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**Assessment of Environmental Control
Technology for Coal Conversion
Aqueous Wastes**

J. A. Klein
R. E. Barker

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ASSESSMENT OF ENVIRONMENTAL CONTROL TECHNOLOGY
FOR COAL CONVERSION AQUEOUS WASTES

J. A. Klein and R. E. Barker

Date Published - July 1978

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ABSTRACT

The commercial design of a coal hydrocarbonization plant was studied to define the problem of wastewater. The wastewater streams were identified and the literature was reviewed to determine the amounts and components of the various wastewater streams. Although no federal effluent guidelines exist for coal conversion plants, the effluent guidelines of related industries were studied so that future effluent guidelines for coal conversion plants could be anticipated. Several cleanup technologies were assessed for their adaptability to coal conversion wastewaters.

1. CONCLUSIONS AND RECOMMENDATIONS

This report defines the wastewater problem in a hydrocarbonization process such as that described in the Coalcon¹ coal conversion flowsheet. Many of the wastewater streams will, theoretically, be completely recycled internally, and thus may not be of concern. Others are fairly well defined, and adequate cleanup technology exists to bring these streams into compliance with any reasonable regulations.

However, many streams are not well characterized either in quantity of flow or in pollutant content. This is particularly true of the organic content (e.g., PNA, phenols) of the cooling tower streams, caused by leaks from process streams to cooling water streams, and the

trace-element content of the ash slurry to the ash pit. These are the streams for which it will be most difficult to apply adequate cleanup technology. Of greatest concern to those involved in wastewater cleanup will be the content of phenols, polynuclear hydrocarbons (PNAs), and trace elements.

It is recommended that:

1. Additional analytical research should be carried out in the characterization of the following critical wastewater streams: (1) runoff from plant grounds and coal storage; (2) water streams from the hydrocarbonization reactor, ammonia stripping, and condensate from the hydrocarbon separation unit; and (3) ash and slag quenching, and sluicing water and leachate from stored ash and slag.
2. Additional reliability studies should be conducted to quantify leak rates into the cooling water through the many heat exchangers that will be needed in a coal conversion plant.
3. Future research studies should be conducted to determine acceptable effluent limits for PNAs and a variety of trace elements. This should be done from the standpoint of a-best-available technology, as well as based on the relative hazards to human health and the environment of the potential pollutants.
4. Screening tests should be performed to assess the adaptability of a variety of presently available and advanced cleanup technologies to coal conversion wastewaters.

2. INTRODUCTION

In order to commercialize the production of clean (i.e., low-sulfur, low-ash) boiler fuel from coal, the Department of Energy (DOE) is studying

many coal conversion processes. This report describes the wastewater problem of coal conversion using the Coalcon hydrocarbonization design.¹ The design work for the Coalcon hydrocarbonization process was recently suspended for various economic and technical reasons. The Coalcon flowsheet, however, still describes a representative coal conversion process that can be used to determine the wastewater problem. The disposal of wastewater from coal conversion plants is not a trivial problem. To meet the goal of replacing 20% of the present oil consumption in the United States with clean fuels from coal, it will take about 80 large (12,000 to 20,000 tons/day) coal conversion plants.² A coal conversion industry of these proportions would produce a very large amount of wastewater (4×10^8 to 8×10^8 tons/year). Although this is considerably smaller than the wastewater produced in the petroleum refining industry ($\sim 2 \times 10^{10}$ tons/year),^{3,4} it is a significant amount of waste.

Hydrocarbonization is one of the more completely investigated coal conversion technologies and is a likely process for commercialization for the following primary reasons:

1. Only low-sulfur gaseous and liquid products are produced.
2. Hydrocarbonization is a noncatalytic process.
3. There is no difficult solid-liquid separation as in the Solvent Refined Coal (SRC), COED, Synthoil, and H-COAL processes.

For these reasons, an environmental evaluation of hydrocarbonization is a timely project.

As of December 1977, no evaluations of environmental control technology for the hydrocarbonization process were available. However, evaluations of other processes have been published. Exxon Corporation has published evaluations of several gasification and liquefaction processes⁵⁻¹⁵ in conjunction with the Environmental Protection Agency (EPA). Under contract with the EPA, Booz-Allen Applied Research Corporation has also published an evaluation of several clean fuel processes.¹⁶ Other coal conversion environmental evaluations have also been published.^{17,18}

Coal conversion aqueous wastes are often compared with their counterpart in the coke production industry. For this reason, the phenolic and light-oil components of the wastewater are well characterized and have generally been anticipated. Hydrocarbonization will produce greater quantities of these pollutants and will have more serious ammonia, hydrogen sulfide, and trace-element problems.

This report represents an effort to identify the sources, composition, and hazardous level of the aqueous effluents from coal hydrocarbonization. In addition, existing and anticipated effluent guidelines for coal conversion have been evaluated. Present commercial and developing technologies have been assessed for their ability to treat these aqueous wastes.

3. PROCESS DESCRIPTION

Hydrocarbonization denotes contacting of coal and gaseous hydrogen (usually in a fluidized bed) at intermediate temperatures (425 to 650°C) and pressures (≤ 100 atm). Hydrocarbonization was developed in the 1950s

and 1960s by Union Carbide Corporation to produce chemical feedstocks. A 20-ton/day pilot plant was successfully operated in the early 1960s using a low-sulfur, nonagglomerating coal.¹⁹ The hydrocarbonization process was not commercialized at that time because it could not compete with the cheaper petroleum feedstocks that were available in 1964.

The proposed hydrocarbonization scheme calls for the conversion of 628 tons of coal per hour to liquid and gaseous products, as well as ammonia and elemental sulfur by-products. The product breakdown is shown in Table 3.1. The solid hydrocarbonization char is totally consumed for process hydrogen production and process heat generation in a Texaco partial-oxidation gasifier and conventional steam plant.

Figure 3.1 is a schematic diagram of the hydrocarbonization process. Table 3.2 is a description of the streams shown in Fig. 3.1. In the following discussion, the numbers in parentheses refer to the streams listed in Table 3.2. The flow rates have either been taken directly from or have been calculated from material balance information in ref. 1. More detailed process descriptions are available.^{1,20}

Run-of-mine coal (stream 1) is delivered and stored in one of two types of storage. Live storage is short-term storage from which the coal will be used in a relatively short period of time. Dead storage refers to additional long-term storage that is to be used in case the normal delivery of coal is stopped. The coal (stream 4) is taken from storage and is crushed, dried, pressurized to 555 psi, and heated to about 325°C. The dried, heated coal (stream 12) is then fed by lock hoppers to the hydrocarbonizer, which operates at 560°C and 555 psia with a hydrogen partial pressure at the gas inlet of 527 psia. The

Table 3.1. Hydrocarbonization product summary^a

Product	Production rate (per day)	Heating value as percent of coal feed
Heavy fuel oil	13,153 bbl	22.67
Gasoline fraction	6,788 bbl	9.56
LPG product	4,387 bbl	4.94
Pipeline SNG	105 x 10 ⁶ scf	30.01
Anhydrous ammonia	48.4 tons	0.26
Sulfur (elemental)	352.4 tons	<u>0.77</u>
Total heat feed retained in products (thermal efficiency)		68.21

^aData adapted from ref. 1, p. 2-44.

Fig. 3.1. Schematic-hydrocarbonization plant.

Table 3.2. Identification of hydrocarbonization process streams

Stream No.	Stream description
1	Coal from mine, 628 tons/hr
2	Rainwater to coal storage
3 ^a	Rainwater runoff from coal storage, 530 lb/hr
4	Coal feed to crushing, 628 tons/hr
5	Coal to boiler, 35.1 tons/hr
6	Coal to hydrocarbonization, 593 tons/hr
7	Dry flue gas to coal drying, 1,080,428 lb/hr
8	Wet flue gas to sulfur recovery, 1,092,112 lb/hr
9	Steam from char cooling, 5000 lb/hr
10 ^a	Contaminated condensate, 125,000 lb/hr (steam made from contacting water with hot char)
11	Steam, 60,642 lb/hr
12	Pressurized coal, 1,089,167 lb/hr
13	Heavy fuel oil to storage, 211,779 lb/hr
14	Water (to be converted to steam by char contact)
15	Light fuel oil, 78,936 lb/hr
16	Char and transport steam, 5000-lb/hr steam, 513,144-lb/hr char
17	Hydrogen gas, 208,106 lb/hr
18	Light gases from reactor, 397,069 lb/hr
19 ^a	Reactor aqueous product, 105,056 lb/hr to ammonia stripping
20	Steam from hydrocarbonization to pressurization, 85,274 lb/hr
21	Agglomerates, approx 160-lb/hr char
22	Ammonia-rich vapor stream to ammonia recovery
23 ^a	Condensate recycle, 12,331 lb/hr
24	Ammonia product, 4067 lb/hr
25 ^a	Wastewater from ammonia stripping to char slurring, 175,000 lb/hr
26	Gas from ammonia stripping to acid gas removal, 472,000 lb/hr (ethane, methane, H ₂ S, etc.)

Table 3.2 (continued)

Stream No.	Stream description
27 ^a	Wastewater recycle, 52,000 lb/hr
28	Steam, 18,000 lb/hr
29	H ₂ S-rich stream to sulfur recovery, 13,300 lb/hr
30	Steam, 20,000 lb/hr
31	Water, 32,000 lb/hr
32	Clean gas to hydrogen purification, 380,000 lb/hr
33	LPG product to storage, 34,600 lb/hr
34	Synthesis gas to methanation, 168,917 lb/hr
35	Hydrogen recycle to reactor, 32,895 lb/hr
36	SNG product to storage, 206,282 lb/hr
37 ^a	Wastewater, 38,000 lb/hr
38	Makeup hydrogen from Texaco unit, 162,865 lb/hr
39	Char-water slurry to Texaco unit, 354,663-lb/hr char, 250,292-lb/hr water
40	Makeup water to char slurrying, ~75,000 lb/hr
41	Sluicewater return from ash pond
42 ^a	Ash slurry to pond from Texaco unit, 86,581 lb/hr, 10% H ₂ O
43 ^a	Gasifier water jacket blowdown, 1715 lb/hr
44	Steam, 70,000 lb/hr
45	Makeup water, 68,430 lb/hr
46	Quench evaporation
47	Char to Texaco unit, 354,663 lb/hr
48	Char to boiler, 158,481 lb/hr
49	Boiler flue gas to sulfur recovery, 1,574,284 lb/hr
50	Sulfur recovery flue gas feed, 2,666,396 lb/hr
51	Desulfurized flue gas to stack, 3,527,940 lb/hr
52	Ash sluicewater return, 308,331 lb/hr
53 ^a	Ash slurry to ash pit, 34,259-lb/hr ash, 308,331-lb/hr water

Table 3.2 (continued)

Stream No.	Stream description
54	Sluicewater makeup
55	Boiler feed water, 1,623,800 lb/hr
56	Steam, 1,593,800 lb/hr
57 ^a	Boiler blowdown, ~30,000 lb/hr
58 ^a	Contaminated rainwater runoff of plant grounds
59 ^a	Cooling tower blowdown, 358,000 lb/hr
60	Cooling tower losses
61	Cooling tower makeup, 4,081,000 lb/hr
62	River water, 5,658,500 lb/hr
63	Boiler feed water, 3,410,000 lb/hr
64	Potable water, 150,000 lb/hr
65	Wastewater to Texaco unit, 50,000 lb/hr
66 ^a	Clarifier blowdown, 70,000 lb/hr
67 ^a	Blowdown from demineralizer, 265,000 lb/hr
68	Water to ammonia recovery, 89,300 lb/hr
69	Turbine condensate
70	Boiler feed water return
71	Steam
72	Sulfur product, 15,720 lb/hr
73	NaSO ₄ product, 528 lb/hr
74	Air to incineration, ~900,000 lb/hr

^aDenotes wastewater stream.

solids residence time in the reactor is ~25 min. The unreacted solids and char (stream 16) are cooled and sent to the hydrogen-production or steam-generation units. The reactor overhead product is quenched with a recirculating oil scrub and fed to a 40-tray fractionator. The fractionator bottoms (stream 13) is a heavy, high-boiling boiler feed, and the overhead product is separated into gas (stream 18), light oil (stream 15), and aqueous phases (stream 19). The light oil is the low-boiling "gasoline fraction" and is sent to product storage. The aqueous phase is steam stripped to remove ammonia for recovery and is sent to the hydrogen production gasifier (stream 25). The gas phase (stream 18) and the overhead from the ammonia stripper (stream 22) are sent to a gas cleanup section for removal and recovery of ammonia (using the U.S. Steel Phosan-W process) and hydrogen sulfide (using the Rectisol process). The anhydrous ammonia (stream 24) is sent to product storage, and the hydrogen sulfide (stream 29) is sent to the Aqua-Claus plant for sulfur recovery. The gas is cryogenically separated to hydrogen (stream 25) for recycle to the reactor, an LPG product (stream 33), and a synthesis gas. The char from hydrocarbonization and char cooling (stream 47) is gasified in a Texaco partial oxidation unit to produce makeup hydrogen for hydrocarbonization (stream 38) with the excess hydrogen and carbon monoxide (stream 35) added to the main product gas stream. The remainder of the char (stream 48) is burned in the boiler to produce process heat. The sulfur dioxide is scrubbed from the stack gas (stream 49) in a regenerative absorption system and sent to the Aqua-Claus plant for reduction to elemental sulfur (stream 51).

4. IDENTIFICATION OF WASTEWATER STREAMS

The hydrocarbonization plant has 15 major wastewater streams. The main sources of wastewater are coal storage, hydrocarbonization aqueous product, and ash handling streams. In the Coalcon design,¹ most of the wastewater is utilized in the plant, including all the organically contaminated water. Although data on the composition of the wastewater streams are lacking, the composition of the various streams has been postulated based on an analysis of similar streams in similar processes.

All organically contaminated aqueous streams are recycled within the process, and a method for destruction or recovery of the organics is provided. Some ash sluicing water overflows the ash pond and enters the river via a percolation bed during periods of very high rainfall (e.g., a 10-year, 24-hr precipitation event). This stream is very low in organic contaminants but may contain toxic trace elements; however, it has been shown²¹ that soil used in percolation beds is a very effective sorber of trace elements (>95% retention of trace elements in 5 to 20 ft of soil).

In this design, a sizeable volume (~130,000 lb/hr) of water is discharged to surface water. This stream contains some water treatment wastes, treated cooling tower blowdown, and the effluent from the sanitary waste treatment plant. The main wastewater streams (see Fig. 3.1) of concern to this report are discussed below.

4.1 Coal Storage Runoff

Rainwater runoff from coal storage piles (stream 3) is a significant water quality hazard. A 90-day supply, or ~1.3 million tons of coal, is

kept in storage. The average rainwater runoff from this 30 to 40-acre supply is about 530 lb/hr. Water percolating through the pile can react with sulfur-bearing mineral matter by a mechanism not totally unlike that of acidic coal-mine drainage. The sulfuric acid formed in these reactions then dissolves salts from the coal.

In its investigation of electric power generation,²² the EPA studied drainage from coal storage piles, and Table 4.1 summarizes these results. Plants 6, 7, and 8 used high-sulfur coal and have the most acidic drainage; plants 9, 10 and 11 used a very low-sulfur coal, which resulted in near neutral drainage. The EPA did not report the size of the coal storage piles, the location of the plants, nor the amount of rainfall received during the tests.

Based on this information, it is estimated that the drainage from a coal storage pile using Illinois No. 6 coal would have a pH of 2 to 5 and a total suspended solids concentration count of approximately 100 to 400 mg/liter. Since the drainage is fairly acidic, significant amounts of trace metals (e.g., mercury, cadmium, zinc, arsenic, lead, chromium, copper) are expected to be leached into the water. The concentrations of these metals will probably be higher than the standards set by the U.S. Public Health Service for drinking water and current discharge limits. A more complete discussion of trace elements is found in Sect. 5.2.

The Coalcon design¹ calls for the coal pile runoff (stream 3) to be stored and reclaimed as makeup slurry water for the Texaco gasification unit. Recycling the runoff from coal storage routes water with a low pH and high concentrations of suspended solids and trace elements to

Table 4.1. Coal storage-pile drainage discharge concentrations (mg/liter)^a

Plant	pH	BOD	COD	TDS	TSS	NH ₃	NO ₃ ⁻	P	Total hardness	SO ₄ ²⁻	Cl ⁻	Al ³⁺	C ⁻	Cu	Fe	Mg	Zn	Na
1	2.8	0	1080	720	610	0	0.3		130	525	3.6		0	1.6	0.168		1.6	1260
2	2.8	0	1080	720	610	0	0.3		130	525	3.6		0	1.6	0.168		1.6	1260
3	3	10	806	7,743	22	1.77	1.9	1.2	1109	5,231	481		0.37			89	2.43	160
4	4.4		85	3,800	200	1.35	1.8		1850	861			0.05		0.06	174	0.006	
5	7.8	3	1099	247	3302	0.35	2.25	0.23		133	23						0.08	
6 ^c	2.7									6,837					0.368			
7 ^c	2.1			28,970	100					19,000		1200	15.7	1.8	4,700		12.5	
8 ^c	2.8			44,050	950					21,920		825	0.3	3.4	93,000		23	
9 ^d	6.7														1.0			
10 ^d	6.6														1.05			
11 ^d	6.6														0.9			
Effluent limits ^e	6-9				35.0							2.0			3.5		0.2	

^aValues derived from ref. 22, p. 165

^bAs CaCO₃.

^cPlant uses high-sulfur coal.

^dPlant uses very low-sulfur coal.

^eSee columns under "Coal mining," Table 6.1 in this report.

the gasifier. The organic portion of the waste is utilized in the gasifier as hydrogen production feedstock, and the inorganics ultimately go to the ash pond.

Although the Coalcon flowsheet¹ and other coal conversion schemes are based on coal storage equal to a 90-day supply, it is not clear that such a large supply is needed. Since hydrocarbonization produces a storable product (as opposed to coal-fired power plants), such a plant can provide deliveries from product storage for some time (the Coalcon flowsheet¹ requires a product storage capacity equal to 3 days of production for the SNG, LPG, light and heavy oils, ammonia, and sulfur products) in the event of an interruption of the coal supply. Furthermore, if the plant output is used by an interruptible consumer a smaller amount of coal storage may be used. In any case, the need for some downstream storage is evident since circumstances other than an interruption of the coal supply can cause production to stop. The optimum size of coal and product storage capacities are beyond the scope of this study and will not be discussed further.

4.2 Coal Pressurization Condensate

Stream 10 (125,000 lb/hr) is the condensate from the steam pressurization section. This steam (stream 20) is produced by contacting liquid water with hot char from the reactor and may be contaminated with phenolics, other organics, ammonia, and hydrogen sulfide. Since there are no available data on the composition of this stream or a similar stream, only an estimation of the composition of the contaminants in stream 10 is possible. The Coalcon flowsheet¹ shows this stream being sent to the gasifier as char slurry makeup water.

4.3 Hydrocarbonization Product Water

The reactor overhead product from hydrocarbonization contains a significant quantity of water vapor that passes overhead in the product separation fractionator and is condensed and decanted from the hydrocarbon stream. This aqueous stream (stream 19), often known as sour water, is one of the major water quality hazards of coal conversion. Its large flow (~105,000 lb/hr) and high concentration of contaminants make it an important stream to consider. Although no analysis of either the Coalcon product water stream or a hydrocarbonization process similar to Coalcon has been reported, data are available from similar processes.

U.S. Steel²³ has reported an analysis of water formed in their Clean Coke Process hydrocarbonizer. This reactor was operated at a temperature of 593°C, a total pressure of 80 psia (~50% H₂), and yielded 4.5% product water (based on coal feed). This analysis, shown in Table 4.2, indicates potentially recoverable amounts of phenolics and ammonia.

The FMC Corporation has developed the COED²⁴ process, which is a staged pyrolysis process not drastically dissimilar from hydrocarbonization. In the COED process, the coal-char is heated at successively higher temperatures in a reducing atmosphere. COED produces two product-water streams; an analysis of these streams,²⁵ produced by two feedstocks, is shown in Table 4.3. A more detailed compound breakdown of the major organic species in the first-stage liquor has been reported²⁶ and is shown in Table 4.4. Although these two analyses show different concentrations for phenol, the higher concentrations are probably more representative.

Table 4.2. Analysis of clean coke
hydrocarbonization product water^a

Component	Concentration (mg/liter)	Effluent standards ^b (mg/liter)
CNS ⁻	1,171	
CN ⁻	74	0.02-0.1
SO ₄ ²⁻	2,050	
S ²⁻	562	0.02-0.2
NH ₃	33,320	0.8 -5.0
Phenol	3,200	} 0.03-0.3 (total)
o-Cresol	700	
m, p-Cresol	1,500	
Xylenols	500	

^aValues derived from ref. 23, p. 43.

^bSee columns under "Anticipated regulations," Table 6.1 in this report.

Table 4.3. Analysis of product water from the COED process^a

	Concentrations (wt%)			
	First-stage liquor		Second-stage liquor	
	Utah subbituminous	Illinois No. 6	Utah subbituminous	Illinois No. 6
Carbon	0.17		2.0	
Nitrogen	0.01	0.05	0.88	0.93
Sulfur	0.01	0.07	0.13	0.18
Entrained oil	0.01		0.2	0.0-0.5
Suspended solids	0.03	0.49	0.64	1.09
Phenol	9.2 ppm	0.00	0.40	0.38
(pH	8.1	3.6	9.0	8.8)

^aValues derived from ref. 26, p. 155.

Table 4.4. Analysis of first-stage water from the COED process^a

Compound	Concentration (ppm)
Phenol	2060
<u>m</u> , <u>p</u> -Cresol	1830
<u>o</u> -Cresol	650
Acetic acid	602
2,5-Dimethylphenol	217
3,5-Dimethylphenol	240
3,4-Dimethylphenol	873
2,6-Dimethylphenol	30
<u>o</u> -Ethylphenol	34
2,3-Dimethylphenol	26
Propionic acid	94
Butyric acid	40
Valeric acid	30
Hexanoic acid	32

^aValues derived from ref. 26, p. 13.

A gasification process called Synthane is being developed at the Pittsburgh Energy Research Center (PERC), and much analytical data are in the literature.²⁶⁻²⁹ Although gasification of coal is fundamentally different from hydrocarbonization, the Synthane process is similar because the coal is fed into free-fall in a hot, hydrogen-rich atmosphere in which the coal is devolatilized. These devolatilization products are probably similar to hydrocarbonization products. Table 4.5 summarizes the Synthane product water analyses performed at PERC²⁷ for several different coals. Table 4.6 summarizes a more detailed analysis of organic compounds in the Synthane product that was made at ORNL.²⁶

Based on these analyses, it is possible to extrapolate the composition of the hydrocarbonization product water. It will have a pH of approximately 8 to 10, and may be up to 1% phenolics. Carboxylic acids may be present in concentrations of 500 to 1000 ppm with appreciable cyanate (10 to 200 ppm) and thiocyanate (100 to 2000 ppm) concentrations. The stream will be rich in ammonia, possibly as much as 3%, with H_2S concentrations in the range 200 to 1500 ppm as sulfide. Up to 1% suspended or entrained insoluble oils and grease may be present. The condensate should be free of solids, since the vapor stream will have passed two cyclone stages and a venturi scrubber. The fines collected in the cyclone will be recycled to the hydrocarbonization reactor or the gasifier. Only the more volatile trace elements (e.g., mercury, arsenic) will be found in the hydrocarbonization product water. These trace elements are discussed in more detail in Sect. 5.2.

The Coalcon flowsheet¹ shows that the hydrocarbonization product water (stream 19) is sent to a steam stripping column for the recovery

Table 4.5. Analysis of Synthane product water^a for several gasifier feedstocks and comparison with effluent standards (concentration in mg/liter)

Coal	Illinois No. 6 coal	Wyoming subbituminous coal	Illinois char	North Dakota lignite	Western Kentucky coal	Pittsburgh steam coal	Effluent standards ^b
Suspended solids	600	140	24	64	55	23	3-15
Phenol	2,600	6,000	200	6,600	3,700	1,700	0.03-0.3
COD	15,000	43,000	1,700	38,000	19,000	19,000	20-350
Thiocyanate	152	23	21	22	200	188	
Cyanide	0.6	0.23	0.1	0.1	0.5	0.6	0.02-0.1
NH ₃	8,100	9,520	2,500	7,200	10,000	11,000	0.08-5.0
Chloride	500		31				0.2
Carbonate	6,000						
Bicarbonate	11,000						
Total sulfur	1,400						
(pH)	8.6	8.7	7.9	9.2	8.9	9.3	6-9)

^aValues derived from ref. 27, p. 3.

^bSee columns under "Anticipated regulations," Table 6.1 in this report.

Table 4.6. Major organic constituents
of Synthane product water^a

Component	Concentration (mg/liter)
Phenol	2070
<u>m</u> , <u>p</u> -Cresol	1830
<u>o</u> -Cresol	670
Acetic acid	619
2,5-Dimethylphenol	248
3,5-Dimethylphenol	225
3,4-Dimethylphenol	94
2,6-Dimethylphenol	44
<u>o</u> -Ethylphenol	33
2,3-Dimethylphenol	32
Propionic acid	63
Butyric acid	18
Valeric acid	10
Hexanoic acid	16
α -Naphthol	10
β -Naphthol	32

^aValues derived from ref. 26, p. 13.

of ammonia and sulfur. Ammonia is recovered from the water for economic reasons, and any sulfur left in the water after stripping is recovered in the treatment of the synthesis gas produced in the gasifier. After stripping, the stream (stream 25) is somewhat larger due to steam condensation, and it contains less NH_3 and H_2S and is slightly depleted in phenolics.

4.4 Acid-Gas Removal and Hydrocarbon Separation Recycles

Stream 23 is a small, aqueous condensate stream formed in the hydrocarbon separation section when the gas stream is cooled to 13°C . This stream should be free of H_2S and NH_3 and may contain some light hydrocarbon liquids that passed the earlier recovery steps. The Coalcon flowsheet shows this stream returning to the decanter in the hydrocarbonization section for recovery of any hydrocarbon values.

Stream 27 is formed by regeneration of the activated carbon beds located in the gas outlet of the acid-gas removal section. The beds are designed to scavenge small quantities of sulfur that would be destructive to downstream catalysts, but they also sorb light hydrocarbons and aromatics. The adsorption beds are operated semicontinuously, with regeneration when the effluent gas quality begins to decline. For this reason, the quantity of the regeneration wastes (i.e., frequency of regeneration) and the concentration of contaminants depends very strongly on the effectiveness of the upstream gas treatment. Assuming that gas leaving the acid-gas removal section is 50-ppm H_2S , the regeneration wastewater may contain up to 0.1% dissolved H_2S . The regeneration waste stream probably contains some dissolved light aromatics and some suspended light oils (>5 ppm). The Coalcon flowsheet¹ shows recycle of this stream

to the decanter in the hydrocarbonization section for sulfur recovery and utilization of hydrocarbon values.

4.5 Methanation Product Water

Stream 37 is the water stream produced in the methanation section where residual CO and CO₂ are converted to methane by the following reactions.

Approximately 38,000 lb of water per hour is formed by this reaction. It is anticipated that this stream will be free of contaminants, and one design for a commercial gasification plant³⁰ used this water for boiler feed. However, the Coalcon flowsheet does not identify the destination of this stream.

4.6 Ash Slurries

Streams 53 and 42 are the boiler ash and gasifier ash slurries. These streams contain most of the inorganics contained in the coal feed to the system. Although the boiler and gasifier operate quite differently, the ash formed in both operations is similar. The major ash constituents of two samples of Illinois No. 6 coal are shown in Table 4.7.³¹ The ash composition is different in two samples from the same seam, and such differences will probably be more marked in samples from other seams. Sample No. 2 is somewhat anomalous in the high content of iron. In addition to the major ash constituents, all coals have relatively large amounts of many trace elements. Most of the trace-element content of the

Table 4.7. Major ash compounds^a as percent ash

Illinois No. 6 coal	Sample No. 1	Sample No. 2
SiO_2	50.0	17.5
Al_2O_3	22.2	9.2
Fe_2O_3	10.75	64.13
TiO_2	0.94	0.44
CaO	9.00	4.05
MgO	1.14	0.38
Na_2O	0.35	0.26
K_2O	2.20	0.97
SO_3	1.56	1.84
Ash content of coal (% dry coal)	14.36	9.59

^aValues derived from ref. 31, pp. 49 and 75.

feed coal ultimately goes to the ash slurries and the ash pond, either in solution or in the solid phase. Table 4.7 shows the results of an analysis of coal ash formed in an air atmosphere at 950°C, which is similar to the ash formed in a boiler furnace or partial oxidation gasifier.

One study concerned with leaching of ash materials was done by the Radian Corporation²¹ for the Electric Power Research Institute. This report presents data from batch ash-leaching experiments using ash obtained from five power plants and ash-pond-water analysis for four power plants.

The ash leaching data were obtained by contacting a mixture of 20-wt % ash and deionized water for 24 hr in a closed container. Table 4.8 shows a summary of the ash leachate trace-element results. The major species in the ash leachate are shown in Table 4.9. The pH of the leaching solution can alter equilibrium trace-element leaching data. The Radian report also gives data on the analyses of ash pond water, and coal and makeup water for three of the plants studied. Table 4.10 summarizes those results. Additional information on the coal properties used in the tests is given in Table 4.11.

Farnsworth et al.³² have published an analysis of the ash sluicing water from a commercial Koppers-Totzek (K-T) gasifier, which is an entrained flow, slagging gasifier that operates at atmospheric pressure. Although the Texaco unit in the Coalcon process is different from the K-T gasifier, the ash sluicing water should be of similar composition. Table 4.12 shows the analysis of ash sluicing water to and from the gasifier.

Table 4.8. Comparison of equilibrium concentrations of trace elements in coal-ash leachate^a and effluent standards

	Station					Effluent standards ^b
	1	2	3	4	5	
Bottom ash, wt %	20	20	20	50	100	
Precipitator ash, wt %	80	80	80	50		
pH	12.5	9.5	12.2	12.0	8.2	6-9
<u>Element (mg/liter)</u>						
Sb	0.006	0.018	0.033	0.022	0.0087	
As	<0.002	0.084	0.015	0.072	0.006	0.25
Ba	40	<0.3	<0.3	<0.3	<0.3	2.0
Be	0.003	0.00064	0.0007	0.001	0.00026	
B	0.03	16.9	0.21	1.1	0.048	
Cd	<0.001	0.0025	<0.01	<0.001	0.0011	0.15
Cr	<0.001	0.21	0.11	1.0	0.14	0.1-1.0
F	2.3	1.4	2.0	17.3	1.4	14
Ge	<0.01	<0.01	<0.01	<0.01	<0.01	
Hg	0.0006	0.0005	0.015	0.0003	0.0003	0.0005
Pb	0.0068	0.0027	0.024	0.0043	0.0063	0.1
Mn	<0.002	<0.002	<0.002	<0.002	<0.002	1.0
Mo	0.047	0.052	0.05	0.69	0.010	
Ni	<0.05	0.015	0.025	<0.05	0.46	1.0
Se	0.009	<0.0005	0.033	0.47	<0.0005	1.0
V	<0.1	<0.1	<0.1	<0.2	<0.1	
Zn	0.038	0.025	0.19	<0.005	0.0175	1.0
Cu	<0.005	0.031	0.092	0.013	0.015	1.0

^aValues derived from ref. 21, p. 20.

^bSee columns under "Anticipated regulations," Table 6.1 in this report.

Table 4.9. Ions present in ash sluicing waters^a

Species	Concentration (mg/liter)
Ca	900
Na	72
K	4
Mg	1
Total Fe	1
OH	800
CO ₃	70
Cl	10
SO ₄	10
NO ₃	2

^aValues derived from ref. 21, p. 28.

Table 4.10. Trace-element fate^a for coal-fired steam generating plants

Element	Station No. 2					Station No. 3					Station No. 4				
	Coal (ppm)	Bottom ash (ppm)	Fly ash (ppm)	Ash pond liquor (mg/l)	Makeup water (mg/l)	Coal (ppm)	Bottom ash (ppm)	Fly ash (ppm)	Ash pond liquor (mg/l)	Makeup water (mg/l)	Coal (ppm)	Bottom ash (ppm)	Fly ash (ppm)	Ash pond liquor (mg/l)	Makeup water (mg/l)
Sb	0.34	1.3	1.5	0.005	0.008	0.82	0.72	2.5	0.003	<0.001	0.08	<1.0	4.4	0.007	<0.002
As	8.7	8.3	74	0.02	<0.0004	3.5	8.0	56.6	0.003	0.004	0.87	4.4	61	0.004	0.006
Ba	100	700	700	<0.3	<0.3	100	750	750	<0.3	<0.3	440	5600	15,000	<0.3	<0.3
Be	1.3	4.7	7.5	0.003	0.003	2.1	7.9	13.1	0.0004	0.0004	0.29	0.40	5.2	0.002	0.001
B	36.5	80.0	274	0.233	0.112	62.1	120	392	0.47	0.019	37.7	83.2	1,040	0.41	0.25
Cd	0.05	0.41	1.4	0.0005	0.0004	0.30	0.86	5.3	0.0001	0.0009	0.11	1.1	4.2	0.0001	<0.0001
Cr	1.2	14.7	3.6	<0.0008	<0.001	3.4	11.0	28.0	<0.0006	0.003	1.8	15.6	8.9	0.004	0.09
F	193	72.2	83.9	0.35	0.18	144	61.0	210	0.43	0.90	78.5	44.6	2,880	0.43	2.72
Ge	2.9	1.0	12.1	0.02	<0.1	4.4	1.8	25.1	0.02	0.02	0.48	<0.1	9.2	<0.1	<0.1
Hg	0.199	0.215	<0.010	0.001	<0.001	0.212	0.056	0.146	0.0322	0.0014	0.131	<0.010	<0.010	<0.001	0.013
Pb	1.4	12	17	0.02	0.02	4.3	4.9	27	0.03	0.04	0.15	1.0	4.0	0.018	0.02
Mn	60.4	281	242	0.02	0.016	41.5	297	273	0.004	0.06	26.2	56.7	374	0.10	0.19
Mo	1.3	7.5	5.4	0.004	0.02	0.39	5.4	5.9	0.04	0.03	0.87	3.2	12	0.012	0.01
Ni	12.9	66.8	75.1	<0.01	0.0079	18.7	101	108	<0.015	<0.015	3.67	14.5	92.9	0.078	0.16
Se	2.24	0.495	3.27	0.0044	0.0003	3.15	0.287	14.7	0.0088	0.00085	0.98	0.14	16.4	0.0030	0.0017
V	<16	<98	<100	<0.10	<0.10	<13	<100	<25	<0.2	<0.2	<13	<100	<100	<0.2	<0.2
Zn	68.6	<49	102	0.02	0.09	68.1	343	854	0.035	0.13	16.2	<8.0	386	0.12	0.40
Cu	22.2	141	113	<0.004	<0.004	28	112	59	0.007	0.026	5.2	68	238	0.090	0.16

^aValues derived from ref. 21, pp. I-27-29, I-33, I-34.

Table 4.11. Coal analysis from Radian^a study

Station	Heating value (Btu/lb dry coal)	Ash content (wt %)	Sulfur content (wt %)
1	9,250	10	0.4
2	10,000	16	4.0
3	10,000	25	4.3
4	9,500	10	4.0
5	9,000	25	5.2

^aValues derived from ref. 21, p. I-27.

Table 4.12. Comparison of ash sluicing water from a Koppers-Totzek gasifier^a with effluent standards^b

Component	Water to gasifier (mg/l)	Water from gasifier (mg/l)	Effluent standards ^b (mg/l)
CaO	78	101	
MgO	97	161	
Na	17.5	17.5	
K	5.6	8.8	
Zn	0.01	0.03	1.0
Fe	0.05	0.22	1.0
NH ₄	0.32	157	0.8-5.0
NO ₂	0.02	0.13	
NO ₃	58.2	3.32	
PO ₄	1.89	0.81	
Cl	18	85	0.1
SO ₄	42	216	
CN	0.26	0.52	0.02-0.1
COD	14	18	20-350
SiO ₂	14.8	16.0	
TSS ^c	14	4612	3-15
Cu	0.01	0.01	1.0
(pH	8.8	8.8	6-9)

^aValues derived from ref. 32, p. 126.

^bSee columns under "Anticipated regulations," Table 6.1 in this report.

^cTotal suspended solids.

It is estimated that the ash sluicing water will contain a large amount (6000 to 200,000 mg/liter) of suspended solids and have a pH of 8 to 13. The concentration of ammonia, phenols, and oils will be near zero. The water will contain many trace elements in varying concentrations, some of which may be too high for discharge to local surface waters.

4.7 Boiler and Cooling Tower Blowdown

The Coalcon plant utilizes two sources of boiler blowdown. The water jacket of the Texaco gasifier is the source of a small blowdown (stream 43), and stream 57 is blowdown from the char furnace boiler. Blowdown refers to a "draw-off" from a recirculating stream to keep the amount of dissolved solids low enough to prevent scaling and corrosion of heat exchange tubes.

Some data on the nature of pollutants have been reported in a study made for the EPA.²² These data represent "grab" samples from several streams of three different petroleum refineries, but this information has limited usefulness. Table 4.13 shows the pollutant concentrations of the boiler and cooling tower blowdown for the three refineries studied. The boiler blowdown is slightly basic and only slightly contaminated with process fluids. The Coalcon flowsheet¹ calls for the boiler blowdown to be utilized as a portion of the cooling tower makeup water.

Table 4.13 also shows that the cooling tower blowdown (stream 59) will be similar to the boiler blowdown. Process fluids can enter the cooling water via leaks in heat exchange equipment; when these contaminants are stripped out of the cooling tower, an air pollution

Table 4.13. Analyses of refinery wastewater^a

Sampling point	Refinery	Sample No.														
		123			123			123			123			123		
		COD(mg/liter)			Sulfide(mg/liter)			Ammonia(mg/liter)			Phenol(mg/liter)			pH		
Boiler blowdown	A	72	76	98	<0.1	<0.1	<0.1	0.7	0.5	0.7			0.01	11.5	11.6	11.8
Boiler blowdown	B	148	156	108	<0.1	<0.1	<0.1	1.2	1.05	1.20	T ^b	1.2	T ^b	11.3	11.0	10.5
Boiler blowdown	C	453	615	970	<0.1	<0.1	<0.1	45	40	43	0.34	0.20	0.15	10.4	10.8	10.7
Catalytic cracker cooling tower blowdown	A	96	153	205	<0.1	<0.1	<0.1	79	80	80			T ^b	6.5	6.1	6.3
Catalytic cracker cooling tower return	B	74	156	54	<0.1	<0.1	<0.1	0.6	1.25	3.0	0.05	0.08	T ^b	6.2	7.7	6.7
Petroleum condenser cooling tower blowdown	B	148	129	72	<0.1	<0.1	<0.1	6	8	8.5	0.20	T ^b	T ^b	6.5	8.0	6.9
Distillation cooling tower blowdown	C	<0.1	28	20	<0.1	<0.1	<0.1	20	30	40	<0.1	<0.1	<0.1	6.8	6.8	7.3
Catalytic cracker cooling tower blowdown	C	10	9	10	<0.1	<0.1	<0.1	22	35	38	<0.1	<0.1	<0.1	6.4	7.7	7.2
Alkylation cooling tower blowdown	C	<0.1	18	20	<0.1	<0.1	<0.1	35	40	4.5	<0.1	<0.1	<0.1	6.1	4.3	6.4

^aValues derived from ref. 4, pp. 105-110.^bTrace.

problem results. A study by the U.S. Public Health Service³³ states that hydrocarbon emissions from cooling towers at petroleum refineries average 9 lb/day for each 1000 gal per minute of cooling water circulated. The Coalcon design¹ calls for circulation of ~311,000 gal of cooling water per minute; on this basis, one may estimate a hydrocarbon emission from the cooling tower to the atmosphere of 2800 lb/day. Since the source of the data in Table 4.13 does not specify whether the cooling water samples are taken before or after the cooling tower, the values in that table may not represent the true organic concentrations in the cooling water. This is an area in which the few data that exist should be studied more thoroughly. In the Coalcon design,¹ the cooling tower blowdown (stream 59) is coagulated and settled, sent to an ion exchange operation, and then discharged to the river. The ion exchange treatment is used to recover valuable chromate compounds that are added to the cooling water to prevent fouling of heat exchangers by microorganisms.

4.8 Water Treatment Wastes

The water treatment for process and potable water produces two waste streams. These streams are similar to those that are handled routinely in most petroleum and chemical plants as well as municipal water plants. Water from the river (stream 62) is mixed with alum, lime, and polyelectrolytes in the flocculator; it is agitated to form a slurry of precipitated minerals from the water and residual solids from the river. This slurry is sent to a clarifier that separates the stream into a clear overflow and an underflow (stream 66) which contains the solids formed in the flocculator. In its study of coal fired power plants, the EPA²² has studied water treatment wastes; Table 4.14 is a

Table 4.14. Characterization of water treatment wastes^a

	Mean (mg/liter)	Standard deviation (mg/liter)
Clarification underflow		
TSS ^b	25,213	53,060
Fe	352	572
Ion exchange waste		
TDS ^c	7,408	11,550
SO ₄ ²⁻	2,085	3,859
Cl ⁻	1,708	4,603
Na ⁺	3,112	6,448
NH ₃	558	1,572

^aValues derived from ref. 22, p. 134.

^bTotal suspended solids.

^cTotal dissolved solids.

summary of the EPA findings. The underflow has a high solids content consisting primarily of dissolved and suspended solids from the river. The underflow is also expected to have a high pH, since flocculation and clarification using lime works best at a pH of 9 to 12.^{34,35} In the Coalcon flowsheet,¹ the clarifier underflow is sent to the ash pond as ash sluicing makeup.

The clear overflow from the clarifier is treated in an ion exchange bed to reduce the mineral content of the water. The ion exchange bed is periodically regenerated, producing a small ion exchange waste stream (stream 67). Table 4.14 also shows the EPA findings for ion exchange wastes from water treatment plants for coal-fired power plants. In the Coalcon design,¹ the ion exchange wastes are sent to the holding pond and then discharged to surface waters. It is not clear whether this water is of sufficient quality to be discharged; more likely, the ion exchange wastes will need to be sent to the ash pond.

4.9 Plant Runoff and Washdown

The water pollution potential of rainwater runoff from plant grounds and washdown of process areas is difficult to quantify. The rainwater runoff may contain suspended oils and dissolved phenols, as well as suspended solids. These contaminants are expected to be dilute, but this water probably cannot be discharged directly to surface waters. The Coalcon design¹ assumes that 5600 ft² of process area will require periodic washdown for health and safety reasons. This washdown will produce a fairly small waste stream similar to the contaminated rainwater runoff. Coalcon proposes to reclaim the rainwater runoff from plant

grounds and process area washdown streams by feeding it to the Texaco gasifier as char-slurry makeup water.

5. MAJOR CONTAMINANTS

From the preceeding descriptions of the wastewater streams found in a coal conversion facility, it is assessed that the major classes of contaminants present are phenolics, trace elements, and polynuclear aromatic hydrocarbons (PNA). These three groups will have the greatest impact on the type (or types) of control technology to be utilized. Although it is obvious that little more than generalizations can be made concerning which contaminants will be present without actually analyzing the wastewater, the types and quantities of these materials should be investigated.

5.1 Phenols

Any aqueous stream contacting coal or one of the various organic streams contains a variety of organics, predominantly phenols. However, as indicated under the various wastewater streams previously described, the stream containing the largest quantity of phenols is the hydrocarbonization product water. Tables 4.2 to 4.6 show the large variety of phenolic compounds found in coal conversion wastewater and indicate that the anticipated amount of phenols will be significant, with concentrations in the 2000 to 6000-ppm range.

It is apparent from these tables that phenol removal efficiencies of 99.9% are not adequate to achieve the anticipated effluent regulations for total phenol of 30 to 300 ppb. The recommended level of

phenol in drinking water is even lower at 1 ppb. Phenols are highly toxic, and this toxicity is increased when chlorine is added to the water, as is the case with most wastewater treatment facilities. Concentrations below 100 ppb can cause undesirable tastes and odors, and amounts of 1 ppb can impart objectionable tastes following marginal chlorination.³⁶

The large amount of phenolics present will not be all phenol. Those wastewater streams for which a breakdown is available (Tables 4.2, 4.4, and 4.6) indicate that phenol makes up 35 to 54% of the total, cresols are 37 to 48%, and xylenols are 8 to 23%. Not included in these analyses were the dihydric phenols (catechol, resorcinol, etc.), or the trihydric phenols (phloroglucinol, pyrogallol, etc.). These were either not present or were present at extremely low levels; Tables 4.4 and 4.6 indicate they were not expected in the samples and therefore were not included in reference standards.

The above variety in the type of phenolic compounds present is often ignored and the total amount is summarized as phenol, but the differences are important in an evaluation of any kind of wastewater cleanup technology to be employed. Solvent extraction methods such as "Phenolsolvan" tend to renew all the phenolics, thus producing a "phenol" product that is really a mixture of compounds. Additional (and often expensive) separation steps may then be required to produce a pure, economically valuable phenol product.

Similarly, in phenol degrading biological oxidation units, performance varies with the type of phenolic compounds present. Chambers et al.³⁷ investigated the biological oxidation of various

phenols by phenol-adapted bacteria. They found that the mono- and dihydric phenols, with the exception of the xylenols, were easily oxidized, and the trihydric phenols were very resistant to degradation by these bacteria.

It is obvious that the type of phenolic compounds present may determine the type and degree of wastewater treatment that is required. Although future regulations will probably group all phenolic compounds together, as determined by some standard analytical technique, it will be important to completely characterize the phenolic compounds that may be present.

5.2 Trace Elements

In recent years, the public has been concerned about the release of trace elements, primarily heavy metals and halogens, into the environment. All coals contain many trace elements in varying concentrations. Due to the large throughput of coal, sizeable quantities of trace elements can potentially be released to the environment from coal conversion plants. The occurrence of trace elements in the more common coals is well documented.^{31,38,39} Tables 5.1 and 5.2 summarize the content of trace and minor elements of Illinois No. 6 coal.³⁸ These tables show that the trace and minor elements must not be discharged directly to the environment, but must be disposed of in an environmentally acceptable manner.

Although it is not now possible to use data such as those in Tables 5.1 and 5.2 to accurately predict the fate of the trace and minor elements in a coal conversion process, several studies have been

Table 5.1. Trace-element content of Illinois No. 6 coal^a
and comparison with effluent standards^b

Element	Av conc in coal		Throughput ^c (lb/day)	Effluent standards ^a (lb/day)
	ppm	lb/10 ³ tons		
As	7.6	15.2	228	3.6
B	129.0	258.0	3870	
Be	1.6	3.1	48	
Br	15.4	30.7	462	
Cd	3.9	7.8	117	2.1
Co	8.2	16.4	246	
Cr	16.0	32.1	480	1.5-15
Cu	14.8	29.6	444	15
F	58.6	117.0	1758	210
Ga	3.1	6.3	93	
Ge	5.9	11.8	177	
Hg	0.18	0.36	5.4	0.006
Mn	53.6	107.0	1608	15
Mo	9.0	18.0	270	
Ni	22.2	44.4	666	15
P	43.6	87.2	1308	
Pb	28.6	57.1	858	1.5
Sb	1.0	1.9	30	
Se	2.0	4.1	60	15
Sn	4.2	8.4	126	
V	33.4	66.8	1002	
Zn	450.0	900.0	13500	15
Zr	54.8	110.0	1644	

^aValues derived from ref. 38, pp. 7-10.

^bWastewater effluent standards and 15,000 tons of coal feed per day. See columns under "Anticipated regulations," Table 6.1 in this report.

^cBased on 15,000 tons of coal feed per day.

Table 5.2. Minor element content of Illinois No. 6 coal^a

Element	Av conc in coal (%)	Throughput ^a (10 ³ lb/day)
Al	1.34	402
Ca	0.78	234
Cl	1.04	312
Fe	1.87	561
K	0.17	51
Mg	0.05	15
Na	0.06	18
Si	2.64	792
Ti	0.07	21

^aValues derived from ref. 38, pp. 11-12.

^bBased on 15,000 tons of coal feed per day.

made on the fate of the trace elements. A trace-element analysis for the ORNL Bench-Scale Hydrocarbonizer has been published.^{40,41} The results of this work are summarized in Table 5.3. The reactor temperature and holding time are similar to that of the Coalcon design;¹ however, because the product recovery system is quite different, the oil-aqueous splits could be very different in the Coalcon process.

The Synthane process is a high-BTU gasification process, but the reactor products are similar to those of hydrocarbonization. Again, due to a higher reactor temperature and differences in product recovery schemes, the trace-element data from the Synthane PDU are not directly applicable to hydrocarbonization; however, they do help reveal overall trends in the fate of the trace elements. Workers at the Pittsburgh Energy Research Center (PERC)⁴² have made an effort to analyze all major streams in the Synthane PDU and have reported trace-element balances, which are summarized in Tables 5.4 and 5.5. The mass balances shown in Table 5.5 are off by as much as a factor of 5, because the analytical technique used is considered to be accurate to approximately a factor of 3. Condensate from the Synthane process has been analyzed by a more accurate method.^{27,29} These results are shown in Table 5.6.

Workers at the Institute of Gas Technology (IGT) have studied the fate of trace elements in the Hygas gasification process⁴³ which has two stages of hydrogasification and one stage of electrothermal gasification at increasing temperatures of 650, 950, and 1000°C. The trace-element analyses and proximate analyses are shown in

Table 5.3. Fate of trace elements^a in ORNL hydrocarbonization unit and effluent standards (weight ppm)

Element	Coal	Char	Oil	Sour water	Effluent standards ^b
Ba	510.0	1570.0	10.0	0.4	2.0
Cd	0.2	0.9	0.1	< 1.0	0.15
Cr	7.0	18.0	3.0	0.1	0.1-1.0
Cu	9.0	17.0	2.5	0.06	1.0
Fe	1700.0	3800.0	95.0	1.0	1.0
In	0.2	0.7	0.1	< 1.0	
Mo	0.2	1.1	0.1	0.01	
Ni	5.0	10.0	7.0	1.0	1.0
Pb	3.0	7.0	0.2	0.003	0.1
Sr	320.0	490.0	4.0	0.1	
Tl	0.3	0.4	0.1	0.02	
Zn	6.0	14.0	1.5	0.06	1.0

^aValues derived from ref. 40, p. 5.

^bSee columns "Anticipated regulations," Table 6.1 in this report.

Table 5.4. Trace-element analysis for the Synthane Process^a
(ppm)

Element	Illinois No. 6 feed coal	Char	H ₂ O	Effluent standard ^b
Al	2,200	1,900	0.007	
As	1.2	4.2	<0.001	0.25
B	86	280	20	
Ba	150	110	0.08	2.0
Ca	>10,000	>10,000	2.7	
Cl	130	20	220	0.2
Cr	120	190	0.018	0.1-1.0
Cu	35	34	0.003	1.0
F	400	240	36	15
Fe	>5,000	>10,000	0.12	1.0
Hg	0.11	0.04	0.029	
K	5,000	4,400	0.36	
Mg	1,700	3,200	0.63	
Mn	200	300	0.075	1.0
Na	1,900	>8,200	6.3	
Ni	21	25	0.007	1.0
P	110	1,100	0.034	
S	>5,000	2,200	0.97	
Se	1.3	4.4	0.11	1.0
Si	>10,000	>10,000	4.7	
Sr	6.9	65	0.07	
Zn	8.3	89	0.078	1.0

^aValues derived from ref. 42, pp. 12-15.

^bSee columns under "Anticipated regulations," Table 6.1 in this report.

Table 5.5. Fate of trace elements in the Synthane gasification process^a

Element	Condensate (%)	Tar (%)	Char (%)	Filter fines (%)	Recovery (%)
As	0.1	3.0	60.2	4.9	69.0
B	120.6	0.6	58.6	0.6	180.3
Be	0.0	0.2	280.8	5.0	286.1
Cd	0.0	0.0	509.7	11.5	521.0
Cl	258.3	0.02	4.7	0.09	263.2
Cr	0.0	0.1	69.3	0.4	69.8
F	14.5	0.0	27.0	3.0	44.5
Hg	47.4	10.6	15.7	0.9	75.4
Mn	0.0	0.0	22.9	0.2	23.2
Ni	0.1	0.4	78.8	2.2	81.4
P	0.1	0.3	152.7	0.1	153.1
Pb	0.0	1.2	326.3	6.2	333.7
Se	40.8	0.6	206.5	19.5	267.3
U	0.0	0.1	49.4	2.0	51.4
V	0.0	0.1	42.3	1.7	44.1
Zn	0.3	0.1	42.4	0.7	43.5

^aValues derived from ref. 42, p. 20.

Table 5.6. Comparison of effluent standards and two trace-element analyses for the Synthane aqueous condensate^a

Element	Concentration (mg/liter)		Average	Effluent standards ^b
	No. 1	No. 2		
Ca	4.4	3.6	4.0	
Fe	2.6	2.9	3.0	1.0
Mg	1.5	1.8	2.0	
Al	0.8	0.7	0.8	
Se	0.401	0.323	0.360	1.0
K	0.117	0.204	0.160	
Ba	0.109	0.155	0.130	2.0
P	0.082	0.092	0.090	
Zn	0.044	0.083	0.060	1.0
Mn	0.036	0.038	0.040	1.0
Ge	0.032	0.061	0.040	
As	0.044	0.028	0.030	0.25
Ni	0.023	0.034	0.030	1.0
Sr	0.033	0.024	0.030	
Sn	0.025	0.026	0.020	
Cu	0.016	0.020	0.020	1.0
Cb	0.007	0.005	0.006	
Cr	0.004	0.002	0.003	0.1-1.0
V	0.004	0.002	0.003	
Co	0.001	0.002	0.002	

^aValues derived from ref. 27, p. 4.

^bSee columns under "Anticipated regulations," Table 6.1 in this report.

Table 5.7. Although the hydrogasification char is similar to hydrocarbonization char, direct use of these numbers to predict the content of hydrocarbonization trace elements would be misleading.

The Coalcon plant has been designed in such a way that the greatest portion of the trace elements will end up in the ash sluicing water either in solution or in the solid phase of the slurry. However, small amounts of some of the more volatile elements (e.g., mercury, chlorine, selenium, arsenic, lead, cadmium) may get into other streams. It is not now possible to predict the amounts of some of the elements known to form compounds with the organics (e.g., vanadium, germanium) that will be in the oil products. Some trace elements tend to concentrate on the surface of small particles present in gas effluent streams,⁴⁴ but we cannot predict whether these will be significant problems in a hydrocarbonization plant.

5.3 Polynuclear Aromatic Hydrocarbons

Coal conversion, particularly hydrocarbonization and carbonization processes, produce large amounts of polynuclear aromatic hydrocarbons (PNAs) in the heavy tar fractions. This has been a cause for concern, since many of the larger ringed PNA compounds produced are suspected of being highly carcinogenic and mutagenic. These PNAs are only slightly soluble in water, but are considered hazardous even at low concentrations. Furthermore, PNAs are not removed by the common wastewater treatment processes and may not be amenable to microbial destruction.⁴⁵ Therefore, it will be important to segregate and recycle aqueous streams containing PNAs to prevent their discharge to the environment.

Table 5.7. Trace element and proximate analysis of Hycas products^a

Product	Raw Pittsburgh No. 8 coal	Pretreated coal	Second stage char	Electrothermal char	Total loss (%)
<u>Based on coal feed (ppm)</u>					
Hg	0.27	0.19	0.06	0.01	96
Se	1.7	1.0	0.65	0.44	74
As	9.6	7.5	5.1	3.4	65
Te	0.11	0.07	0.05	0.04	64
Pb	5.9	4.4	3.3	2.2	63
Cd	0.78	0.59	0.41	0.30	62
Sb	0.15	0.13	0.12	0.10	33
V	33.0	36.0	30.0	23.0	30
Ni	22.0	11.0	10.0	9.1	24
Be	0.92	1.0	0.94	0.75	18
Cr	15.0	17.0	16.0	15.0	0
Proximate analysis (as received, wt %)					
Moisture	1.4	3.7	0.8	0.2	
Volatile matter	38.6	22.4	2.2	2.1	
Ash	11.6	12.3	22.1	45.0	
Fixed carbon	43.4	61.6	74.9	52.7	

^aValues derived from reg. 43, pp. 13, 21.

Very little reliable data are available concerning the PNA concentration in coal conversion process streams; however, all streams that contact the organic products (including washdown and rainwater runoff) are likely to contain PNAs and should be treated accordingly.

6. GOVERNMENTAL REGULATIONS

The Federal Water Pollution Control Act of 1972 requires the EPA to establish guidelines for technology-based effluent limitations which must be achieved by point sources of discharge into the navigable waters of the United States. At the present time, federal regulations for the control of pollutants in wastewater streams are issued as industry-specific rules. Since no coal conversion industry exists as yet, the only guidelines as to what future federal regulations might be can be obtained by comparing existing similar industries. These industries include iron and steel (coke making), petroleum refining, steam electric power generating, and coal mining. All of these industries utilize various operational units that would be common to a coal conversion industry.

6.1 Existing Regulations

One requirement of the Water Pollution Control Act requires the achievement (by not later than July 1, 1977) of effluent limitations for point sources that are based on the application of the best practicable control technology currently available (BPCTCA). This level is generally based on the average of the best existing performance.⁴⁶

A second section also requires the achievement (by not later than July 1, 1983) of effluent limitations for point sources that are based

on the application of the best available technology economically achievable (BATEA),⁴⁶ which will result in further reasonable progress toward the national goal of eliminating the discharge of all pollutants. Best available technology is not based on an average of the best performance within an industry category, but will be determined by identifying the very best control and treatment technology employed by a specific point source.

Effluent limitations for new sources are specified by the degree of effluent reduction achievable through the application of the best available demonstrated control technology (BADCT). New facilities will not be constructed until new source performance standards (NSPS) have been published. Existing federal regulations for four industries are tabulated in Table 6.1, both in units as written in the regulation and in units that can be compared to coal liquefaction. Effluent limitations for new sources are the guidelines that are listed except for coal mining where the BPCTCA limits are the only guidelines available.

Generally, the BATEA guidelines are the most stringent, either being equivalent to the new source standards or, in the case of petroleum refining, only about 25% of the new source guidelines for most pollutants. In some cases, substitution of the BATEA guidelines would noticeably lower the anticipated limits, especially for biological oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, phenols, NH_3 , and hexavalent chromium.

The range for any one pollutant varies widely from industry to industry. Part of this may be due to the conversion of units, but a significant factor is that existing federal regulations tend to allow

Table 6.1. Wastewater effluent regulations

Pollutant parameter	Petroleum ^a refining		Electrical ^c generating		Steel/Coke ^e		Coal mining ^g		Illinois state regulation ⁱ (ppm)	Anticipated regulations (lb/10 ⁶ lb)		
	(lb/10 ³ bbl)	(lb/10 ⁶ lb) ^b	(ppm)	(lb/10 ⁶ lb) ^d	(lb/10 ³ lb)	(lb/10 ⁶ lb) ^f	(ppm)	(lb/10 ⁶ lb) ^h		Low	High	ppm ^d
TSS	1.20-15.4	1.80-23.1	30	15	0.0104	7.18	35	0.24	15	1	7	3-15
Phenols	0.010-0.125	0.015-0.188			0.0002	0.138			0.3	0.01	0.15	0.03-0.3
Oil and grease	0.44-5.8	0.66-8.72	15	7.5	0.0042	2.90			15	0.5	3	1-16
CN					0.0001	0.069			0.025	0.01	0.05	0.02-0.1
NH ₃	0.28-11.0	0.42-16.5			0.0042	2.9			2.5	0.4	2.5	0.8-5
S ²⁻	0.008-0.10	0.012-0.15			0.0001	0.069				0.01	0.1	0.02-0.2
Trace elements												
Al							2.0	0.0138				
Mn							2.0	0.0138	1		0.5	1.0
Ni							2.0	0.0014	1		0.5	1.0
Cl			0.2	0.1							0.1	0.2
Pb									0.1		0.05	0.1
F									15		7	15
Ba									2.0		1	2.0
Ag									0.1		0.05	0.1
Cd									0.15		0.07	0.15
Cu			1	0.5					1		0.5	1.0
Total Fe			1	0.5			3.5	0.024	2		0.5	1.0
Dissolved Fe							0.3	0.0021	0.5		0.25	0.5
Hg									0.0005		0.0002	0.0005
As									0.25		0.12	0.25
Total Cr	0.037	0.055							1.0	0.05	0.5	0.1-1
Cr ⁶⁺	0.0025	0.0038							0.3	0.003	0.1	0.007-0.3
Zn							0.2	0.0014	1.0		0.5	1.0
Se									1.0		0.5	1.0
BOD	11.4-18.9	2.1-28.3							30	2	15	4-30
COD	7.1-131	10.6-196								10	150	20-350
(pH)	6-9		6-9		6-9		6-9		5-10		6-9	6-9)

^aValues derived from ref. 47.^bBased on 3 bbl of oil per ton of coal.^cValues derived from ref. 48.^dBased on 0.5 lb of water-to-river per pound of coal.^eValues derived from ref. 46.^fBased on 0.69 lb of coke per pound of coal.^gValues derived from ref. 49.^hBased on 37x10⁶ gal of runoff/5.50 x 10⁶ tons of coal = 6.71 gal per ton of coal.ⁱValues derived from ref. 50.

an industry that emits more of a certain waste product to have a higher limit for that waste product than an industry that does not produce as much.

Another complicating factor is that private industry expects regulations to be written in terms of pounds of effluent per pound of feedstock (or product) rather than in what would seem to be a simple concentration (ppm). This does, however, allow for very concentrated effluent streams from plants that tend to discharge a minimum of wastewater. The regulations listed in Table 6.1 have therefore been converted to a pounds-per-pound of coal feedstock basis.

6.1.1 Iron and steel industry

In the iron and steel industry, coke making is often an integral part of the total process and specific regulations have been written for this operation.⁴⁷ In the Coalcon flowsheet,¹ the hydrocarbonization, ammonia recovery, ammonia stripping, and acid-gas removal steps are all similar to those in coke production. Regulations are listed for pH, total suspended solids (TSS), phenols, oil and grease, cyanide, and ammonia on a pound of effluent per pound of product coke basis. These were converted to a pound of coal basis by assuming 0.69 lb of coke per pound of coal.

6.1.2 Petroleum refining

Steps in the coal conversion process such as methanation, sulfur recovery, acid-gas removal, and ammonia recovery are similar to operations in many refineries. Effluent limits are given for pH, BOD, COD, TSS, oil and grease, phenols, ammonia, sulfide, and chromium.⁴⁸ Regulations have been established on the basis of pounds of effluent

per barrel of feedstock. A variety of conversion factors could have been used, but it has been assumed that 1 ton of coal is roughly equivalent to 3 bbl of petroleum.

6.1.3 Steam electric power generation

The Coalcon flowsheet has an integral steam generation plant associated with it, and effluent standards for coal-fired electric power generating stations should be applicable.⁴⁹ In this case, regulations for TSS, oil and grease, chlorine, copper, and iron are given on a concentration basis. The conversion factor used was 0.5 lb of final wastewater per pound of coal.

6.1.4 Coal mining

Any overlap between the operations conducted in coal mining and those of a hydrocarbonization facility would be relatively minor and essentially limited to coal handling and coal pile runoff. Effluent limits are for a variety of trace elements and are given as milligrams per liter.⁵⁰ In this case, a conversion factor of 0.00167 lb of water per pound of coal throughput was used. This number only holds for the coal pile runoff and is obviously only a small part of the total plant wastewater. A 90-day supply of coal was assumed to be present in the coal pile.

The only other Federal regulations in effect are those for drinking water which were set by the U.S. Public Health Service (USPHS). Although these standards were designed for use in regulating the quality of water supplied to common carriers engaged in interstate commerce, they have become the standard for all public water supplies in the country through adoption by the various state health departments.

Some of these standards are mandatory requirements, other are recommended limits. In addition, the American Water Works Association adopted a series of potable water quality goals which, in some cases, are more exacting than the USPHS standards. Also, additional limits for a variety of substances have been suggested for inclusion in the next version of the Drinking Water Standards. All these are included in Table 6.2. It is important to note that these are standards for receiving bodies of water and not effluent streams, (i.e., no credit is given for any dilution effect).

6.1.5 State regulations

Most states have written regulations to enforce limitations on the quality of wastewater that can be discharged to various bodies of water within their boundaries. However, most of these regulations are based on the minimal quality level permitted in a particular body of water and not on a plant-effluent basis. These limits usually vary depending on the type of use (e.g., recreation, drinking water supply) for the body of water. Any discharge that would tend to raise the water pollutant levels above the predetermined level would be disallowed.

Illinois, which has attracted a number of demonstration coal conversion units, is one of the few states that has set actual discharge limits for a variety of pollutants.⁵⁵ These limits are given in parts per million and can be converted by using the conversion factor of 0.5 lb of final wastewater per lb of coal feedstock.

6.2 Anticipated Regulations

The proposed anticipated regulations are based on the various existing regulations for other related industries. In most cases, a

Table 6.2. Drinking water standards (ppm)

Constituent	Mandatory ^a	Recommended ^b	Goals ^c	Suggested ^d
Al			0.05	
Sb				0.05
As	0.05	0.01		
Ba	1.0			
B				1.0
Cd	0.01			
Cl ⁻		250		
Cr ⁶⁺	0.05			
Cu		1.0	0.2	
CN ²⁻	0.20			
F ⁻	1.4 - 2.4			
Fe		0.3	0.05	
Pb	0.05			
Mn		0.05	0.01	
Hg	0.002			
Se	0.01			
Ag	0.05			
Zn			1.0	
Phenols		0.001		

^aData derived from ref. 51.

^bData derived from ref. 52.

^cData derived from ref. 53.

^dData derived from ref. 54.

range of values has been indicated because of the large variation between existing industries in the amount of pollutant that can be released. Usually the high end of the range has been determined by the highest existing regulation for an industry that would not emit an excessive amount of that particular pollutant. Lower limits have been determined by the smallest limits for a related industry. In no cases were limits based on an estimation of any future technology.

7. CLEANUP TECHNOLOGIES

The complexity of the various aqueous streams from a coal conversion plant such as the Coalcon hydrocarbonization plant has made the "best" processes for waste cleanup somewhat doubtful. At the same time, the sure enactment of stricter effluent standards has put pressure on new coal conversion processes to dispose adequately of their wastes. A variety of treatment processes are suitable for use in a coal conversion plant, as shown below. This list is not complete, but is probably representative.

Activated sludge	Flotation
Trickling filters	Oil separation
Aerated lagoons	Stripping
Biological fluidized beds	Solvent extraction
Neutralization	Adsorption
Coagulation and flocculation	Combustion
Ozonization	Wet oxidation
Chlorination	Filtration and ultrafiltration
Ion exchange	Reverse osmosis
Sedimentation	Electrolysis
Ultraviolet activation	

Many of these processes will require some form of pretreatment. Some will also be used to produce clean process and potable water for the plant. A few of the most useful processes for hydrocarbonization waste-

water cleaning are discussed below in relation to their adaptability to the specific pollutants found in these wastewaters. Only those technologies that show promise of immediate application to coal conversion wastewaters have been investigated. Some (e.g., neutralization or oil separation) will definitely be applied to some wastewater streams, are commercially available, and will need little or no modification. Others (e.g., electrolysis and uv activation) are of such a nature that little application is seen for the immediate future.

7.1 Biological Degradation

The most widely used method to control aqueous organic pollutants are those that can be grouped under the broad category of biological degradation. In its various forms, biological degradation can include everything from dumping raw wastewater into the nearest waterway and letting the natural purifying properties of the environment take charge, to highly sophisticated reactors that utilize specially selected bacteria that would be unable to survive under natural conditions. The biological means have included a wide variety of bacteria of the aerobic and anaerobic types, algae, and even higher-order plants such as water hyacinths. Reactors have varied from the simple natural or man-made ponds to complicated, tapered-fluidized-bed reactors. Cost and reliability are such that when organics need to be degraded, biological means are usually the method of choice, whether the industry is iron and steel or municipal sewage disposal.

Normally, the following items are considered in the design of a biological oxidation process:

Need for pretreatment. In some situations, a simple filtering or settling step can vastly improve the performance of a biological oxidation unit. Special pretreatment other than neutralization may occasionally be needed for the particular bacteria to perform under optimal conditions. This may include sparging to remove excessive dissolved gases such as NH_3 , H_2S , or CO . In some cases, this step may be so difficult it will preclude the use of biological treatment such as with some metal pickling wastes.

Need for flow equalization. This step may be necessary to equalize any changes in volume or composition of flows. This can be a major problem where a variety of different process plants can be operating at different times. In other cases, such as in municipal sewage treatment, only flow equalization may be a problem.

Need for stream dilution. Most compounds, even those being used by the bacteria as a carbon source, can be detrimental at excessive levels. In these cases, a simple recycle may prove necessary even though it can add considerable pumping costs to the unit and increases the size and capital cost.

Need for stream nutrification. Although many bacterial strains can survive and even grow under stressful environmental conditions, the addition of nutrients such as trace elements, phosphorus, and nitrogen are often needed for optimal cell growth and pollutant degradation.

Type of biological oxidation unit to be considered. A variety of biological oxidation units in various stages of development are available.

These include trickle-bed filters, complete mix tanks, aerated lagoons, simple holding ponds, and fluidized-bed systems. Each type has its advantages such as efficiency, cost, and operating difficulty.

Oxidation or retention time needed. Each of the above types of biological unit will require a characteristic contact time depending on the process stream to be treated. Times may range from several minutes to several days.

If biological oxidation is to be considered for the treatment of hydrocarbonization wastewater, the needs listed above should be examined in connection with the specific problems arising from hydrocarbonization.

Various pretreatment steps will definitely need to be included if any ammonia recovery or removal steps have not reduced the NH_3 concentration below the level of 1500 to 2000 ppm that most bacteria can tolerate.⁵⁶ Some untreated wastewater from the hydrocarbonization reactor may be as high as 30,000 ppm. Although this level will be diluted before discharge, the quantities of NH_3 may still be too high. Suspended matter will be present but should not consist of particles large enough to cause concern.

Flow equalization should not be a major problem. In most conversion processes, the individual units that produce wastewater will either all be operating or the entire system will be shut down. Variations in the flow rates may exist, but compositions should remain relatively constant, especially for commercial units. The problem will need to be carefully examined in pilot plant and demonstration units, because fluctuations in operating conditions will produce large deviations in the composition of wastewaters.

In complete mix tanks, aerated lagoons, and simple holding ponds the outflow concentration is equal to the steady-state reactor concentration. Stream dilution is already occurring and no additional dilution will be needed. However, for trickle-bed filters and fluidized beds, stream dilution will have to be included in the system design. Expected phenol levels to 6000 ppm greatly exceed the 200 to 300-ppm level tolerated for optimum phenol removal.^{57,58} Recycling of effluent would probably be the optimum way of achieving the necessary amount of dilution.

Stream nitrification is likely to be only a minor problem. The large variety of chemicals found in hydrocarbonization wastewater will probably contain many of the trace elements needed (Tables 4.8-4.10, 4.12). A rough rule of thumb is that the ratio between BOD_5 (where "5" indicates days), nitrogen, and phosphorus should be 100:5:1. The large amount of NH_3 present should provide the necessary nitrogen. Phosphorous may need to be added to achieve the above ratio. However some experimental data from the ORNL hydrocarbonization experiment would indicate that much of the necessary phosphorous may also be present. In this case, a hydrocarbonization quench water containing 8150-ppm carbon also contained 20-ppm phosphate.

In choosing a biological oxidation unit to treat hydrocarbonization wastewater streams, various parameters such as installed costs, operating costs, and efficiency will have to be considered. The following expression was developed as the result of a survey made by the Dow Chemical Company in 1973. It can be considered applicable to coal-

conversion wastewater treatment for estimating the total annual operating costs:

$$Q (43.1) + \left(\frac{Q}{812} \right)^{0.6} (88,800) \quad ,$$

where Q is the organic loading in lb/day.⁵⁹ Since the reference hydrocarbonization plant produces 1.0×10^6 gal of water per day at 5000-ppm phenol, the above expression results in \$0.17 per pound of phenol, or approximately \$7000 per year per 10^6 gal of water. If an inflation-correction factor of 1.39 (1973-1977) is used, it will result in \$0.24 per pound of phenol and \$9700 per year per 10^6 gal of water.

In 1969, the South Tahoe Public Utility District, South Lake Tahoe, California, built an advanced wastewater treatment facility.³⁴ This plant treated organic constituents for \$0.07/lb or \$2700 year⁻¹ 10^6 gal. Using an inflation-correction factor of 2.15 (1967-1977) results in \$0.14/lb and \$6000 year⁻¹ 10^6 gal. These numbers compare quite reasonably with those above considering the different types of facilities involved.

The oxidation or retention time needed is a strong function of the type of reactor chosen, but there is usually a range of times for any one type of unit. Factors to be considered include the degree of removal required, and hydraulic loading. Many of the components present in hydrocarbonization wastewater may be quite refractory to biological oxidation, especially during the short oxidation times required in trickle-bed filters and fluidized beds. On the other hand, the several-day residence times that would be needed in aerated lagoons

will possibly allow the polymerization of phenols into PNA with the possibility of having higher PNA levels in the effluent than the feed.

Apparently, the potential application for biological oxidation of hydrocarbonization wastewater is very good. Numerous experiments have shown that phenol levels, the major contaminant in hydrocarbonization wastewater, can be reduced by up to 99.9% to levels as low as 20 ppb.^{57,60} Trace metals and PNA would be more refractory, although previous work has shown that up to 50 to 90% of heavy metals such as cadmium, lead, copper, nickel, mercury, iron, and zinc can be removed by biological oxidation.⁶¹⁻⁷¹ The metals would be tied up in organic sludge that is produced as a by-product. PNAs seem to be relatively untreated and, in fact, may be increased for those units that have long residence times.⁷²

Several other areas are of concern in the application of biological oxidation, including the need for elevated temperatures, especially during the cooler months of the year. Temperatures of 25° to 35°C seem to be optimum for most biological systems and, in some cases, temperatures of 45° to 60°C are desirable, with a temperature of at least 10°C being necessary.⁷³⁻⁷⁶

Another case of concern is by-product disposal. The carbon content of the wastewater streams will be converted to some extent by changes in operating conditions, but some biomass in the form of sludge will be produced. This sludge will contain live and dead bacteria with the possible presence of a high concentration of heavy metals. Some form of land disposal or incineration will need to be provided. In the past, this sludge has often been applied to agricultural lands, but the high concentration of metal will probably preclude this disposal technique.⁷⁷⁻⁸⁰

7.2 Chlorination and Ozonation

Several chemical oxidation processes are presently being used to treat both wastewater and drinking water. These processes include chlorine treatment and ozonation. Gaseous chlorine, chlorine dioxide, and sodium hypochlorite have been used as final polishing steps in wastewater treatment and as a method of supplying residual bactericidal potential. However, the advisability of using chlorine in treating wastewater heavily laden with phenolics is highly questionable. Many authorities have discussed the formation of chloroderivatives of phenolics, and several have commented on the toxicity of these compounds.⁸¹⁻⁸⁴

When PNAs are chlorine treated, a significant reduction in concentration can be expected. Sforzolini⁸⁵ indicated that chlorine as chlorine water showed an effective reduction in a variety of PNAs of 100% for 3,4-benzopyrene to 15% for 3,4-benzofluoroanthene. Both Sforzolini⁸⁵ and Muller and Reichert⁸⁶ have shown that chloroderivatives are formed in the process, and, although Muller and Reichert have shown that some chloroderivations of carcinogenic PNAs are not carcinogenic, it would seem wise to avoid chlorinating known toxic and carcinogenic compounds.

Ozone, a very strong oxidizing agent, is used to oxidize hydrocarbons to simple organic compounds or to completely oxidize them to inert compounds such as water and carbon dioxide. These simpler compounds usually have fewer undesirable effects such as color, malodor, toxicity, or carcinogenic effects. When a wastewater containing hydrocarbons is subjected to ozone treatment, a situation similar to that shown in Fig. 7.1 is usually observed.⁸⁷

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Fig. 7.1. Typical ozonation curve.

An initial period, a, is usually explained by the conversion of complex hydrocarbons to simple oxidation products. The slope b represents the oxidation of hydrocarbons to the final carbon dioxide and water products. The last segment, c, often has a slope near zero and can be interpreted as the simple recombination of ozone back to oxygen with very little carbon being oxidized during this period. The process is usually only 30 to 60% efficient; that is, only 30 to 60% as much carbon dioxide is produced as the stoichiometry of the ozone reactions would indicate.

Apparently, ozone treatment is one of the few means of achieving reasonable reductions in PNA content without producing other questionable compounds. Reichert⁸⁸ found that when 3,4-benzopyrene in water at concentrations of 1 to 100 mg/liter was placed in contact with ozone at concentrations of 0.5 to 1.5 mg/liter for 30 min, it decreased in content by ~99%. Sforzolini et al.⁸⁵ showed effective reduction in a variety of PNAs ranging from 100% for 3,4-benzopyrene and 11,12-benzofluoroanthene to 70% for 3,4-benzofluoroanthene. Unlike the similar tests with chlorine, there was no evidence of new compounds being formed when ozone was used.

A wide variety of ozone generation equipment is available for commercial use, and progress is being made on upgrading the effectiveness of these generators.⁸⁹ However, present indications are that the complete oxidation of hydrocarbons cannot be achieved economically with ozone.^{87,90} If either a very small amount of hydrocarbon needs to be treated, or if only a small amount of degradation is needed, as would be the case when a complex toxic compound can be degraded to a slightly

less complex nontoxic compound, ozonization may have an advantage.

In 1973, Kroop⁹¹ reported costs for the ozone degradation of phenol wastes of approximately \$0.75/lb, or about \$1.00/lb at today's prices. Three other references for phenol removal by ozone^{87,92,93} give ozone requirements of 2 to 3 lb of ozone per pound of phenol. If the ozone is \$0.30/lb (including capital costs for ozone generation), the equivalent is \$0.60 to \$0.90 per pound of phenol.

7.3 Coagulation and Flocculation

Impurities in coal conversion wastewater vary in size from dissolved substances that are a few angstroms to suspended materials that are a few hundred microns. Normally sedimentation is used to remove a large fraction of these particles; but, because many of these substances are too small for gravitational settling to be effective, the aggregation of these particles into larger masses that settle more readily is essential for successful sedimentation. This process of agglomeration is often termed coagulation.

Much confusion is associated with the terms coagulation and flocculation because they are often used interchangeably. Coagulation is the chemical reaction resulting in the production of complex hydrous oxides. It is very fast and only requires enough time to disperse the chemical coagulation agents throughout the liquid. Flocculation is usually applied to the agglomeration of coagulated solids to produce solids that can be settled or filtered. It is during this process that much of the colloidal material not involved in the chemical reaction of the coagulant can be agglomerated. This agglomeration may be improved

by stirring the water to increase the number of collisions between coagulated particles, in which case, it is necessary to keep the precipitate in suspension long enough for the agglomeration to occur. Camp⁹⁴ and Hudson⁹⁵ have discussed the various details of flocculator design.

Coagulation can frequently occur under natural conditions. In biological treatment processes, the microorganisms aggregate themselves to a point at which they will settle out. Under some conditions, the agglomerated sludge can even absorb colloidal organic substances in wastewater in a shorter time than is required to remove these materials by biological oxidation.

Several investigators have indicated that as much as 80% of the COD of some wastewater streams may be contained in particles that are colloidal or larger in size, and up to 50% of the total organic carbon in the effluent of biological treatment plants may be colloidal.⁹⁶ In addition to exerting an oxygen demand, these colloidal materials can severely impair the efficiency of ion exchange, adsorption, and membrane processes used to remove soluble substances as a final polishing step.⁹⁷

Traditionally, lime, alum, iron salts, or, more recently, poly-electrolytes have been used for this coagulation process. Lime reacts with the bicarbonate in the water to form insoluble calcium carbonate as in the following reaction:

As the pH increases due to the resulting alkalinity, other compounds will begin to precipitate. One of the first will be magnesium hydroxide:

Magnesium hydroxide normally precipitates when the pH is in the range 9 to 11; it is a gelatinous material that can remove many colloidal particles as it settles. Magnesium is often present in significant quantities and is also added as an impurity to the lime.

Calcium carbonate can be recalcined to recover the calcium oxide content. However, in cases where large amounts of organics and/or heavy metals may have been removed from the wastewater, the recalcining may allow for the creation of a new air pollution source or for the reintroduction of heavy metals back into the waste stream.

When alum, $\text{Al}_2(\text{SO}_4)_3$, is added to alkaline wastewater, the following reaction occurs:

In this case the addition of alum tends to lower the pH.

In some situations, the addition of both lime and alum can be used first to raise the pH and then to lower it, although the dense chemical sludges thus produced may be difficult to thicken and dewater.

Iron coagulation relies on the reaction between the ferric ion and the dissolved phosphate ion. This reaction can be useful for municipal residential wastewaters that contain significant quantities of phosphorous, but may not be helpful for coal conversion wastewaters.

Polyelectrolytes can be used as primary coagulants, but normally their application is limited to use as coagulation or flocculation aids.

Under certain conditions, lime or alum, alone or in combination, may produce a fine, slow-settling precipitate. In these cases, a variety of commercially available polymers, such as those produced by Calgon, Nalco, and Dow, produce a rapidly settling precipitate.

Of secondary importance in most sewage treatment facilities, but possibly of immense importance in coal conversion wastewater cleanup, is the ability of coagulants to remove heavy metals. Calculations in the literature have shown that when Pb^{2+} , Cu^{2+} , and Cr^{3+} are precipitated, they leave a concentration of about 1 ppm at a pH of ~7. A pH of ~9 to 9.5 is needed to reduce the concentration of Zn^{2+} , Ni^{2+} , and Cd^{2+} to below 1 ppm.⁹⁸

Lime coagulation, by nature of its raising the pH to a point at which many of the trace metals form insoluble hydroxides, results in a reduction in the concentration of these metals. Culp and Culp⁹⁹ summarized the available data and listed removals of 80 to 99.9% for a wide variety of metals. Where the dissolved metal is in an organic form, removal efficiencies were much lower, often less than 10%. In addition, filtration to remove residual particulate matter can often provide additional removal of heavy metals. For example, Culp and Culp reported additional literature values of 2.6 to 95% for seven metals with the use of filtration.

Alum coagulation is usually not considered as effective as lime in metal removal, but one study showed metal removal of 18 to 99% for five metals (lead, copper, magnesium, Cr^{6+} , Cr^{3+} , cadmium, and zinc). Nickel was not removed.⁹⁸

Costs for coagulation and flocculation vary widely depending on the wastewater to be treated. Assuming a representative dose of 3.3 lb per 1000 gal of effluent (400 mg/liter), and a price of \$50 per ton of lime (including capital equipment costs), a cost of \$80 per million gallons of effluent is obtained.^{34,100} Assuming that coagulation would remove 50% of the organic matter present, this would be less than \$0.01/lb removed.

7.4 Solvent Extraction

Recently, several researchers^{101,102} have worked on a variety of solvents for phenol removal in both typical solvent extraction systems and dual solvent processes (polar solvent-volatile solvent). In all cases, it is necessary to identify and quantify the major pollutants present in order to choose the appropriate solvents. Regardless of the high-distribution coefficients reported for many of these systems, the Lurgi Phenosolvan process seems to be the only one that has been commercialized. Lurgi developed this process in the 1940s, and about 30 commercial Phenosolvan plants have since been installed in the coke production and petroleum industries. This process uses isopropyl ether as the solvent in multistage mixer settlers. The phenol-rich solvent is usually distilled to recover solvent for reuse and is then stripped to remove and recover any residual solvent. The dephenolized aqueous phase is also gas-stripped to recover solvent. Although the solvent for this type of contactor is chosen because of its high-distribution coefficient for phenol, other types of organics will also be stripped out of the aqueous phase.

A recent article on the Phenosolvan process discussed its applicability to coal gasification wastewater.¹⁰³ The Phenosolvan process should remove 99.5% of the monohydric phenols (e.g., phenol, cresol, xylenol), 60% of the polyhydric phenols (catechol, resorcinol), and 15% of other organics. This may leave an aqueous stream that might contain as much as 20 ppm of monohydric phenols, 500 ppm of polyhydric phenols, and 1800 ppm of other organics. The crude phenol produced may have a composition of 80% monohydric phenols, 15% polyhydric phenols, and 5% other organics.

Although a significant amount of phenol and other organics can be removed by the Phenosolvan process, a large quantity of polyhydric phenols and other organics remain in the effluent stream. The process would seem to be advantageous only if a moderate reduction in phenolic content is needed to allow an additional waste treatment plant to operate, or where a salable crude phenol can be produced economically. The first case will still be expensive, and there is some question whether the crude phenol produced is of a quality to be used as a chemical feedstock.

A recent review¹⁰¹ indicated that if the value of the recovered phenol is greater than \$3/1000 gal, then recovery is promising. At 5000 ppm of phenol, this is equal to \$0.07 per pound of phenol compared with bulk prices of \$0.26 per pound of phenol.¹⁰⁰ Product upgrading may, however, prove to be quite expensive, and the remaining contaminants in the aqueous stream will require treatment.

7.5 Sorption

Adsorption of dissolved organics on activated carbon is a well-developed water treatment process. Activated carbon adsorption has been used both in treatment of industrial wastes and for polishing of potable water. In addition, activated carbon adsorption processing has the potential to recover the removed "pollutants" in an economically valuable form. Sorbents other than activated carbon (e.g., polar macroreticular resins and hydrogasification or hydrocarbonization char) are potentially useful for removal and/or recovery of dissolved pollutants, whereas activated carbon systems have exhibited several problems. For example, they are known to be costly, and they involve some extensive solids handling problems (i.e., in most cases the carbon must either be transferred between the sorption vessel and the regeneration vessel or it must be disposed of).

Activated carbon treatment of wastewater is a well-developed and growing treatment process, especially at the pilot and demonstration levels.¹⁰⁴⁻¹⁰⁹ Although these references (and others too numerous to catalog) provide an excellent base of experience, there has been less experience with wastewater streams similar to those normally found in a hydrocarbonization plant. Baker et al.¹¹⁰ have reported a successful activated carbon treatment plant that operates with an industrial waste high in cresylics (which are likely to be found in hydrocarbonization wastewater). In addition, the carbon was regenerated in such a way that the valuable cresols were returned to the upstream process, allowing this "waste treatment process" to actually show a profit. This plant was of reasonable size (~40 gal/min) and operated on a fairly

concentrated waste (0.3 to 0.5% cresylics). Workers at Reichhold Chemicals, Inc. (RCI),¹¹¹ have operated a larger carbon treatment plant (350 gal/min) with a more dilute waste stream (phenol, 420 ppm; COD, 3773 mg/liter). They have shown good success and operability using an activated carbon system, which was found to be superior to an activated sludge system that was also tested. The workers at RCI also found that regeneration of the carbon with acid or caustic solutions was, at best, partially effective for this wastewater.

Workers at Hercules Inc.¹¹² have successfully operated a commercial-scale (2.6×10^6 gal/day) activated carbon secondary treatment unit. This unit was operated on naval stores wastewater containing oily waste (COD, 750 mg/liter; TOC, 203 mg/liter, phenol, 4.7 mg/liter). The plant appeared to remove a large quantity of organic species and showed about 70% removal for some trace metals (nickel, zinc, cadmium, copper, chromium). The carbon was regenerated in a multiple-hearth furnace with a 3 to 5% loss of carbon per cycle. The regenerated carbon was shown to be slightly more active than virgin carbon, and no information was given on the fate of the trace metals in the regeneration process. A German study^{56,113} of activated carbon treatment of coking wastes includes results of some pilot plant studies. The coking wastewater is probably similar to hydrocarbonization wastewater (50 to 3200 mg/liter phenol, plus ammonia, cyanides, etc.).

There will be a large incentive in a hydrocarbonization plant (or any coal conversion plant producing a solid carbonaceous residue) to replace activated carbon in the treatment step with char. Researchers at PERC¹¹⁴ have reported good adsorption of Synthane wastes on Synthane

char. The use of char as an adsorbent would remove the need for a carbon regeneration step in the waste treatment flowsheet. The spent char can be used as fuel for a gasifier or boiler thereby recovering the dissolved pollutants as fuel. The use of hydrocarbonization char as an adsorbent in a wastewater treatment step is an area that warrants further study.

In addition to activated carbon and hydrocarbonization char, there is a class of neutral macroreticular resins which may be useful in wastewater treatment in coal conversion plants. These resins act similarly to activated carbon in sorption characteristics but are composed of a synthetic styrene polymer. Research has shown that these resins have a high affinity for phenolics and PNA, but their high cost may make neutral resins unattractive for wastewater treatment.

Although much work has been done on the sorption characteristics of phenolics on activated carbon, very little information is available on sorption of PNA. However, some pertinent information on the effects of trace elements is available. A radiochemical study of adsorption of inorganic ions carried out at the Japan Atomic Energy Research Institute tested activated carbon adsorption for 44 elements as a function of pH. Some of the important trace elements in wastewater treatment (arsenic, selenium, lead, mercury) were omitted. In addition, this study was carried out with laboratory stock solutions that did not contain other contaminants which may effect sorption.

Additional information on activated carbon sorption of inorganic species is found in water and sewage treatment literature.¹¹⁵⁻¹¹⁷ These studies have concentrated on four elements (silver, cadmium,

chromium, selenium) and show varying degrees of removal (~95% for silver, cadmium, and chromium, and ~40% for selenium). There is also some speculation¹¹⁶ that the sorption of the trace inorganics may be enhanced by the presence of organic species.

No discussion of sorption can be complete without consideration of regeneration. The carbon or other sorbent must be regenerated (or reactivated) when saturated to allow for another cycle of adsorption; otherwise, the sorbent is discarded and fresh sorbent is used. Loven¹¹⁸ lists five classes of regeneration processes which can be placed in two groups, chemical and thermal.

Thermal regeneration refers to heating the carbon to vaporize the adsorbed organics. For adsorbed volatile organics, steam stripping is sufficient to regenerate the carbon; however, when heavier species are present, as is the case in most wastewater treatment processes, more severe heating is necessary. In this case, the adsorbed materials are pyrolyzed, carbonized, and gasified at temperatures to 2000°F. This processing can be carried out in rotary kilns, multiple-hearth furnaces,¹¹⁹ transport reactors,^{120,121} or similar equipment. Hutchins¹²²⁻¹²⁴ has published papers on the costs associated with thermal regeneration.

Chemical regeneration refers to washing the carbon with a solvent or reactive solution to remove the adsorbed material. This technique is especially applicable when the dissolved "waste" can be economically utilized if recovered. However, chemical treatment may not be severe enough to fully regenerate carbons from hydrocarbonization waste processing. As mentioned earlier, washing with acid and caustic solutions did not adequately regenerate carbon used in waste treatment

of a stream similar to that found in hydrocarbonization.¹¹² However, regeneration of adsorbed phenolics using sodium hydroxide solution has been demonstrated to be profitable.^{110,125} Calculations in one of these reports¹²⁵ show that sodium hydroxide regeneration can compete with thermal regeneration, even without recovery of a valuable by-product. If an activated carbon treatment was to be used on hydrocarbonization by-product water, chemical regeneration would probably be inadequate to regenerate the carbon. It may be possible, however, to partially regenerate the carbon with sodium hydroxide, thereby recovering a relatively uncontaminated phenolic by-product and further reactivating the carbon by other means.

Activated carbon is considered moderately expensive, with cost estimates of \$0.40 to \$6.00 per pound of phenol (most estimates are in the \$0.50 to \$1.00/lb range) for carbon adsorption--thermal regeneration, and either reactive or solvent recovery methods become economical at high concentrations of phenol.¹²⁶ This wide range of values makes cost comparisons difficult.

7.6 Membrane Processes

Several separation processes involving membranes have been studied, but only reverse osmosis, ultrafiltration, and electrodialysis will be considered here. In reverse osmosis and ultrafiltration, the separation is achieved by passing the water through a membrane with the concentrated solute (or particulates) left behind; conversely, in electrodialysis, the solutes pass through the membrane (via an electric potential driving force) leaving the purified solvent behind. These membrane processes, although considered expensive, may

be useful in upgrading wastewater for inplant reuse. Although no tests of membrane purification have been performed on streams such as those derived from coal conversion, general reviews based on related experience are available.¹²⁷

In electrodialysis, only ionic species in the feed permeate the membrane. For this reason, electrodialysis is usually used in demineralizing and deashing solutions such as the desalination of water. Hence electrodialysis could be used as a sidestream treatment to remove electrolytes from a recirculating stream. Although electrodialysis is routinely used for demineralizing water solutions with a high-organic content,¹²⁸ the effects of phenolics and PNA are not known. No data have been reported on the electrodialysis of streams similar to those found in coal conversion plants, and electrodialysis is apparently not applicable to coal conversion wastes, with the possible exception of cooling tower wastewaters.

Reverse osmosis^{129,130} and ultrafiltration¹³¹ have been studied in depth as a means for treatment of liquid wastes. Both reverse osmosis and ultrafiltration processes have been tested on oily wastewater. The study of reverse osmosis¹³² showed good rejections of oil, COD, and total dissolved solids, but a poor (50%) rejection of phenol. The ultrafiltration study¹³³ considered only oil rejection, which was quite high. The ultrafiltration process produced an oil stream that was suitable for reuse or as fuel. However, phenol rejections for membrane processes are not promising. One work shows poor (8 to 45%) removals for reverse osmosis,¹³² and little rejection of phenol can be expected using ultrafiltration. Another study of organically contaminated

wastewater¹³⁴ showed no rejection of phenols but recorded varying rejections (0 to 90%) for 37 other organic solutes. The aromatic alcohols tested in this study showed very poor rejections, indicating that reverse osmosis would have little or no effect on many of the oxygenated hydrocarbons found in the wastewater from a coal conversion plant.

Since reverse osmosis has long been used for desalting brackish water, it may find its best use in a coal conversion plant. Chian and Fang¹³⁵ have made a study of the feasibility of using reverse osmosis as treatment for reuse of cooling tower blowdown. The use of reverse osmosis for treating blowdowns and ash pond water, which can be quite similar in composition to brackish water, looks promising and should be considered in more detail. Reverse osmosis treating of these streams will be an expensive means of producing feed water, but may be necessary in arid regions.

It is difficult to estimate the economics involved in membrane processes. Communications with various vendors of reverse osmosis equipment have optimistically discussed numbers in the range \$2000 to \$6000/10⁶ gal. At ≥80% phenol removal, this would be approximately \$0.05 to \$0.15 per pound of phenol. However, this still produces a concentrated mixed phenols-aqueous stream that needs further concentration and processing, and a dilute aqueous stream that contains unacceptable levels of organics, which would necessitate additional cleanup.

8. SUMMARY

A hydrocarbonization process¹ has been studied to assess environmental control technology for coal conversion wastewaters. The first phase of this program was the identification of the sources, magnitudes, and character of the wastewater streams. Fifteen major wastewater streams were identified. Table 8.1 summarizes the magnitudes and characteristics of the major wastewater streams. A brief description of these streams as well as other major plant streams can be found in Table 3.2. Of the 15 major wastewater streams, only 2 present serious environmental problems not routinely encountered in industry today. These are the hydrocarbonization condensate (stream 19) and the ash sluicing waste from the gasifier (stream 42). The hydrocarbonization product water, as seen in Table 8.1, is high in phenolics, ammonia, cyanide, thiocyanate, and other sulfur compounds. This stream will present a significant wastewater treatment problem unless the stream can be recycled internally, which would be the case if it can be used as a feed to the hydrogen production unit. The gasifier-ash sluicing water will probably be similar to ash sluicing water from coal-fired power generating plants. However, the large quantity of toxic trace elements may be more easily dissolved from ash produced at the lower-temperature and reducing conditions encountered in gasification.

In addition to the flowsheet study, the coal conversion literature was surveyed to obtain information on wastewater streams from processes similar to hydrocarbonization. Processes for which pertinent wastewater information is available include COED, Synthane, U.S. Steel Clean Coke, and other similar processes. These sources have been used to

Table 8.1. Identity of hydrocarbonization waste streams

Waste stream No.	Flow rate (lb/hr)	pH	Total suspended solids (ppm)	Phenolics (ppm)	soluble hydrocarbons (ppm)	Ammonia (ppm)	Hydrogen sulfide (ppm)	Trace ^a elements (ppm)	Other solubles (ppm)	Oil and grease (ppm)
3	530 ^b	2-5	100-4000	~0	~0	0.3-2.0	~0	C	SO ₄ ²⁻ ~20,000 Metal sulfides	~0
10	125,000	7-10	~0	100	<50	<50	<10	A	CN <20 SCN <50	Trace
19	105,056	8-10	~0	10 ³ -10 ⁴	500-1000	5000-30,000	200-1000	B	CN 10-200 SCN 100-2000	<10,000
23	12,331	5-9	~0	Trace	Trace	Trace	0	A	~0	Trace
25	175,000	5-9	~0	200-6000	100-600	<100	<25	B	CN 6-120 SCN 60-1200	<6,000
27	52,000	5-9	~0	<10	<5	Trace	<1000	A	~0	Trace
37	38,000	~7	~0	~0	~0	~0	~0	A	~0	~0
42	86,581	8-13	6000-200,000	~0	~0	<200	~0	C	CN, SCN <1 ppm	~0
43	1,715	9-12	~0	0-1.2	0-1	<1-50	<0.1	A	Salts 10-500	~0
53	342,590	8-13	6000-200,000	~0	~0	~0	~0	C	~0	~0
57	30,000	9-12	~0	0-1.2	0-1	<1-50	<0.1	A	Salts 10-500	~0
58	160,000	5-9	50-4000	Trace	Trace	Trace	~0	B	Salts traces CN and SCN	<50
59	358,000	7-10	<200	0.1	Trace	1-80	0.1	A-B	Salts ~2400	Trace
65	70,000	9-12	15,000-150,000	0	COD ≈ 500-10,000	0	0	B-C	Salts 2000-12,000	0
67	265,000	~7	Trace	0	~0	0	0	A	Salts 4000-18,000	0

^aA, little or no trace-element content; B, possibly undesirable trace-element content; C, significant trace-element content.

^bBased on 90-day reserve storage pile.

estimate the concentration data in Table 8.1. Tables 8.2 through 8.10 summarize the data and identify the source of the data for each of the water quality criteria shown in Table 8.1. Scaling of these data could be misleading unless flows, temperatures, pressures, methods, and other pertinent information are considered. Each table presents the data for one water quality index. For each stream in these tables, the data source (i.e., pilot plant, laboratory studies, etc.) and the reference are listed with a description of the data (space permitting), average, or range of data. In addition, a reliability-applicability index is included. This column represents a judgment (possibly somewhat subjective) as to the pertinence of the data from that particular source. This judgment considers such factors as the relation of the data source to hydrocarbonization (e.g., certain data from another pyrolysis process are more applicable than similar data from a low-BTU gasification process) and the scale of the investigation producing the data (i.e., for our purposes, pilot plant data are considered more reliable than laboratory-scale data).

Federal effluent limitation guidelines applicable to coal conversion have also been estimated by reviewing the effluent limits of related industries. These anticipated regulations are tabulated on two bases in the last two columns of Table 8.11: mass of pollutant per mass of coal, and concentration of pollutant in the effluent stream. Federal regulations use the former basis for effluent limitation guidelines, whereas some states and most of the scientific community use the latter basis.

Table 3.2. Data sources for pH

Stream No.	Comments	Data source (ref.)	pH	Reliability-applicability ^a
3	Analyses of coal storage runoff	22	2-8 overall 2-5 high-sulfur coal	A
10	No data available but assumed to be similar to stream 19		7-10	B
19, 25	Analyses of COED pilot plant first- and second-stage condensate	25	3.6-9	A
	Analysis of Synthane PDU condensate	27	8.6-9.3	A
37	Water of methanation, free of contaminants	30	~7	A
42, 53	Batch equilibrium experiments with ash from coal fired power plants	21	8.2-12.5	B
	Analysis of ash quenching water from Koppers-Totzek gasifier	32	8.8	A
43, 57	Analyses of boiler blowdown from coal fired power plants	22	9-11	A
	Analyses of boiler blowdown from petroleum refineries	4	10-12	A
58	No data available, assumed to be approximately neutral		5-9	C-B
59	Analyses of cooling water from petroleum refineries; this could be highly variable due to the number and magnitude of process leaks.	4	6-8	B
66	Typical value for lime coagulation sludge	34, 35	9-12	A
	Typical value for alum coagulation sludge	22	5-9	A
67	Typical value for ion exchange waste		~7	A

^aA, very reliable-applicable; B, intermediate; C, marginally reliable-applicable.

Table 8.3. Data sources for suspended solids

Stream No.	Comments	Data source (ref.)	TSS (mg/liter)	Reliability-applicability ^a
3	Analyses of coal storage runoff	22	100-4,000	A
10	No data available			
19	Assumed to be low due to product recovery configuration		~0	A
23	Assumed to be near zero since this stream is condensate from a stream that has been washed and cooled		~0	A
25, 27	Assumed to be near zero since this stream was formed from clean streams		~0	A
37	Water of methanation is free of suspended solids	30		
42, 53	Analyses of ash handling water in coal fired power plants	22	6,000-200,000	A
43, 57	Boiler blowdown very low in suspended solids	22	~0	A
58	No data available, assumed similar to stream 3		50-4,000	C-B
59	Upper limit for suspended solids in recirculating cooling water	22	<400	A-B
66	Typical values for clarifier sludge from lime or alum flocculation	22	15,000-150,000	A-B
67	No data available, assumed ~0		~0	A-B

^aA, very reliable-applicable; B, intermediate; C, marginally reliable-applicable.

Table 8.4. Data sources for phenolics

Stream No.	Comments	Data source (ref.)	Concentration (mg/liter)	Reliability-applicability ^a
3	Analyses of runoff from coal storage	22	0	A
10	No data available, assumed to be similar to stream 19, but more dilute		<100	C
19	Analyses of U.S. Steel, Clean Coke Process PDU, condensate	23	6000	A
	Analyses of FMC CED pilot plant second-stage condensate	25	0-4000	A
	Analyses of FMC CED pilot plant first-stage condensate	26	6000	A
	Analyses of PERC-Synthane PDU condensate	27	2000-6000	B-A
	Analyses of PERC-Synthane PDU condensate	26	~5000	B-A
23	No data available, assumed to be zero because of nature of the stream		~0	B-A
25	No data available, but only small amount of phenolics is lost in the ammonia stripper		200-6000	B-A
27	No data available			
37	Water of methanation free of phenolics	30	~0	A
42, 53	Ash slurries found to have no phenolics	22, 32	~0	A
43, 57	Analyses of boiler blowdown from petroleum refineries	4	0-1.2	A
58	No data available, assumed to be present in small quantities		Trace	C
59	Analyses of cooling water from petroleum refineries	4	<0.1	B
66, 67	Water treatment wastes will reflect the phenolic content of river water; should be near zero		~0	A

^aA, very reliable-applicable; B, intermediate; C, marginally reliable-applicable

Table 8.5. Data sources for soluble hydrocarbons

Stream No.	Comments	Data source (ref.)	Concentration (mg/liter)	Reliability-applicability ^a
3	Analyses of runoff from coal storage		COD = 100	B
10	No data available			
19	Analyses of FMC COED pilot plant, first-stage condensate	26	~800	B
	Analyses of PERC Synthane PDU condensate	26	~800	B
	Analyses of PERC Synthane PDU condensate	27	COD = 2000-5000	B
23	No data available, assumed near zero, due to nature of the stream		~0	A
25	No data available but only small amount of soluble hydrocarbons will be lost in the ammonia stripper		100-600	A
27	No data available			
37	Water of methanation free of hydrocarbons	30	~0	A
42, 53	Ash slurries found to be very low in soluble hydrocarbons	22, 32	~0	A
43, 57	Analyses of boiler blowdown from petroleum refineries	4	COD = 100-1000	B
58	No data available, should be present in small quantities		Trace	C
59	Analyses of cooling water from petroleum refineries	4	COD = 100-200	B
66	Analyses of water treatment wastes	22	COD = 500-10,000	B
67	Demineralizer wastes free of hydrocarbon contamination	22	~0	B

^aA, very reliable-applicable; B, intermediate; C, marginally reliable-applicable.

Table 8.6. Data sources and comments for ammonia

Stream No.	Comments	Data source (ref.)	Concentration (mg/liter)	Reliability-applicability ^a
3	Analyses of runoff from coal storage	22	0.3-2.0	A
10	No data available			
19	Analyses of U.S. Steel clean coke PDU condensate	23	33,000	A
	Analyses of PERC Synthane PDU condensate	27	2500-11,000	B
23	No data available, assumed to be small due to nature of the stream		Trace	B
25	Calculated, assuming 97 to 98% removal in ammonia stripper		<100	A
27	No data available, assumed to be small due to nature of the stream		Trace	A
37	Water of methanation free of ammonia	30	~0	A
42, 53	Analyses of ash quenching water from Koppers-Totzek gasifier	32	154	A
43, 57	Analyses of boiler blowdown from petroleum refineries	4	<1-50	A
58	No data available			
59	Analyses of cooling water from petroleum refineries	4	<1-80	A
66, 67	Water treatment wastes will reflect amount of ammonia in river water, should be small		~0	C

^aA, very reliable-applicable; B, intermediate; C, marginally reliable-applicable.

Table 8.7. Data sources for hydrogen sulfide

Stream No.	Comments	Data source (ref.)	Concentration (mg/liter)	Reliability-applicability ^a
3	Analyses of runoff from coal storage shows no dissolved H ₂ S, but some sulfides and sulfates are present	22	~0	A
10	No data available			
19	Analyses of U.S. Steel clean coke PDU condensate	23	562 (total sulfide)	B
	Analyses of FMC COED pilot plant first- and second-stage condensate	25	0.01-0.18% (total sulfur)	B
	Analyses of PERC Synthane PDU condensate	27	1400 (total sulfur)	B
23	No data available, but no H ₂ S will be present due to the nature of the stream		0	A
25	No data available, H ₂ S assumed to be stripped out with NH ₃		<25	B
27	No data available, but since this stream is formed by regeneration of the sulfur sorption beds, a large amount of sulfur is expected		1000	C
37	Water of methanation free of sulfur contamination	30	0	A
42, 53	No data available, but H ₂ S or sulfide are not likely to be present in ash sluicing waters		~0	A
43, 57	Analyses of boiler blowdown from petroleum refineries	4	<0.1	A
58	No data available, but some sulfides probably present		Trace	C
59	Analyses of cooling water from petroleum refineries	4	<0.1	A
66, 67	Water treatment wastes will reflect quality of river water, probably no H ₂ S present		~0	A

^aA, very reliable/applicable; B, intermediate; C, marginally reliable/applicable.

Table 8.8. Data sources for trace elements

Stream No.	Comments	Data source (ref.)	Concentration (mg/liter)	Reliability-applicability ^a
3	Analyses of runoff from coal storage	22	Cl 3-500 Cr 0.06-16 Cu 1.5-3.5 Mg 80-175 Zn ~0-23	A A A A A
10, 19, 25	Trace-element concentration should be similar to ORNL Hydrocarbonization and Synthane condensates; see Tables 5.3-5.6	40,27,42		
23, 27	No data available, probably free of trace-element contamination		~0	B
37	Water of methanation free of trace-element contamination	30	~0	A
42, 53	Batch leaching studies of coal-fired power plant ash	21	See Table 4.8	B
	Analyses of ash sluicing water from coal fired power plants	21	See Table 4.10	A
43, 57, 59	No data available, trace-element contamination from coal is unlikely			
58	No data available			
66, 67	No data available, but water treatment wastes are likely to contain trace elements found in river water			

^aA, very reliable-applicable; B, intermediate; C, marginally reliable-applicable.

Table 8.9. Data sources for other soluble contaminants

Stream No.	Comments	Data source (ref.)	Concentration (mg/liter)	Reliability-applicability ^a
3	Analyses of runoff from coal storage	22	SO ₄ , 100-22,000	A
10	No data available			
19	Analyses of U.S. Steel clean coke PDU condensate	23	CN, 74 SCN, 1171	A A
	Analyses of PERC Syntthane PDU condensate	27	CN, 0.1-0.6 SCN, 20-200	B B
23, 27, 37	No data for these streams			
25	No data for this stream, but will contain CN and SCN from stream 23			
42, 53	Ash sluicing stream saturated with Ca, Al, Mg, Fe salts	22		
	Analyses of ash quenching water from Koppers-Totzek gasifier	32	CN, 0.52	A
43, 57	Typical values for boiler blowdown	22	Salts, 10-500	A
58	No data available			
59	Typical value for recirculating cooling water	136	Salts, <2400	A
66	Typical value for clarifier sludge	22	Salts, 2000-12,000	A
67	Typical value for demineralizer waste	22	Salts, 4000-18,000	A

^aA, very reliable-applicable; B, intermediate; C, marginally reliable-applicable.

Table 8.10. Data sources for suspended oil and grease

Stream No.	Comments	Data source (ref.)	Concentration (mg/liter)	Reliability-applicability ^a
3	No oil or grease in coal storage runoff	22	C	A
10	No data available			
19	Analyses of FMC COED condensate ^b	25	0-0.5%	B
23	No data available, no oil or grease expected due to nature of the stream		~0	B
25	See note on stream 19			
27	No data available, but only a very small amount expected due to the nature of the stream		Trace	C
37	Water of methanation not contaminated	30	~0	A
42, 53	No data available, but no oil or grease expected		~0	B
43, 57, 58	No data available, but trace contamination expected due to leakage		Trace	B
59	No data available, some contamination expected		Trace	C
66, 67	No data available, no contamination expected		~0	B

^aA, very reliable-applicable; B, intermediate; C, marginally reliable-applicable.

^bThe oil and grease concentration is entirely dependent on the efficiency of the phase separator used, the design of which is unknown.

Table 8.11. Summary of hydrocarbonization wastewater data

Effluent parameter	Total waste (lb/day) ^a	Main sources	Maximum conc (ppm)	Hazard level ^b		Existing treatment-technology available	Anticipated regulations	
				Envir	Human		(lb effluent/10 ⁶ lb coal)	ppm
pH				2	1	Neutralization	6-9	6-9
TSS		Coal storage, ash handling, and water treatment	200,000	2	1	Clarification and sedimentation	1-7	3-15
Phenolics	2500-25,000 (may be recovered)	Hydrocarbonization	6,000	3	3	Liquid-liquid extraction and biological oxidation (expensive and unproven for coal conversion wastes)	0.01-0.15	0.03-0.3
Other soluble hydrocarbons (benzene, fatty acids)	250-2500	Hydrocarbonization	1,000	2	2		BOD, 2-15 COD, 10-150	4-30 20-350
Oil and grease	1500-15,000	Leaks, plant washdown and hydrocarbonization	10,000	2	2	Separators	0.5-8	1.0-16
Dissolved gases (NH ₃ , H ₂ S, etc.)	Recovered for sales	Hydrocarbonization and acid-gas treatment	NH ₃ , 30,000 H ₂ S, 1,000			Stripping columns	0.4-2.5 0.01-0.1	0.8-5.0 0.02-0.2
Other soluble contaminants	CN 1-240 SCN 3-3000		100 1200	3	3		0.01-0.05	0.02-0.1
Trace elements		Ash handling and coal storage				None		
Ag	1		c	1-3	1-3		0.05	0.1
As	228		c	1-3	1-3		0.12	0.25
Ba	150		c	1-3	1-3		1.0	2.0
Cd	117		c	1-3	1-3		0.07	0.15
Cr	480		c	1-3	1-3		0.05-0.5	0.1-1.0
Cr ⁶⁺			c	1-3	1-3		0.003-0.1	0.007-0.3
Cu	444		c	1-3	1-3		0.5	1.0
Fe	561,000		c	1-3	1-3		0.5	1.0
Hg	5.4		c	1-3	1-3		0.0002	0.0005
Mn	1608		c	1-3	1-3		0.5	1.0
Ni	666		c	1-3	1-3		0.5	1.0
Pb	858		c	1-3	1-3		0.05	0.1
Se	60		c	1-3	1-3		0.5	1.0
Zn	13,500		c	1-3	1-3		0.5	1.0
PAH	2-50	Hydrocarbonization, leaks, and spills		2	3	None	Unknown	

^aBased on coal feed 15,000 tons/day (3 x 10¹⁰ lb/day).^bHazardousness: 1, fairly innocuous; 2, undesirable; 3, very hazardous.^cDue to recycling of ash slurry water, no estimates of maximum concentration are shown.

Table 8.11 also summarizes production rates, sources, maximum concentrations, and hazard level of each effluent parameter. This table is a condensation of the data presented in Tables 8.1-8.10.

A number of cleanup technologies relevant to the cleanup of coal conversion aqueous effluents have been assessed for their adaptability to the specific pollutants found in coal hydrocarbonization wastewater. A summary of these processes, shown in Table 8.12, lists the potential applicability, economics, raw material requirements, process compatability, operating conditions, state of development, environmental problems, energy requirements, and availability of each. The economics of the various processes, shown graphically in Fig. 8.1, compare the cost per pound of organic material degraded or removed to the remaining residual organic concentration. In most cases, the organic level is equivalent to the phenolic content. Indications are that almost any level of removal can be achieved if one is willing to pay the cost. The optimum amount of cleanup will require much future interaction between industry, environmental control technology developers, human and environmental effects assessors, and federal effluent regulations administrators.

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Table 8.12. Summary of control technologies

	Biological oxidation	Adsorption	Ozonation	Coagulation- flocculation	Solvent extraction	Membrane processes
Potential applicability	High	High	Moderate	High	Moderate	Low
Economics	\$0.15-\$0.25/lb phenol \$6000-\$10,000/10 ⁶ gal	\$0.50-\$1/lb phenol	\$0.60-\$1/lb phenol	>\$0.01/lb organic \$80/10 ⁶ gal	\$0.07/lb phenol \$3000/10 ⁶ gal	\$0.05-\$0.15/lb phenol \$2000-\$6000/10 ⁶ gal
Raw materials	None to little	Charcoal or other sorbers	None	Lime or other agents	Solvent	Membrane material
Process compatibility	Moderate to high	High	High	High	Moderate	Low to moderate
Operating conditions	Moderate temperature and pH	Moderate, except for regeneration	Little known	Moderate	Moderate	Moderate
State of development	High	Moderate to high	Fair	High	Moderate to high	Moderate
Additional environ- mental problems	Disposal of sludges	Disposal of spent sorber	No trace- element remover	Disposal of sludges, heavy metal sludges	Little to none if product salable ^a	Concentrated aqueous waste stream
Energy requirements	Low	Low (except for regeneration)	High	Low to moderate	Moderate to high	Moderate to high
Process availability	High	High	Moderate	High	Moderate to high	Moderate to high

^aAn aqueous stream with contaminants in excess of regulations will require additional treatment; product stream will need to be disposed of if not salable.

Fig. 8.1. Economic costs of environmental control technologies for aqueous coal conversion wastes.

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