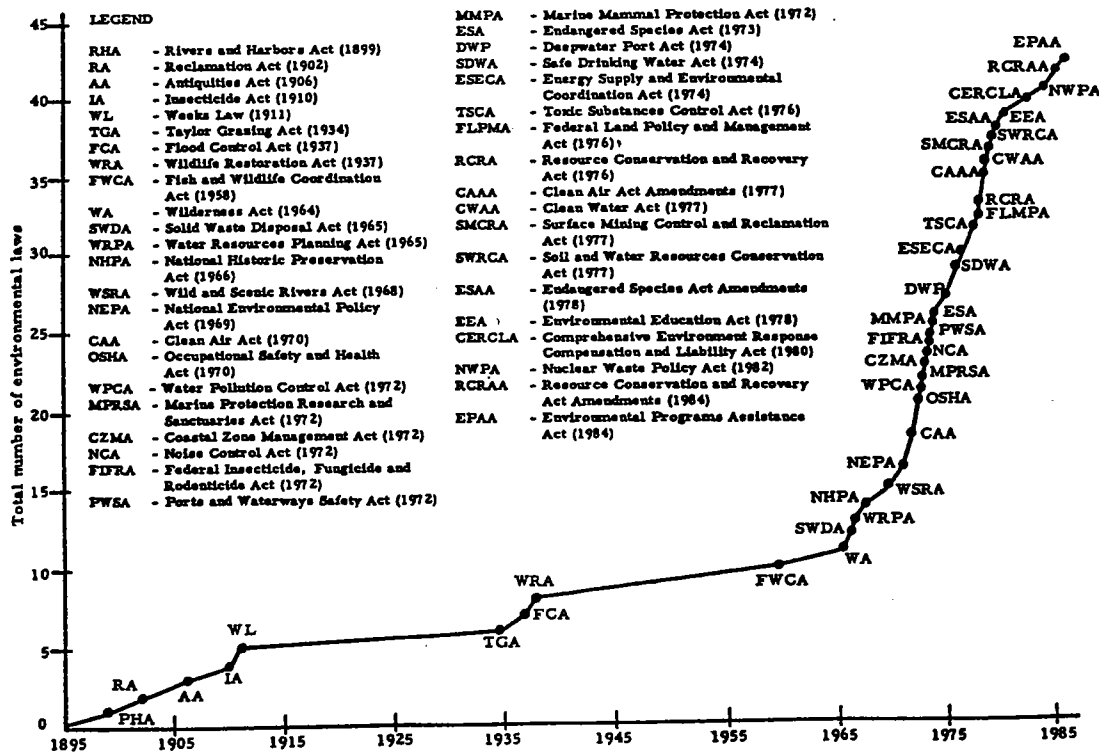


Fig. 9. 2-1. US laws on environmental protection (Ref. 1).

[†]This chapter has been written by Edward S. Rubin.

research and 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: (1) standards defining acceptable environmental quality and (2) 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 coal-gasification systems, though in many cases environmental quality standards also play a major role, particularly in plant siting.

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 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-

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)

Table 9.2-2. National ambient air-quality standards; codified at 40 CFR Part 50.

| Pollutant | Primary Standards | Averaging Time | Secondary Standards |
|--|---|---|--|
| CO | 9 ppm 35 ppm | 8-hr ^a 1-hr ^a | None |
| Lead | 1.5 µg/m ³ | Quarterly average | The same as the primary |
| NO ₂ | 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 |

^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 µm. Ranges of 24-hr standards of 150-250 µg/m³ and annual standards of 50-65 µg/m³ were proposed. An annual secondary TSP standard in the range of 70-90 µg/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.

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.

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-emission 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

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

| 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 9.2-4. 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 limit 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 new source performance standards do not currently cover coal-gasification facilities, so that wastewater 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.

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

| Promulgated | Forthcoming [†] |
|---------------------|--------------------------|
| 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 |

[†]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 considerably 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, NO_x, 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 wastewater 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.

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.

[†]Power generation represents an environmental worst case since the coal-gas 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 gas into a useful form, which reduces the environmental consequences at the gasification facility.

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

| Air | Water | Land |
|------------------|--|-----------------|
| SO ₂ | NH ₃ | Slags |
| NO _x | φOH | 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 | |
| HCl | TDS | |
| HCN | pH | |
| Metals | H ₂ S | |
| Organics | S ₂ O ₃ ⁼ | |
| | SO ₄ ⁼ | |
| | Cl ⁻ | |
| | F ⁻ | |
| | Alkalinity | |
| | Oils/grease | |

← Hazardous or toxic substances →

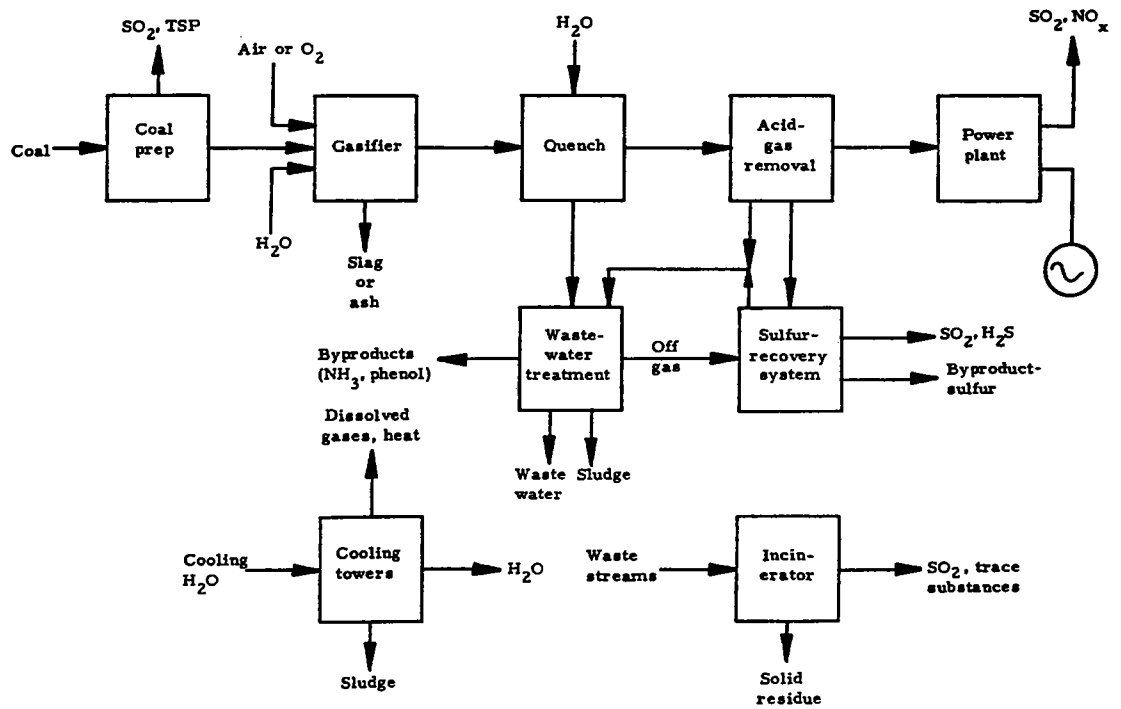


Fig. 9.3-1. Typical environmental control and emissions for coal-gasification processes.

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_x).

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 program⁶⁻⁸ 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 (CH_3SH), ethyl mercaptan (C_2H_5SH), and carbon disulfide (CS_2) 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.

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 thiocyanate (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 N_2). No vapor-phase volatile amines or 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 facilities 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.

Table 9.3-2. Coal and coal-gasification facility type (Ref. 6).

| 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) | Worcester, 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 |

[†] 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 general 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 quench-waters, 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 sulfides).

Table 9.3-3. Comparison of coal-gasification facilities for EPA studies (Ref. 6).

| Process | Chapman | Wellman-Galusha (Fort Snelling) | Wellman-Galusha (Glen-Gery) | Riley | Foster-Wheeler/STOIC | Lurgi-type (Kosovo) | KRW PDU | Koppers-Totzek (Modderfontein) | Koppers-Totzek (Ptolemais) | Texasco (Ruhrchemie) |
|--|---------|---------------------------------|-----------------------------|-------|----------------------|---------------------|---------|--------------------------------|----------------------------|----------------------|
| COAL HANDLING | | | | | | | | | | |
| Receive prized coal | X | X | X | X | X | X | X | X | X | X |
| Crush/pulverize | | X | | | X | X | | | | |
| Screen | | X | | | X | X | | | | |
| Thermal drying | | | | | | X | | | | |
| Slurrying | | | | | | X | | | | |
| Air classifying | | | | | | X | | | | |
| COAL FEEDING | | | | | | | | | | |
| Lock hoppers | | X | X | X | X | X | X | X | X | X |
| Screw feed/entrainment | | | | | | | | | | |
| Slurry pumping | X | | | | | | | | | |
| Barrel valve | | | | | | | | | | |
| GASIFICATION | | | | | | | | | | |
| Atmosphere (A)/pressurized (P) | A | A | A | A | A | P | P | A | A | P |
| Moving-(M)/fluid-(F)/entrained-bed (E) | M | M | M | M | M | M | F | E | E | E |
| Thin bed (T)/deep bed (D) | T | D | D | T | D | D | D | - | - | - |
| Slagging (S)/agglomerating (A)/dry ash (D) | D | D | D | D | D | D | A | S | S | S |
| Single-stage (S)/two-stage (T) | S | S | S | S | T | S | S | S | S | S |
| Co-current (C)/counter-current (CC) | CC | CC | CC | CC | CC | CC | CC | C | C | C |
| Air blown (A)/O ₂ blown (O) | A | A | A | A | A | O | O | O | O | O |
| GAS CLEANUP | | | | | | | | | | |
| Cyclones | X | X | X | X | X | | X | | | |
| ESP | X | | | | | X | | X | X | X |
| Quench/scrubbing | | | | | | X | | X | X | X |
| Acid gas removal | | | | | | X | | X | X | X |
| ASH REMOVAL/HANDLING | | | | | | | | | | |
| Lockhoppers | X | | | X | X | X | X | | | X |
| Ash plow | | | | | | | | | | |
| Slide valve | X | X | X | X | X | X | X | X | X | X |
| Water quench | X | X | X | X | X | X | X | X | X | X |
| Conveyor/drag chain | X | X | X | X | X | X | X | X | X | X |

^aNot applicable.

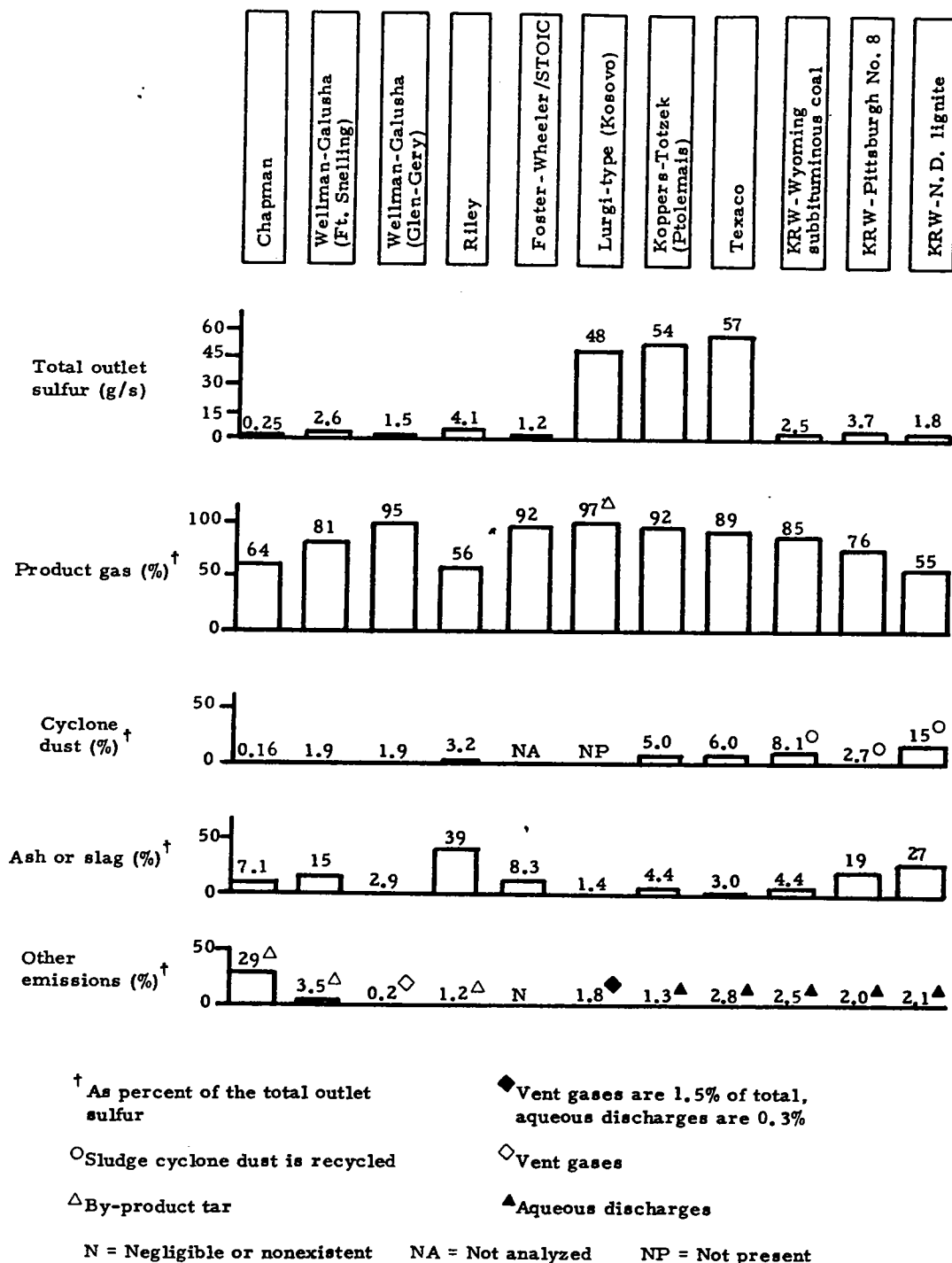
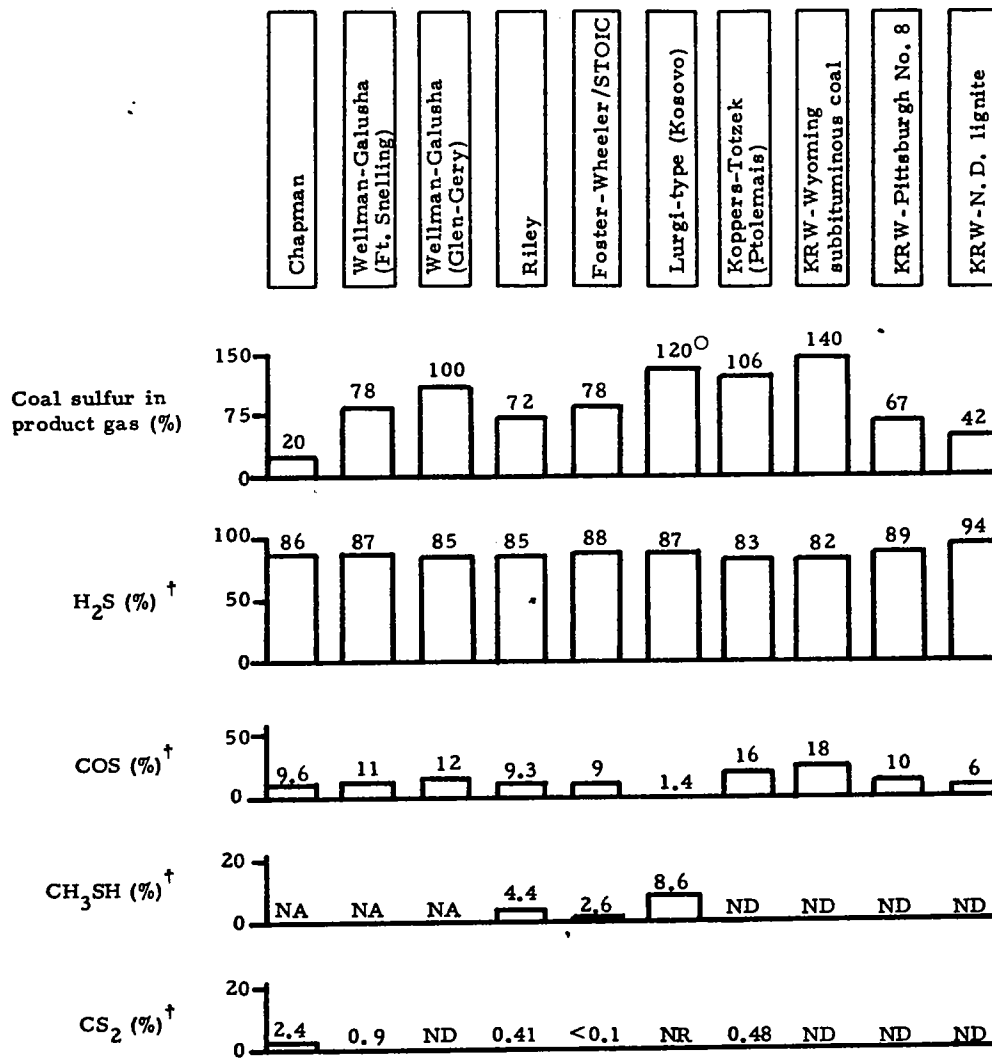


Fig. 9.3-2. Sulfur distribution among outlet streams (Ref. 6).



† Percent of product gas sulfur

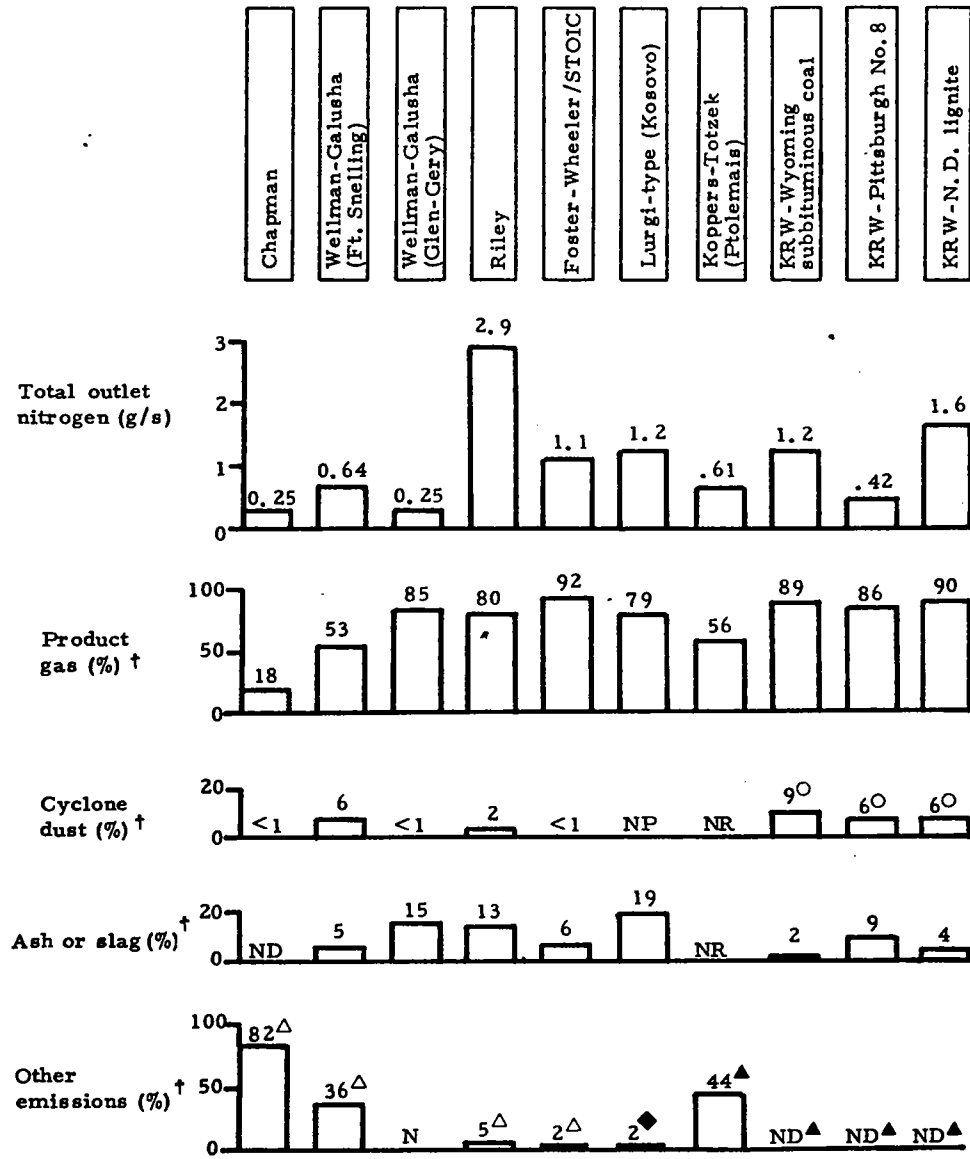
NA = Not analyzed

^oCrude product gas, includes tar/oil

ND = Not detected (< ~ 3 ppmv)

NR = Not reported

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



† As percent of the total outlet nitrogen

◆ Vent gases are 1.9% of total, aqueous discharges are 0.2%

○ Sludge cyclone dust is recycled

▲ Aqueous discharges

△ By-product tar

N = Negligible or nonexistent

ND = Not detected

NP = Not present

NR = Not reported

Fig. 9.3-4. Nitrogen distribution among outlet streams, excluding N₂ (Ref. 6).

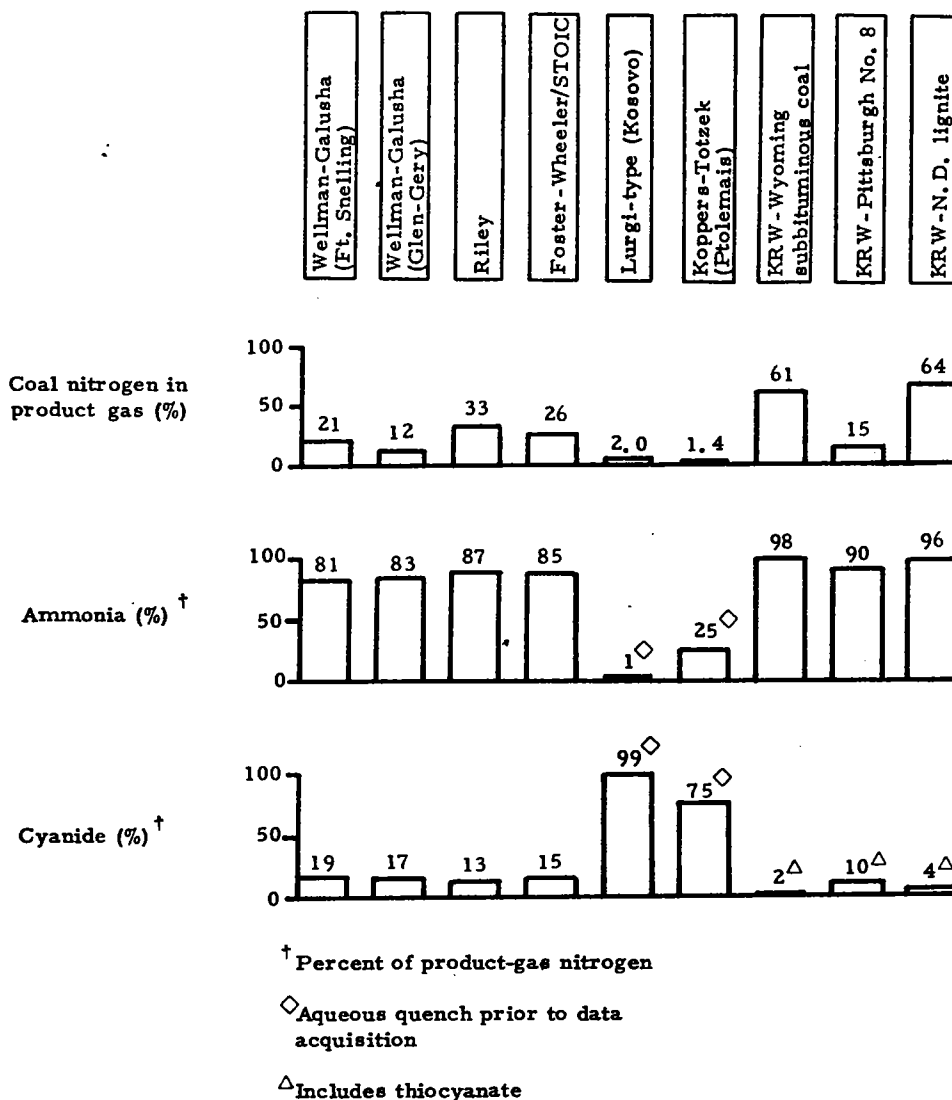


Fig. 9.3-5. Distribution of vapor-phase nitrogen species (Ref. 6).

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. Wastewater 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 confirm 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.

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

| 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 ^e | 0.9 | NA ⁱ | g | g |

^aLurgi gasifier at Westfield, Scotland.
^bCoarse graded (6-32 mm).
^cFine graded (2-10 mm).
^dRuhrkohle/Ruhrchemie in Oberhausen-Holten, FRG.
^ePulverized (< 2 mm).
^fSteam flow rate is taken as the sum of fresh makeup slurry water, coal moisture, and water in additives and flocculants.
^gNegligible.
^hTVA projections.
ⁱNA - data not available

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

| Gasification system | Riley | Chapman | Wellman-Galusha at Fort Snelling | Koppers-Totzek at Modderfontein | | | | KRW-PDU | | |
|--|-------------------|------------------|----------------------------------|------------------------------------|------------------------------------|-----------------------|-----------------------|---------------------|-----------------|---------|
| | Ash pan | Separator liquor | Cyclone-dust quench-water | Compressor condensate ^b | Compressor condensate ^c | 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 | 8.1 | 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 | d | <1 | 12 | 70 | 20 | 4,600 | 3,100 | 1,000 |
| Hardness as CaCO ₃ | | | | 60 | 46 | 691 | 554 | | | |
| Alkalinity as CaCO ₃ | | 2,140 | | 2,990 | 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 | | 185 | | | | | 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 ⁻ | ND ^e | 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 ₂ O ₃ ⁼ | | | | 4.8 | 7.8 | 18.5 | 16.4 | | | |
| SO ₃ ⁼ | | | 12 | <1 | <1 | <1 | <1 | 10 | 10 | 12 |
| SO ₄ ⁼ | 1,380 | 1,000 | 55 | 56 | 49 | 461 | 541 | 225 | | 65 |
| PO ₄ ⁻³ | 0.06 | 60 | 0.1 | 2 | 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 | |
| NO ₂ ⁻ | | | <0.01 | | | | | | | |
| Fluoride | 0.71 | 200 | 2 | | | | | 1.8 | 25 | 30 |
| Total sulfur | 18 | | | | | | | | | |
| NH ₃ fixed | <30 | | | | | | | | | |
| Carbonate | 2x10 ⁶ | | | | | | | | | |

^aUnits are mg/l unless otherwise noted.^bPurified sewage used as process feedwater.^cCooling tower makeup water used as process feedwater.^dBlanks mean parameter not analyzed.^eND - not detected.

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

| Gasification system | Lurgi at Sasolburg | | | | Lurgi at Westfield | | Lurgi-type at Kosovo | | |
|-------------------------------|--------------------|----------------------|---------------------|-------------------|-------------------------|-------------------------|----------------------|------------|---------------------------------|
| | 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 (μmho/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 | 720 | 170 | g | | 220 | 330 | | | Trace |
| SO ₃ ⁼ | 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 |
| NO ₂ ⁻ | 0.15 | 0.03 | 0.04 | | | | | 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 | | | |
| NH ₃ - 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 | | | | | | | 570 | 14,200 | 8,060 |
| Tar & oils | | | | | | | | <400 | |

^a Units are mg/l unless otherwise noted.^b Wastewater associated with Pittsburgh #8 coal.^c Wastewater associated with Montana Rosebud coal.^d Includes coal bunker vent-gas scrubber and ash-lock vent-gas scrubber blowdowns.^e TDS measured at 180°C.^f Blanks mean parameter not analyzed.^g Possible analytical interferences.

Table 9.3-7. Trace elements in fixed-bed coal-gasification wastewaters (Ref. 7).^a

| Gasification system | Foster-Wheeler/STOIC | Lurgi at Sasolburg | | | | Lurgi-type at Kosovo | | Riley | Chapman | Wellman-Galusha at Fort Snelling |
|---------------------|----------------------|--------------------|----------------------|---------------------|-------------------|----------------------|----------------------|------------------|------------------|----------------------------------|
| | Type of wastewater | Raw-gas liquor | Extracted-gas liquor | Stripped-gas liquor | Coal-slurry water | Cyanic water | Phenosolvan effluent | Ash pan | Separator liquor | Cyclone-dust quench-water |
| | Method of analysis | SSMS ^b | ICPES ^c | ICPES | ICPES | SSMS | SSMS | AAS ^d | SSMS | SSMS |
| Aluminum | 30 | <50 | <50 | <50 | <50 | 70 | 100 | e | ND | MC ^{f,g} |
| Antimony | ND ^h | <2 | 85 | 36 ⁱ | <2 ⁱ | ND | ND | | 70 | <60 ⁱ |
| Arsenic | 30 | 1,800 ⁱ | 1,700 ⁱ | 1,700 ⁱ | 170 | 90 | 20 | 21 | 800 | 120 ⁱ |
| Barium | 4,000 | 200 | 80 | 110 | 1,900 | 20 | 50 | 170 | 300 | 570 ^g |
| Beryllium | ND | <0.5 | <0.5 | <0.5 | <0.5 | ND | ND | | ND | ND |
| Boron | 400 | 32 | 26 | 28 | <9 | 20 | 100 | | 9,000 | 900 ^g |
| Bromine | 100 | | | | | 100 | 9 | | ND | 40 |
| Cadmium | ND | <2 | <2 | <2 | 51 | ND | ND | <1 | 5 | <5 ^g |
| Calcium | MC | 3,200 | 1,900 | 2,900 | MC | ND | 6,000 | | 2,000 | MC ^g |
| Cerium | ND | | | | | ND | ND | | 3 | 2 |
| Cesium | <1 | | | | | 4 | ND | | 1 | 4 |
| Chlorine | 700 | | | | | 4,000 | 1,000 | MC | 200 | MC |
| Chromium | 40 | 1,500 | 2,800 | 3,900 | <1 | 9 | 5 | <1 | ND | <5 ^g |
| Cobalt | 5 | <6 | <6 | <6 | <5 | ≤3 | 3 | | ND | 9 |
| Copper | 20 | <1 | 15 | 19 | <1 | 20 | 30 | 6 | 10 | 12 ^g |
| Fluorine | 50 | | | | | 300 | 4,000 | 530 | 2,000 | 2,000 |
| Gallium | 20 | | | | | ND | ND | | ND | 20 |
| Germanium | ND | | | | | 20 | 30 | | ND | 7 |
| Iodine | 7 | | | | | 400 | 20 | | 300 | 6 |
| Iron | 9,000 | 430 | 520 | 5,600 | MC | 4,000 | 500 | 1,900 | 1,000 | 4,900 ^g |
| Lanthanum | ND | | | | | 8 | ND | | 1 | ND |
| Lead | 10 | <2 ⁱ | <2 ⁱ | 61 ⁱ | 83 ⁱ | 8 | 70 | 1.3 | ND | 99 ^g |
| Lithium | 200 | <1 | 18 | 28 | 140 | 2 | 3 | | 3 | 40 |
| Magnesium | 300 | 510 | 460 | 1,000 | MC | MC | 2,000 | | 2,000 | MC |
| Manganese | <1 | <1 | <1 | <1 | <1 | 40 | 10 | 58 | ND | <1 ^g |
| Mercury | 4.2 ⁱ | 660 ⁱ | 79 ⁱ | 6.2 ⁱ | 1.9 ⁱ | ND | ND | 0.5 | <0.0003 | 0.4 ⁱ |
| Molybdenum | 20 | <2 | <2 | <2 | <2 | ND | ND | | ND | 4 |
| Nickel | 2 | <3 | 4 | 3 | <3 | 7 | 80 | | 8 | <20 ^g |
| Niobium | 2 | | | | | ND | ND | | 8 | ND |
| Phosphorus | 100 | <200 | <200 | <200 | 3,200 | ND | 80 | | MC | 400 |
| Potassium | 6,000 | <40 | <40 | 2,400 | <40 | 7,000 | 1,000 | | MC | MC |
| Rubidium | 30 | | | | | <1 | ND | | ND | 20 |
| Scandium | <2 | | | | | ≤2 | ≤5 | | 2 | ND |
| Selenium | 40 | 600 ⁱ | 300 ⁱ | 89 ⁱ | 9 ⁱ | ND | 30 | <7 | 2,000 | 6 |
| Silicon | 400 | 7,900 | 7,700 | 7,800 | MC | 1,000 | 1,000 | | 2,000 | 2,000 |
| Silver | ND | <2 | <2 | <2 | <2 | ND | ND | 14 | 2 | 2 |
| Sodium | 200 | 6,000 | 6,500 | 6,100 | MC | >4,000 | 4,000 | | ND | MC ^g |
| Strontium | MC | 14 | 3 | 15 | 1,900 | 10 | 20 | | ND | 1,100 ^g |
| Sulfur | >9,000 | | | | MC | MC | MC | | ND | MC ^g |
| Tellurium | 4 | | | | | ND | ND | | ND | ND |
| Thallium | ND | <2 ⁱ | <2 ⁱ | <2 ⁱ | <2 ⁱ | ND | ND | | ND | ND |
| Thorium | <10 | | | | | 40 | 10 | | ND | ND |
| Tin | ND | | | | | ND | 20 | | 30 | 180 ^g |
| Titanium | 200 | <5 | <5 | 12 ⁱ | 1,800 | ND | 400 | 20 | 10 | 100 ND |
| Uranium | <10 | | | | | ≤10 | ≤30 | | 10 | ND |
| Vanadium | 1 | <3 | <3 | 13 ⁱ | 810 | | 1 | 3 | ND | ND 15 ^g |
| 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 | 35 ^g |
| Zirconium | 10 | | | | | ND | ≤30 | | 10 | 5 |

^a Units are µg/l unless otherwise noted.^b SSMS - spark source mass spectrometry.^c ICPES - induced coupled argon plasma-emission spectrometry.^d AAS - atomic absorption spectrophotometry.^e Blanks mean parameter not analyzed.^f MC - major component in the wastewater, concentration greater than 10,000 µg/l.^g Analyzed by induced coupled argon plasma-emission spectrometry.^h Not detected.ⁱ Analyzed by atomic absorption spectrophotometry.

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

| Gasification system Type of wastewater Method of analysis | Koppers-Totzek at Modderfontein | | | | KRW-PDU | | | Texaco at Ruhrkohle/Ruhrchemie | |
|---|------------------------------------|------------------------------------|-----------------------|-----------------------|-------------------------|-----------------|-----------|--------------------------------|-------------------|
| | Compressor condensate ^b | Compressor condensate ^c | Rectisol ^b | Rectisol ^c | Subbituminous coal | Bituminous coal | Lignite | Settler underflow | Settler underflow |
| | SSMS ^d | SSMS | SSMS | SSMS | AAS ^e /ICPES | AAS/ICPES | AAS/ICPES | SSMS | AAS/ICPES |
| Aluminum | 5 | 9 | 100 | 100 | ND ^f | 1,400 | 2,400 | MC ^h | MC |
| Antimony | ≤ 2 | 10 | < 1 | ND | ND | ND | ND | 90 | 21 |
| Arsenic | 2 | 4 | 20 | 10 | 73 | 300 | 420 | 600 | 480 |
| Barium | 100 | 40 | 200 | 200 | 1,200 | 550 | 470 | MC | 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 | MC | 700 | MC |
| Bromine | 80 | 300 | 30 | 60 | | | | 300 | |
| Cadmium | 3 | 7 | 1 | ND | ND | ND | ND | 70 | 190 |
| Calcium | MC | MC | MC | MC | MC | MC | 8,000 | MC | MC |
| Cerium | ND | 1 | 1 | ND | | | | 1,000 | |
| Cesium | < 1 | ND | < 1 | ND | | | | 70 | |
| Chlorine | 100 | 60 | 200 | 300 | | | | MC | |
| 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 | 740 |
| Dysprosium | ND | ND | ND | ND | | | | 50 | |
| Erbium | ND | ND | ND | ND | | | | 20 | |
| Europium | ND | ND | ND | ND | | | | 10 | |
| Fluorine | 30 | 3,000 | 400 | 3,000 | | | | MC | |
| Gadolinium | ND | ND | ND | ND | | | | 30 | |
| Gallium | < 1 | 3 | < 1 | < 1 | | | | 2,000 | |
| Germanium | 5 | 7 | < 1 | 2 | i | | | 3,000 | |
| Hafnium | ND | ND | ND | ND | | | | 20 | |
| Holmium | ND | ND | ND | ND | | | | 30 | |
| Iodine | 4 | 8 | 8 | 9 | | | | 20 | |
| Iron | 500 | 1,000 | MC | 2,000 | 1,800 | 600 | 2,300 | MC | MC |
| Lanthanum | ND | 1 | 1 | ND | | | | 900 | |
| Lead | 20 | 30 | 20 | 10 | ND | ND | ND | 4,000 | 3,100 |
| Lithium | 3 | 10 | 6 | 3 | | 100 | 44 | 70 | |
| Lutetium | ND | ND | ND | ND | | | | 2 | |
| Magnesium | 1,000 | 2,000 | MC | MC | 28,000 | 7,600 | 55,000 | MC | MC |
| Manganese | 10 | 9 | 50 | 80 | ND | 610 | ND | MC | 2,500 |
| Molybdenum | 30 | 20 | 40 | 20 | ND | ND | ND | 1,000 | 1,100 |
| Neodymium | ND | ND | ND | ND | ND | ND | ND | 100 | |
| Nickel | 4 | 7 | 200 | 100 | ND | ND | ND | 1,000 | 1,050 |
| Niobium | 2 | 5 | 2 | < 1 | | | | 200 | |
| Phosphorus | 70 | 70 | 700 | 1,000 | 1,300 | ND | ND | MC | 5,800 |
| Potassium | MC | MC | 5,000 | MC | 2,700 | 4,300 | MC | MC | MC |
| Praseodymium | ND | ND | ND | ND | | | | 100 | |
| Rubidium | 8 | 3 | 9 | 6 | | | | 2,000 | |
| Samarium | ND | ND | ND | ND | | | | 90 | |
| Scandium | ≤ 1 | ≤ 1 | < 1 | < 1 | | | | 700 | |
| Selenium | 1,000 | 2 | 50 | 40 | 38 | ND | ND | 1,000 | 1,600 |
| Silicon | 300 | 100 | 1,000 | 2,000 | MC | ND | ND | MC | MC |
| Silver | ≤ 2 | 1 | ND | ND | ND | ND | ND | < 6 | |
| Sodium | 2,000 | < 1,000 | > 1,000 | > 2,000 | MC | 8,600 | MC | MC | MC |
| Strontium | 70 | 30 | 300 | 500 | | | | 7,000 | |
| Sulfur | > 2,000 | > 3,000 | > 2,000 | > 4,000 | | | | MC | |
| Tantalum | 2 | ND | ND | ND | | | | 5 | |
| Tellurium | 3 | 3 | ND | ND | | | | 7 | |
| Terbium | ND | ND | ND | ND | | | | 1 | |
| Thallium | ND | ND | ND | ND | ND | ND | ND | 100 | 50 |
| Thorium | < 8 | < 3 | < 3 | < 6 | | | | 200 | |
| Thulium | ND | ND | ND | ND | | | | 4 | |
| Tin | 2 | < 1 | 4 | ND | | | | 100 | |
| Titanium | 30 | 200 | 100 | 200 | 46 | 18 | 110 | MC | MC |
| Tungsten | ND | ND | ND | ND | | | | 50 | |
| Uranium | < 7 | < 3 | 6 | 6 | | | | 300 | |
| Vanadium | 2 | < 1 | 3 | 5 | 20 | 14 | ND | 2 | 1,400 |
| Ytterbium | ND | ND | ND | ND | | | | 20 | |
| Yttrium | ≤ 1 | 1 | < 1 | < 1 | | | | 700 | |
| Zinc | 600 | 1,000 | 6,000 | 5,000 | ND | ND | ND | MC | 1,700 |
| Zirconium | 3 | 10 | < 1 | ≤ 1 | | | | 1,000 | |

^a Units as µg/l unless otherwise noted.

^b Purified sewage used as process feedwater.

^c Cooling tower makeup water used as process feedwater.

^d SSMS - spark source mass spectrometry.

^e AAS - atomic absorption spectrophotometry.

^f ICPES - induced coupled argon plasma emission spectrometry.

^g ND - not detected.

^h MC - major component in the wastewater, concentration greater than 10,000 µg/l.

ⁱ Blanks mean parameter not analyzed.

Table 9.3-9. Organics in fixed-bed coal-gasification wastewaters (Ref. 7).^a

| Gasification system | Chapman | | Foster-Wheeler/ STOIC | Riley | Lurgi-type at Kosovo |
|---|----------------------|-------------|--------------------------|------------------|-----------------------------|
| Wastewater type | Separator 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 ^c | 1500-4700 | ND ^d | ND | - ^e |
| Dimethylphenols (total) ^f | 1,200 | 330-1900 | ND | 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 |
| 1-Naphthol | 5.0 | 3.3-8.5 | ND | ND | ND |
| 2-Naphthol | 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 | - | - | ND | 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/astracene | 2.3 ^h | 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 ^h | 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 |
| 1-Methylnaphthalene | 2.3 | 0.43-4.2 | ND | ND | ND |
| 2,3-Dimethylnaphthalene | 2.3 | 0.65-<4.5 | ND | ND | ND |
| 2,6-Dimethylnaphthalene | 2.2 | <1.3-<3 | ND | ND | ND |
| Indole | 12 | 8-14 | ND | ND | ND |
| 2-Methylindole | 12 | 2.2-16 | ND | ND | ND |
| 3-Methylindole | 2.4 | 0.58-3.6 | ND | ND | ND |
| Diethyl phthalate | ND | - | ND | 1.9 | 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 | - | - | - | - | 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 | - | - | ND |
| m,p-Xylene | 0.15 | 0.124-0.172 | - | - | ND |
| o-Xylene | 0.28 | 0.034-0.184 | - | - | 0.8 |

^a All data as mg/l.^b Average of grab samples.^c One extremely high data point is not included in the average but the compound was identified 6 of 6 times.^d ND means not detected.^e Dashes mean parameter not analyzed.^f Includes 2,4-DMP.^g The portion of 2,4-DMP from the B/N fraction was estimated from the amount found in the acid fraction.^h Probable artifact of sample handling.

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

| Gasification system | Koppers-Totzek at Modderfontein | | KRW-PDU | | | Texaco at Ruhrkohle/Ruhrchemie |
|---|---------------------------------|-----------------|--------------------|-----------------|---------|--------------------------------|
| | Compressor condensate | Rectisol | Subbituminous coal | Bituminous coal | Lignite | Settler-underflow |
| Wastewater type | grab | grab | | | | grab |
| Sample type | grab | grab | | | | grab |
| Acid extractable compounds | | | | | | |
| Phenol | Tr ^b | Tr | 0.19 ^c | - | 0.16 | 0.0026 |
| Dimethylphenols (total) ^d | ND ^e | ND | - | - | - | ND |
| 2,4-Dimethylphenol | ND | ND | - | - | - | ND |
| o-Cresol | ND | ND | ND | - | ND | ND |
| m-Cresol | ND | ND | ND | - | ND | ND |
| p-Cresol | - | - | ND | - | ND | - |
| Total unknown phenols | - | - | - | - | - | - |
| Base-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 ^f |
| 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 | Tr ^f | Tr ^f | - | - | - | ND |
| Di-n-butyl phthalate | 0.006 ^f | 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 | - | - | - | - |
| Total volatile organics | - | - | - | - | - | 0.03-0.05 |

^a All data as mg/l.

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

^c Dashes mean parameter not analyzed.

^d Includes 2,4-DMP.

^e ND means not detected.

^f Probable artifact of sample handling.

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

| Gasifier/wastewater | Bioassay Test Results | | | |
|---|-----------------------|------------------------------------|---|---|
| | AMES ^a | In-vitro cytotoxicity ^b | Freshwater algae ^c EC ₅₀ | Fathead minnow ^d LC ₅₀ |
| Lurgi-type Kosovo/gas liquor | positive | CHO-M | - ^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 | CHO-H | 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% |

^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.

^c*Selenastrum capricornutum*, EC₅₀ - concentration of effluent estimated to cause a 50% decrease in biomass.

^d*Pimephales promelas*, LC₅₀ - concentration of effluent estimated to cause a 50% decrease in the fish population.

^eDashes mean parameter not analyzed.

^fValues expressed as percent concentration of sample in dilution water.

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 tests, 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 concerns 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.

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 H₂S (rather than SO₂), 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 SO₂ 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 H₂S 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 SO₂ and/or H₂S in very low concentrations (several ppm). The largest source of SO₂ from coal gasification arises from the combustion of

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

| Elements: | Facilities ^a | | Range | RCRA Limit |
|------------|-------------------------|------------|-------------------------|------------|
| | High | Low | | |
| Aluminum | F ^c | A | < BC ^b -0.15 | |
| Antimony | - ^c | - | < 0.005-<0.050 | |
| 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 | B | C | 0.099-MC ^d | |
| Chromium | E | D, G | < 0.001-0.3 | 5 |
| Cobalt | F | A | < BC-3.3 | |
| Copper | B | D, G | <0.001-0.1 | |
| Iron | E | D | <0.008-10 | |
| Lead | H | D, F, G, L | <0.002-0.025 | 5 |
| Lithium | G | A | ND ^e -0.29 | |
| Magnesium | B | C | 0.036-MC | |
| Manganese | B | E | 0.001-0.5 | |
| Mercury | - | - | <0.0002-<0.0005 | 0.2 |
| Molybdenum | E | A | < BC-0.1 | |
| Nickel | B, E | A | < BC-0.04 | |
| Potassium | B | I | ND-MC | |
| Selenium | A | C | < 0.001-0.01 | 1 |
| Silicon | B | C | 0.2-MC | |
| Silver | K | D | <0.0005-0.007 | 5 |
| Sodium | D | F | 1.6-140 | |
| Strontium | B | C | 0.06-6 | |
| Titanium | A, B | G, I | < 0.005-0.1 | |
| Vanadium | E | A | ND-0.07 | |
| Zinc | C | A | < BC-4 | |

^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.

^b<BC = less than or equal to blank concentration.

^cAll analyses below detection limit.

^dMC = major component.

^eND- not detected.

the low- or medium-BTU coal-gas product, where the H₂S 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_x 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_x 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.

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 particulate 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.

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 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 zero-discharge 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 circumstances; 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 Wastes

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 plant 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 wastewater treatment and disposal. Cleaned waters from the wastewater-treatment facility are

recycled as cooling-tower makeup-water since no discharges 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 sour-water 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.

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

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

| RCRA EPA Parameters | Ignitability Corrosivity Reactivity | Leachate concentration | Negative Negative Negative 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/l | | ND | 5.0 | (<0.002) |

(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/l | ND | 5.0 | (0.003) |
| Barium, mg/l | 25 | 100 | |
| Beryllium, mg/l | ND | 0.75 | (0.001) |
| Cadmium, mg/l | ND | 100 | (0.05) |
| Chromium, mg/l | 1.6 | 560 | |
| Chromium (+6), mg/l | ND | 5.0 | (0.005) |
| Cobalt, mg/l | 0.14 | 80 | |
| Copper, mg/l | 0.25 | 25 | |
| Fluoride, mg/l | 3.8 | 180 | |
| Lead, mg/l | 0.36 | 5.0 | |
| 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 | | |

ND = not detected.

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 heat-recovery 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 SO_2 , 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 results from compliance and supplemental testing of the incinerator stack gases, as is shown in Tables 9.4-4 and 9.4-5.

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 wastewater-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.

9.5. Research Needs and Priorities

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 facilities? 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 environmental 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 far 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.

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

| Parameter | Units | Emission limit | 1984 Test | 1985 Test |
|---------------------|-------------------|----------------|-----------|-----------|
| Sulfur dioxide | lb/hr | 35 | 33.1 | 16.8 |
| Nitrogen oxides | lb/hr | 140 | 61.2 | 68.9 |
| | ppmv @ 15% oxygen | 50 | 22.8 | 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 |

^a Approval 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.

Table 9.4-3. Cool Water HRSG stack gases: supplemental environmental data (Ref. 10).

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

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.

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

| 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 | |
| Cobalt | ppmv | 0.051 | |
| Iron | ppmv | 7.8 | |
| Magnesium | ppmv | 1.2 | |
| Manganese | ppmv | 0.34 | |
| Mercury | ppmv | 0.12 | |
| Nickel (total) | ppmv | 62 | |
| Silicon | ppmv | 1.7 | |
| Sodium | ppmv | 0.63 | |
| Titanium | ppmv | 0.15 | |
| Zinc | ppmv | 0.37 | |
| Organic compounds detected | | None | |

ND = not detected.

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 regulated by the 1970 Clean Air Act, e.g., SO₂, 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 long-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_x 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.

References

1. S. B. Baruch and J. S. Feher, "Toxic Substances: Future Electric Utility Considerations," Proceedings of the American Power Conference, Vol. 47, Illinois Institute of Technology, Chicago, IL (1985).
2. E. S. Rubin and F. C. McMichael, *Environ. Sci. Technol.* **9**, 112 (1975).
3. J. P. Fillo and M. J. Massey, "Fate of Phenols During the Gasification of Coal," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology IV, 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).
5. 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).
6. 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).
7. 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).
8. A. G. Eklung, "Coal Gasification Environmental Data Summary: Solid Wastes and By-product Tars," Report No. EPA-600/7-86-015c, US EPA, Research Triangle Park, NC (April 1986).
9. V. P. Sabin, "Progress Report on Great Plains Gasification Project," Alternate Energy '86 Conference, Council on Synthetic Fuels, Captiva Island, FL, May 1986; also, private communications with US DoE, Radian Corp., and ERT, Inc. (1986).
10. R. W. Grover et al., "Preliminary Environmental Monitoring Results: Cool Water Coal Gasification Program," National AIChE Meeting, Boston, MA, American Institute of Chemical Engineers, NY (April 1986).