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Wastewater and Sludge Control-Technology Options for Synfuels Industries

Volume 1: Slagging, Fixed-Bed Lignite Gasification

F. J. Castaldi, W. Harrison, and D. L. Ford

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WASTEWATER AND SLUDGE CONTROL-TECHNOLOGY OPTIONS FOR SYNFUELS INDUSTRIES

VOL. 1: SLAGGING, FIXED-BED LIGNITE GASIFICATION

by

Frank J. Castaldi,* Wyman Harrison, and Davis L. Ford*

with an appendix by

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Energy and Environmental Systems Division
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PREFACE

This report is the first in a series of studies of wastewater and sludge control-technology options for synfuels industries. Presented here is an analysis of control-technology options for wastewaters associated with the conversion of lignite to pipeline quality gas using the slagging, fixed-bed gasification process. Subsequent reports will deal with wastewaters from the in-situ production of oil from oil-shale kerogen and tar-sands bitumen.

The Argonne National Laboratory synfuels wastewater environmental control-technology program is a coordinated effort among Argonne, industrial, academic, and consulting-firm specialists in such technology. All work is supported by the Environmental Control Technology Branch, Environmental and Safety Engineering Division, Office of Environmental Compliance and Overview, under the Department of Energy's Assistant Secretary for Environment. The DOE project officer for this report is Fred E. Witmer.

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WASTEWATER AND SLUDGE CONTROL-TECHNOLOGY OPTIONS FOR SYNFUELS INDUSTRIES

VOL. 1: SLAGGING, FIXED-BED LIGNITE GASIFICATION

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ABSTRACT

The options examined were those of zero discharge, partial water reuse with restricted discharge of treated effluents, and unrestricted discharge of treated effluents. Analysis of cost data and performance-analyses data for several candidate secondary-wastewater-treatment unit processes indicated that combined activated-sludge/powdered-activated-carbon (AS/PAC) treatment incorporating wet-air-oxidation carbon regeneration is the most cost-effective control technology available for the removal of organic material from slagging, fixed-bed process wastewaters. Bench-scale treatability and organic-constituent removal studies conducted on process quench waters from a pilot-scale, slagging, fixed-bed gasifier using lignite as feedstock indicated that solvent extraction followed by AS/PAC treatment reduces levels of extractable and chromatographable organics to less than 1 μg/L in the final effluent. Levels of conventional pollutants also were effectively reduced by AS/PAC to the minimum water-quality standards for most receiving waters. The most favored and most cost-effective treatment option is unrestricted discharge of treated effluents with ultimate disposal of biosludges and landfilling of gasifier ash and slag. This option requires a capital expenditure of $8,260,000 and an annual net operating cost of $2,869,000 in 1978 dollars, exclusive of slag disposal. The net energy requirement of 19.6×10^6 kWh/year, or 15.3 kWh/1000 gal treated, is less than 6% of the equivalent energy demand associated with the zero-discharge option.

EXECUTIVE SUMMARY

From among several physicochemical and biological options discussed as appropriate for controlling wastewater and sludge pollution from a slagging, fixed-bed (SFB) gasifier using a lignite feedstock, three treatment-process systems are defined in terms of costs and levels of control. The three options evaluated are (1) zero discharge, where all process wastewaters and storm-water runoff are treated and recycled within the treatment and production facility; (2) partial water reuse with limited discharge of treated effluents; and (3) unrestricted discharge of treated effluents. The flow diagrams for each treatment system are presented in the text (Figs. 15-17).

Recently published data were gathered on state-of-the-art, coal-conversion wastewater treatment technology. These data were supplemented with information obtained from correspondence and discussions with treatment-process licensors and equipment vendors. In addition, special emphasis was placed on the evaluation of activated-sludge/powdered-activated-carbon (AS/PAC) treatment as a possible secondary-treatment alternative.

The zero-discharge option is a modified version of the proposed commercial-scale CONOCO design for treating Lurgi-type, SFB process wastewaters. In that design, all process wastewaters and storm-water runoff are treated and recycled within the treatment facility. The modified version incorporates neutralization as preliminary treatment, before treating with flotation, oil-water separation. The treatment facility employs conventional biological-oxidation, tertiary-filtration, and granular activated carbon (GAC) treatment of process wastewaters that are reused as cooling-tower makeup. The effluent-desalting facilities incorporate forced evaporation of high dissolved solids, cooling-tower blowdowns, filtrate from slag dewatering, and spent-demineralizer regenerant from raw-water treatment. The condensates are used as cooling-tower makeup, while the waste brines are concentrated for further recovery of water and the residuals are chemically stabilized and encapsulated.

The option for partial water reuse is characterized by a treatment system that employs the AS/PAC process, tertiary granular-media filtration, and a membrane desalination process for secondary-effluent desalting. The AS/PAC process incorporates wet-air-oxidation (WAO) carbon regeneration, which also provides for the ultimate disposal of organic sludges from preliminary treatment. The reject brine stream from the candidate membrane-desalination process is sent to a forced-evaporation unit for recovery of water. This distillation process was designed with sufficient capacity to handle such ancillary streams as the filtrate from slag dewatering and the spent-demineralizer regenerant from raw-water treatment. Desalted effluents from the membrane-desalination process would provide low-dissolved-solids make-up water to a cooling tower, while condensates from the evaporator would provide feedwater to the boilers for steam generation. The blowdown from the evaporator would be concentrated and disposed of by subsurface injection into a reservoir with suitable confining strata.

The unrestricted-discharge option provides for the discharge of treated effluents that are characterized by an effluent quality commensurate with the best available technology (BAT) economically achievable for coal-conversion wastewaters. The treatment facility employs the AS/PAC process and incorporates WAO regeneration of spent-carbon sludges. The WAO process also is used to achieve ultimate disposal of organic sludges from primary and secondary oil-recovery units. Secondary effluents undergo granular-media filtration before final discharge to the receiving body. This design option permits unrestricted discharge of cooling-tower blowdowns and neutralized spent-demineralizer regenerants, and these effluents are considered of comparable or better quality than those that would be discharged from a coal-fired, steam-electric power plant regulated by proposed BAT standards required by the Clean Water Act (PL95-217).

The cost of the zero-discharge option is more than four times greater than the unrestricted discharge of treated effluent and would consume over 13 times more energy. More than 80% of the 337 × 10^6 equivalent kWh/yr required by the zero-discharge option would be used in desalinating the secondary-treatment effluents and ancillary streams; this option would consume an equivalent of over 1% of the designed energy output of the gasification facility, while the unrestricted-discharge option would require less than 0.1% of the designed equivalent energy demand. The unrestricted-discharge option, which includes preliminary wastewater treatment and gravity filtration of AS/PAC process effluents, would require a capital expenditure of $8,260,000 (1978 dollars) and an annual net operating cost of $2,869,000. The net energy requirement is 19.6 × 10^6 equivalent kWh/yr or 15.3 kWh/1000 gal treated. The zero-discharge option, which would cost $8.84/1000 gal treated, is nearly four times as expensive as the unrestricted discharge of treated effluent, and has an equivalent energy demand that is over 13 times greater than that of the unrestricted-discharge option. The additional treatment costs associated with the partial reuse of treated effluents far exceed those of complete discharge because the former option would add approximately $1.50/1000 gal to the unit cost of treatment associated with complete discharge, and over 50 equivalent kWh of energy consumed per 1000 gal of wastewater treated.

It was estimated that the partial-water-reuse option would allow a discharge of approximately 145 tons/day of dissolved solids to the receiving water, while nearly 200 tons/day of dissolved solids would be discharged by the unrestricted-discharge option. The zero-discharge option would require disposal of approximately 250 tons/day of waste brine, while over 100 tons/day of waste brine would be generated by the partial-water-reuse option. In addition, all the wastewater-treatment-process options are expected to handle an estimated 3000-4000 tons/day of dry ash and slag associated with the gasifier and the onsite combustion of coal for steam and power generation. The solid residuals generated by both the partial-reuse and zero-discharge options are excessive, and the anticipated cost burden associated with effective solid-waste management would be substantial.

The quantity of refractory chemical oxygen demand (COD) that characterizes the treated-effluent quality associated with the unrestricted-discharge option is estimated to be 22,650 lb/day, while the partial-water-reuse option would discharge as much as 6000 lb/day of residual COD after effluent desalting. The former solids-loading rate reflects the apparent level of residual organics in treated effluents from the AS/PAC process that would be present in the form of refractory organic carbon. On the other hand, detailed gas chromatography (GC) and gas-chromatography/mass-spectrometry (GC/MS) analyses of the organics present in the influent and secondary-treated effluents indicated an excellent reduction of these organics in solvent-extracted, pretreated process gas liquors. Experimental data suggest that a pretreatment by solvent extraction selectively removes a large fraction of the biodegradable organics and that the residual organics in the wastewaters are less readily biodegradable. As a consequence, the AS/PAC process offers an overall advantage for the treatment of SFB coal-gasification wastewaters because it provides a lower effluent residual-organics level in terms of refractory COD than AS treatment alone. Moreover, most of the apparently toxic organic material of treated SFB, coal-gasification wastewaters, as measured by GC/MS, would be reduced to the submicrogram-per-milliliter level with the AS/PAC process. The treated effluent discharges should meet the minimum water quality conditions applicable to most receiving waters regarding such pollutants as ammonia, oil and grease, alkalinity, pH, hexavalent chromium, and phenolics.

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1 INTRODUCTION

1.1 BACKGROUND

Synthetic liquid or gaseous fuels produced from coal offer promise as substitute energy resources to supplement diminishing supplies of petroleum and natural gas. A major advantage of the energy produced from a synthetic fuel over that associated with the direct use of coal is the transfer of environmental problems from the often small, individual end-users to the large, commercial-scale conversion facility. This factor has spurred development of numerous processes for the production of synthetic fuels from coal. A few, such as the British Gas/Lurgi slagging, fixed-bed (SFB) coal-gasification process, have reached commercial status while others are still in various stages of development.

The United States Department of Energy (DOE) has contracted with Continental Oil Company (CONOCO) to design, construct, and operate a demonstration coal-gasification plant capable of converting high-sulfur, bituminous caking coal to high-Btu, pipeline-quality gas. One of the task assignments under the CONOCO contract was to prepare a preliminary design of a commercial-scale plant based on the process selected for demonstration. The British Gas/Lurgi slagging, fixed-bed coal-gasification process was selected primarily because of proven commercial capabilities and its potential for gasifying high-sulfur, bituminous caking coals in an economically and environmentally acceptable manner.

Bituminous coals found in the Appalachian region are difficult to gasify because of their low reactivity. Slagging gasification is accomplished at high temperatures in the bottom of the gasifier, and thus the reactivity of the coal is a minor factor in the gasification process. The British Gas/Lurgi slagging gasifier is based on new technology developed by the British Gas Corporation of London, England, and the Lurgi Kohle und Mineraloeltechnik GmbH of Frankfort, Federal Republic of Germany. The SFB process reacts coal with steam and oxygen at elevated temperatures in the bottom of the gasifier to produce a synthesis gas that flows upward countercurrently to the downward flow of coal under a pressure of 450 psia. The countercurrent flow improves the thermal efficiency of the gasifier. The volatilizing reactions effected by hot gases at the top of the gasifier drive off moisture in the coal. The resultant crude synthesis gas exits at the top of the gasifier.

The initial volatilization of the coal accompanied by gasification occurs in the middle of the gasifier in a temperature range of 1140-1400°F, which is less than the ash fusion temperature. The reactor temperature at the bottom of the gasifier is above the ash fusion temperature; therefore, the coal ash is discharged therefrom as a molten slag. (Steam is the source of hydrogen, and combustion of a portion of the char with oxygen supplies the necessary heat. Temperatures in the upper portion of the gasifier are well below the fusion temperature of the ash, usually between 700 and 1100°F, depending on the type of coal, so the crude gas leaving the gasifier contains tar, oil, naphtha, phenols, and ammonia, plus the unfused ash and coal particulates.)

The exiting crude synthesis gas is quenched and scrubbed in a wash cooler by a recirculating gas liquor stream that removes dust and tar from the gas stream. The resulting cooled gas is transferred by interconnecting piping to a shift converter. Gas from the shift converter is washed to remove naphtha and unsaturated hydrocarbons. Finally, carbon dioxide, hydrogen sulfide, and ammonia are removed, and the gas is methanated and dehydrated, producing a pipeline-quality gas.

CONOCO's conceptual commercial-scale plant was designed to produce 242 million standard cubic feet (MMSCF) per stream day of 960 Btu/SCF pipeline-quality gas from 16,879 tons per day of Illinois No. 6 coal, a bituminous caking coal. This particular coal was selected as a feedstock for the commercial-plant design primarily because it is representative of large reserves found in Illinois, Indiana, and Kentucky, as well as throughout Appalachia in Pennsylvania, West Virginia, Ohio, and Virginia. The proposed demonstration plant is designed to produce 19 MMSCF per stream day of pipeline-quality gas, and would be constucted in Noble County, Ohio.

Several pilot-plant, coal-gasification tests have been conducted in the United States to evaluate design process efficiency and to characterize the constituents present in the process wastewaters. The DOE is sponsoring pilot-plant-scale research on an improved slagging, fixed-bed gasifier at its Grand Forks Energy Technology Center (GFETC) in North Dakota. The GFETC SFB gasifier was tested in 1979 with North Dakota lignite, the feedstock upon which part of the present wastewater control technology is based, and it is planned to test the gasifier in 1981 with bituminous coal. Wastewaters generated from GFETC's SFB gasifier, while not strictly representative of the commercial-scale SFB process, provided useful information for evaluating treatment technology applicable to handling coal-conversion wastewaters characteristic of SFB gasifiers.

1.2 OBJECTIVE AND SCOPE

The present study provides an assessment of control-technology options for treatment of process wastewaters and sludges from the SFB coal-gasification process as designed for the production of high-Btu, pipeline-quality gas.

Principal objectives of the present evaluation are: (1) to specify suitable wastewater pollution abatement technology for the control of contaminated waters from the SFB coal-gasification process; (2) to develop capital and annual operating cost information for candidate wastewater treatment options; (3) to specify the energy requirements of the various treatment options; and (4) to specify the expected levels of treatment performance associated with the candidate treatment options in terms of standard wastewater quality parameters.

CONOCO's conceptual design of a commercial-scale, SFB coal-gasification process provides the basis upon which the treatment technology evaluation is constructed. Wastewaters and solid wastes generated by such a proposed facility are estimated from (1) available pollution control literature and (2) wastewater compositional and treatability information derived from the assessment of GFETC's Run RA-52 quench waters. The former provides a means of comparison between alternative wastewater treatment modes; the latter allows a thorough evaluation of performance levels associated with biological-treatment processes with special emphasis on activated-sludge/powdered-activated-carbon (PAC) treatment as a possible secondary-treatment alternative.

Quantities of wastewater and solid waste used to develop various treatment-process schematics were based on information from CONOCO's conceptual design as prepared for the U.S. Department of Energy, Division of Coal Conversion.[1] Three major treatment-process options are evaluated: (1) zero discharge, (2) partial water reuse with restricted discharge of treated effluents, and (3) total discharge of treated effluents. By definition, the zero-discharge option does not permit release of treated wastewaters to a receiving water. Consequently, water losses from the system would be from cooling-tower evaporation, from water associated with quench ash or slag, and from water present in wet inorganic and organic sludges from water and wastewater treatment. (Provision would be included for collection of leachate and runoff from solid-waste disposal areas for return to the coal-conversion facility for ash quenching or treatment for recycle.) These provisions, in effect, adhere to the concept of zero discharge. It should be noted that the term "zero discharge" describes a complex process of internal recycle and reuse of process and storm-water wastes and does not imply that there is an absence of wastewaters generated by the coal-conversion plant.

Commercial methods for treating wastewaters are investigated in detail for applicability, treatment efficiency, and process limitations. Residual waste streams from the various treatment steps are estimated in order to specify applicable ancillary treatment processes for waste residuals characteristic of the technology employed. Recently published data on the state of the art of coal-conversion, wastewater-treatment technology are supplemented with information obtained from correspondence and discussion with treatment-process licensors and equipment vendors. Much of the treatment-process analysis presented herein is based on best estimates of the volume and composition of each stream requiring treatment and the allowable contaminant levels in the treated effluents.

Capital and annual operating costs are obtained from equipment vendors, treatment-process licensors, and published cost data. Various methods of measuring the effect of inflation on equipment and contruction costs are used to update costs reported in the literature. Factors are developed for estimation of total installed cost when only vendor equipment costs are available. Published capital costs for treatment processes proposed by, among others, the Continental Oil Company,[1] Water Purification Associates,[2] Battelle-Northwest,[3] and Pullman Kellogg[4] are tabulated and compared. Annual operating and maintenance costs, including energy requirements and costs, are estimated from published cost data[3,5-8] and information made available to the authors by equipment vendors.

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2 THE FIXED-BED COAL GASIFICATION PROCESSES

The Lurgi Dry Ash process best represents current state-of-the-art commercial fixed-bed gasifier technology. It is the only commercial process operating at high pressure, usually between 24 and 31 atmospheres. Temperatures within the gasifier are about 1200-1500°F at the middle of the bed and about 1700-2500°F at the bottom. At higher temperatures at the bottom of the gasifier (greater than 2550°F), the coal ash melts and forms a liquid slag. Such slag is characteristic of the Lurgi Slagging Ash gasifier, the type proposed for the CONOCO demonstration plant. Generally, limestone is required in the gasification process to control the viscosity of the molten slag. Since the coal is fed to the top of the gasifier and is gradually heated through stages of devolatilization, gasification, and combustion, the exiting gas contains phenols, oils, and tars.

Advantages claimed for the Lurgi fixed-bed gasifiers are high carbon conversion, low oxygen consumption, and a high throughput. Additionally, the resultant crude synthesis gas has a relatively high methane content (7-12% by volume). The principal disadvantages cited are phenol, oil, and tar production and a high steam consumption. Difficulty is experienced, too, when using coals with low ash-fusion temperatures or those that cake or swell appreciably. Pretreatment for caking coals is available, but its use increases the consumption of steam and oxygen.[4]

2.1 WASTEWATER CHARACTERISTICS

The Lurgi process is proprietary, and no wastewater quality data are available for the gasifier itself. However, waste stream compositions are reported in conceptual designs that are based in turn on operational data for the total process. The generalized block-flow diagram for the Lurgi Slagging Ash process is presented in Fig. 1. This diagram indicates the type of wastewaters that would be generated from the major conversion steps in the process for the production of a high-Btu, pipeline-quality gas. Since the principal concern is with the contaminated wastewaters produced by the process, recycle directly within the process is omitted, and only those streams that would be expected to leave the process battery limits are indicated.

The premise that coal-gasification processes fed with the same coal and operating under the same or similar conditions will generate wastewaters with the same or similar characteristics formed the basis for this evaluation. It is noted that virtually all the tentative commercial-scale, coal-gasification projects currently under consideration for the United States employ a type of Lurgi fixed-bed gasification process. As a consequence, a reasonable amount of data and information on the compositions and quantities for the waste streams from the various types of Lurgi gasification processses are available. An attempt was made in the early stages of the project to derive approximations for the compositions and quantities of process waste streams that characterize both the Lurgi Dry Ash and Lurgi Slagging Ash gasification processes. This task was accomplished by exercising best engineering judgement regarding the evaluation of available published data for the waste streams generated by a Lurgi process. It was conjectured that this information would provide a basis for evaluating the best practicable control

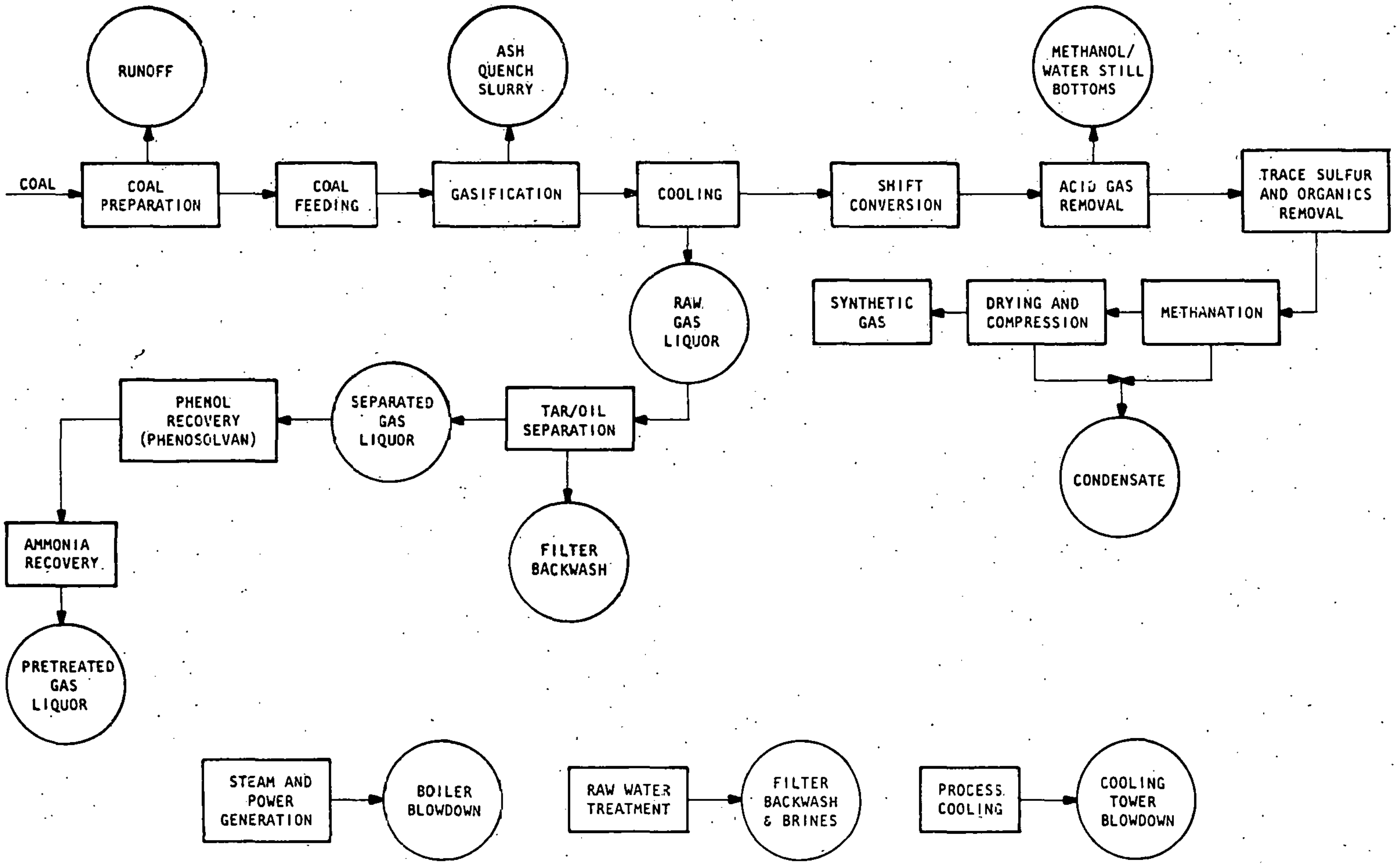

Fig. 1 Process Modules Generating Wastewaters in Lurgi Coal-Gasification Facilities

technology currently available for the abatement of wastewater pollution from SFB coal-gasification processes.

Data[9] for the major pollutant constituents present in gravity-separated Lurgi process gas liquors are presented in Table 1. These data indicate that Lurgi process gas liquors are generally high in phenols, tars, oils, ammonia, biochemical oxygen demand (BOD), and chemical oxygen demand (COD). The data represent pollution levels indicative of gas liquors generated in a Lurgi Slagging Ash, coal-gasification process that uses both bituminous and subbituminous coals as feedstocks. Although it is not known whether the data are characteristic of gas liquors generated from steady-state operation of a Lurgi gasifier, nevertheless, the wide variation in pollutant constituent concentrations for the various wastewater quality parameters indicates that these waste streams are highly dependent on the characteristics of the coal feedstock.

Data[9] for the trace-element composition of Lurgi process gas liquors are presented in Table 2. These data represent the pollutant level of a grab sample of Lurgi gas liquor taken from a process that used a lignite feedstock. The characteristic pollutant levels found[9] in liquors from a Rectisol methanol/water still bottom are presented in Table 3. This source constitutes the second major organic wastewater stream from a Lurgi coal-gasification process. Ancillary process wastewater streams such as the condensates generated from the methanation stage and the gas drying and compression steps are usually used as boiler feedwater, although these streams are sometimes discharged to the wastewater sewer for final processing at the end of the pipe. The trace-element composition and total dissolved-solid content of drainage from two different coal pile sites[10] are presented in Table 4. Usually, runoff from a coal pile is treated separately from the main process wastewater streams since these liquors pose a special treatment problem because of their high dissolved-solids level and iron concentration.

2.2 SOLID WASTE CHARACTERISTICS

Solids handling problems in Lurgi-process coal-gasification plants are of two general types, those related to control of airborne dusts and those related to management of solid process wastes that include spent catalysts. Considering the paucity of available data regarding the composition and quantity of such solid waste streams as those caused by fugitive dust and those from coal-pile runoffs, the data presented herein are limited in their utility. For instance, no data are available concerning possible interactions between coal-refuse and gasification-process ash and slag when these wastes are mixed in a single disposal area. Nevertheless, a lack of data, for example, on the amount of dust escaping from coal handling operations does not deter investigation into acceptable techniques for controlling the dust.

Figure 2 is a schematic diagram of the process modules that would generate solid wastes in Lurgi coal-gasification facilities. The major source of solid waste in a fixed-bed gasification process, other than spent catalyst material, is the ash and slag produced in the gasifier. The elemental composition of ash produced by gasification of both bituminous coal and lignite[9] is presented in Table 5. These data are not specific to an SFB gasifier because they were obtained from the analysis of ash produced in a

Table 1 Major Pollutant Constituents in Gravity-Separated, Lurgi Gas Liquors[a] (all units are mg/L unless otherwise indicated)

	Subbituminous Coal, Montana		Bituminous Coal							
			Illinois No. 6		Illinois No. 5		Pittsburgh No. 8		South African	
Parameter	A	B	A	B	A	B	A	B	A	B
Production rate (lb waste/lb coal)	0.93	0.93	2.11	2.11	1.77	1.77	2.60	2.60	1.06	1.06
pH (units)	9.6	8.3	9.8	8.5	9.5	8.3	9.3	8.2	-	8.9
Ammonia (ppm)										
Free	3,990	14,015	1,700	17,650	1,520	13,970	1,600	14,000	10,600	11,200
Fixed	395	525	280	210	410	330	320	250	150-200	-
Suspended tar and oil	350	650	1,130	1,250	2,150	2,200	300	1,100	5,000	-
Total dissolved solids	4,030	1,765	2,770	1,570	3,180	1,120	1,550	1,240	-	2,460
Total dissolved solids after ignition	45	35	110	35	85	25	105	120	-	-
Sulfide	130	115	25	440	15	490	65	520	-	<0.5
Total sulfur	150	265	180	730	160	930	155	720	-	-
Fatty acids	1,250	1,670	490	280	400	260	275	610	300	-
Carbonate	4,070	19,460	1,280	6,500	680	9,210	1,360	10,740	8,500	-
Total phenols	4,200	4,406	2,200	1,900	2,900	3,750	1,400	2,150	3,250-4,000	-
Monohydric phenols	-	-	-	-	-	-	-	-	-	2,140
Cyanide	2	4	3	11	7	14	1	12	6	-
Thiocyanate	6	15	65	160	79	158	70	185	-	85
Chlorides	45	40	135	75	290	170	240	210	-	-
Biochemical oxygen demand	9,900	13,400	3,800	4,700	6,000	6,200	4,100	5,400	-	-
Chemical oxygen demand	22,700	20,800	10,100	12,000	9,300	10,600	650	7,500	-	12,500
Total organic carbon	-	-	-	-	-	-	-	-	-	4,190

Source: Data obtained from the testing of caking coals at the Westfield, Scotland, Lurgi facility (see Ref. 9).

[a] Analysis on tar-free basis.
Option A = with ammonia stripping.
Option B = without ammonia stripping.

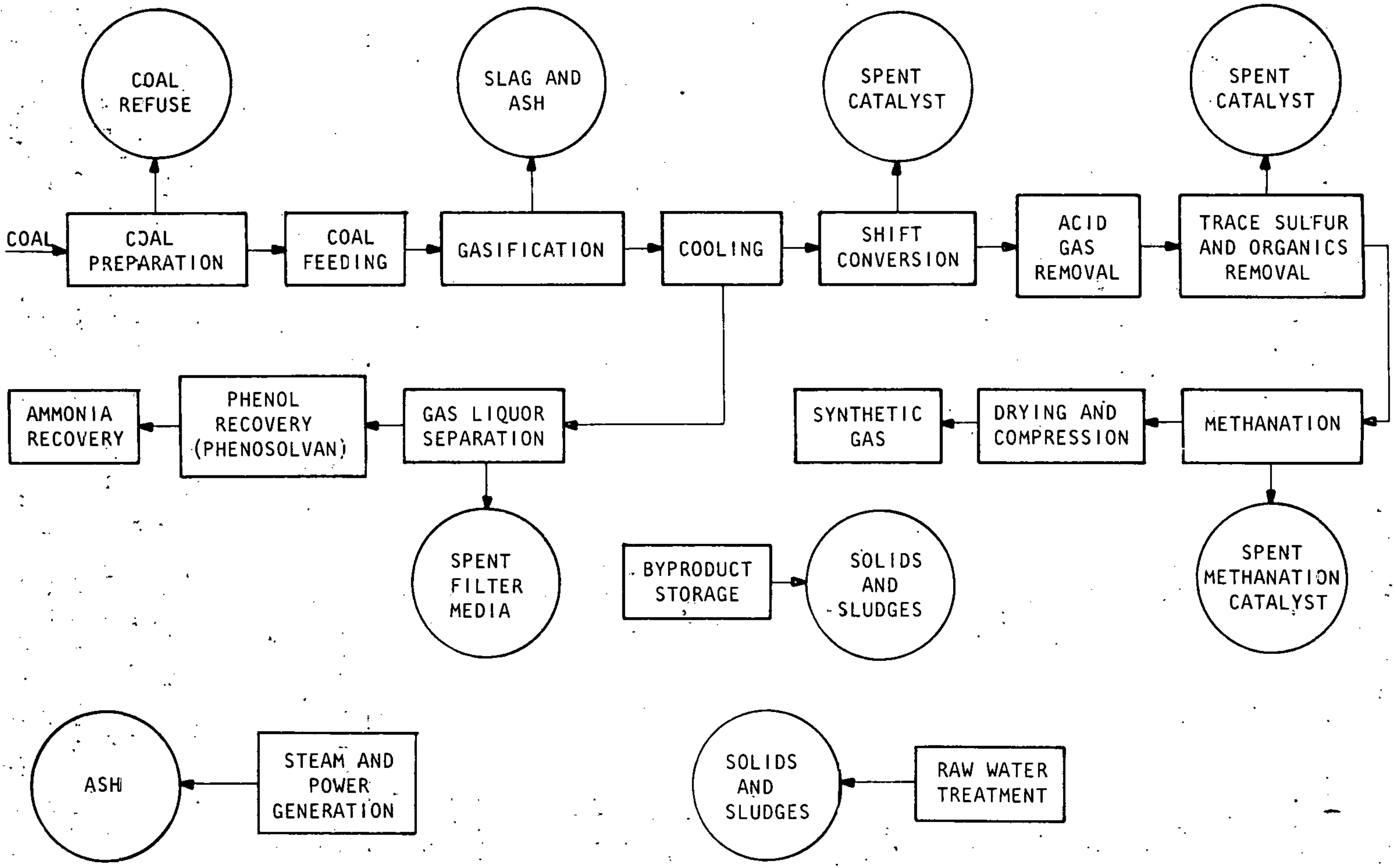

Fig. 2 Process Modules Generating Solid Wastes in Lurgi Coal-Gasification Facilities

Table 2 Composition of Lurgi Process Gas Liquors

Trace Element	Concentration (mg/L)	Composition	Percent
Aluminum	2.9	Moisture	35.98
Arsenic	0.1	Volatile matter	27.21
Barium	0.005	Ash, dry basis	7.42
Boron	0.9	Carbon, dry basis	71.45
Bromine	0.001	Hydrogen, dry basis	4.81
Cadmium	0.2	Oxygen, dry basis	21.01
Calcium	14.6	Sulfur, dry basis	1.26
Cerium	0.006	Nitrogen, dry basis	1.44
Chromium	0.02		
Cobalt	0.001	Btu per pound	7,230
Copper	0.02		
Fluoride	5		
Iron	0.2		
Lead	0.005		
Lithium	0.002		
Magnesium	0.6		
Manganese	0.03		
Mercury	0.17		
Molybdenum	0.04		
Nickel	0.006		
Phosphorus	6		
Potassium	0.8		
Rubidium	0.003		
Scandium	0.006		
Selenium	0.004		
Silicon	117		
Sodium	82.5		
Strontium	0.004		
Titanium	0.02		
Vanadium	0.001		
Zinc	0.2		
Zirconium	0.008		

Source: Data obtained from the testing of a North Dakota lignite feedstock at the Sasol, South Africa, Lurgi facility. See Ref. 9.

Lurgi Dry Ash reactor. It is generally accepted, however, that the ash characteristics for a slagging gasifier would be similar to those for a nonslagging gasifier. The estimated maximum concentration of various trace elements that might be present in ash-slurry leachate[9] is presented among the data in Table 6. Estimations are based on information obtained on the trace-element level that characterized the ash produced from the gasification of lignite in a Lurgi Dry Ash reactor. An analysis[9] of spent methanation catalysts is presented in Table 7. These data indicate that the nickel catalyst used in the methanation reaction can be fouled by the presence of sulfur in the crude synthesis gas. This fouling poses an important design

Table 3 Characteristic Pollutant Levels in Liquors from Rectisol Methanol/Water Still Bottoms at the Sasol, South Africa, Lurgi Facility

Parameter	Quantity
Waste volume generated by unit ($gal/10^3$ scf of feed gas)	0.31
Phenol (mg/L)	18
Cyanide and thiocyanate (mg/L)	10.4
Ammonia (mg/L)	42
Sulfide (mg/L)	trace
Chemical oxygen demand (mg/L)	1,606
pH	9.7
Conductivity (μmhos/cm)	1,111

Source: Ref. 9.

Table 4 Characteristics of Coal-Pile Drainage (all units are mg/L except as noted)

	Coal Pile Site A			Coal Pile Site B		
Parameter	High	Low	Mean	High	Low	Mean
Aluminum	450	60	250	90	20	45
Antimony	1.5	0.09	0.6	0.5	0.1	0.25
Arsenic	0.4	0.05	0.15	0.04	0.006	0.02
Barium	0.5	0.1	0.17	0.5	0.1	0.14
Beryllium	0.07	0.03	0.04	0.03	0.01	0.01
Cadmium	0.001	0.001	0.001	0.003	0.001	0.001
Calcium	500	30	350	700	125	350
Chloride	20	0.08	10	700	17	250
Chromium	0.01	0.005	0.006	0.01	0.005	0.006
Copper	1.5	0.3	0.9	0.5	0.07	0.2
Iron	2,000	250	950	600	250	350
Lead	0.01	-	0.01	0.01	-	0.01
Magnesium	500	17	270	150	22	70
Manganese	50	8	30	12	2	5
Mercury	0.0025	0.001	0.001	0.006	0.001	0.002
Nickel	4.5	0.7	2.5	0.5	0.15	0.3
Selenium	0.03	0.001	0.006	0.006	0.001	0.001
Silicon dioxide	400	45	200	45	2	30
Sulfate	9,000	2,000	5,000	6,500	1,800	3,000
Titanium	1	1	1	1	1	1
Zinc	20	2.5	7	6	1	2.5
Acidity as $CaCO_3$	7,000	300	3,500	4,000	700	1,500
TDS	17,000	2,500	8,000	8,000	300	3,500
TSS	2,000	8	400	700	37	290
pH (units)	3.5	2.25	2.7	3.5	2	2.3
Conductivity (μmhos/cm)	6,500	2,500	4,500	7,000	2,500	3,500

Source: Ref. 10.

Table 5 Composition of Ash Produced by Gasification of Various Coals in Slagging, Fixed-Bed Gasifiers

Element	Bituminous Coal, Illinois No. 6	Lignite, North Dakota
Major compounds and ions (%)^a		
Aluminum trioxide	20.5	24
Calcium oxide	2.3	26
Chloride	0.01	0.007
Ferric trioxide	20.5	11
Magnesium oxide	0.6	7
Potassium oxide	1.8	0.6
Silicon dioxide	49.3	25
Sodium oxide	0.3	8
Sulfite	1.5	3.1
Titanium dioxide	1.0	0.6
Trace elements (ppm)		
Antimony	4.2	33
Arsenic	3	74
Barium	950	8,270
Beryllium	12	6
Boron	355	1,680
Bromine	<1	3
Cadmium	<1.6	0.5
Cerium	140	190
Cesium	11	0.9
Chromium	212	140
Cobalt	34	13
Copper	57	27
Fluoride	<10	191
Gallium	26	53
Germanium	7	2
Lead	45	58
Lithium	42	45
Manganese	1,859	760
Mercury	0.05	0.055
Molybdenum	30	12
Nickel	89	25
Phosphorus	87	3,500
Rubidium	162	35
Scandium	29	4
Selenium	<1	0.5
Silver	<0.4	1
Strontium	370	12,900
Tellurium	–	0.3
Tin	–	4
Tungsten	1.5	2
Uranium	17	7
Vanadium	184	150
Yttrium	–	320
Zinc	400	10
Zirconium	170	520

Source: See Ref. 9.

[a] Dry-weight basis.

Table 6 Estimated Solubility of Elements in Ash from Lurgi Gasification of Dunn County, North Dakota, Lignite

Element	% of Element Leachable	Quantity of Element Solubilized[a] (lb/ton of ash)	Estimated Maximum Concentration of Elements in Ash Slurry Supernatant[b] (mg/L)
Aluminum	0.32	0.29	87
Arsenic	0.74	0.001	0.3
Barium	<0.09	<0.003	0.8
Boron	15.9	0.003	41
Bromine	13	0.003	0.9
Calcium	0.49	1.06	321
Cesium	42	0.001	0.4
Chromium	4.4	0.04	11
Cobalt	1.6	0.001	0.3
Copper	7	0.02	6
Fluoride	4.5	0.001	2.6
Gallium	5.4	0.003	1
Germanium	<1.3	<0.001	0.03
Iron	<0.4	<0.4	<100
Lead	0.31	<0.001	0.06
Lithium	11	0.002	0.6
Manganese	<0.25	<0.01	<3
Mercury	4.4	<0.001	<0.0001
Molybdenum	92	0.23	71
Nickel	1.4	0.002	6
Phosphorus	<0.5	<0.01	<3
Potassium	21	1.3	395
Rubidium	59	0.03	10
Scandium	<0.66	<0.001	<0.2
Selenium	<34	<0.001	<0.17
Sodium	37.1	11.7	3500
Strontium	0.71	<0.1	30
Sulfur	84	17.3	5231
Titanium	<2.3	<0.1	<25
Tungsten	24	<0.002	<0.6
Vanadium	5.2	<0.002	4.7
Zinc	37	0.004	1.2

Source: See Ref. 9.

[a] Estimated for Dunn County lignite ash based on data for Mercer County lignite gasified in Lurgi gasifier at Sasol South Africa.

[b] Assuming that ash slurry contains 0.6 kg ash/kg water.

Table 7 Analysis of Spent Methanation Catalyst[a]

Parameter/Constituent	First Stage Bottom	First Stage Top	Second Stage Bottom	Second Stage Top	Typical Fresh Catalyst
Carbon (%)	3.4	4.7	5.3	4.5	3.4
Nickel (%)	52	61	60	61	60
Sulfur (%)	3.7	0.95	0.13	0.16	0.15
Surface area (m^2/g)	36	69	75	79	150
Total pore volume (cm^3/g)	0.16	0.27	0.27	0.27	0.25
Nickel crystallite size (A)	491	97	89	99	65

Source: Ref. 9.

[a] Catalyst type: Harshaw Ni-0104-T-1/4.

problem when gasifying high-sulfur bituminous caking coals. Because of the heavy metal content of the catalysts, these solid wastes are classified as hazardous materials. It is generally accepted, however, that spent catalyst material would be handled offsite, either for regeneration or ultimate disposal.

2.3 SFB PROCESS GAS-LIOUOR PRETREATMENT

As indicated by the general process schematic presented in Fig. 1, the crude synthesis gas leaving the gasifiers is quenched with water and cooled in vertical tube heat exchangers, while waste heat is recovered to power a boiler to produce high-pressure superheated steam for use in the gasification section.

The following sequence of unit operations describes the elements of gas-liquor pretreatment for phenol and ammonia removal that are characteristic of Lurgi coal-gasification processes:

1. Raw, tarry gas-liquor condensates are sent to tar/oil separation where dusty tar, clear tar, tar oil, and dissolved acid gases are removed from the gas liquor.
2. The clarified gas liquor is transferred to the Phenosolvan unit for phenol recovery.
3. Phenols in the gas liquor from the gasification and gas-cooling sections are extracted from the wastewater with isopropyl ether as the solvent.
4. The solvent is distilled from the phenols and returned to the extractor.
5. The dephenolized wastewater is then stripped with steam in the deacidifier column to remove carbon dioxide.
6. A small gas stream containing hydrogen sulfide is sent to sulfur recovery.

7. Acid gas from the top of the column is sent to the boiler, and the bottoms flow to the ammonia stripper.
8. A gaseous ammonia stream is removed overhead from the ammonia stripper column and converted to an aqueous form sent to storage. The bottom stream of gas liquor is sent to further processing.

The Phenosolvan process removes monohydric phenols as well as polyhydric phenols and other organics.[11,12] Extraction recoveries for coal-gasification gas liquors up to 99.5% for monohydric phenols, 60% for polyhydric phenols, and 15% for other organics are reported in the literature.[4] Stamoudis and Luthy[12-14] reported that the acid fraction of extractable and chromatographable organic material found in gas liquors generated from the HYGAS process of the Institute of Gas Technology and the SFB process of GFETC were composed almost exclusively of phenol and single-ring alkylated phenolic compounds. The types of coal employed were bituminous Illinois No. 6 for the HYGAS process, and Indian Head lignite for the SFB process. The acid fraction represented more than 98.5% of the total identified organics on a mass basis for the HYGAS sample, and 99.3% of the total for the SFB process gas-liquor sample. Phenol and cresols constituted the largest fractions of observed organics.

The composition of the crude phenols extracted from coal-gasification quench waters is often assumed[2,4] to be 95% phenols and 5% other organics on a water-free basis, with the phenols being 85% monohydric and 15% polyhydric. It should be noted that the Phenosolvan process is a licensed process, and the licensor (Lurgi) always includes it as an integral part of the Lurgi coal-gasification process.

After removal of phenols, the gas liquor is steam stripped to remove hydrogen sulfide, hydrogen cyanide, carbon dioxide, and ammonia. Stripping at a high pH value favors ammonia removal; hydrogen sulfide and hydrogen cyanide are removed at a low pH. When steam stripping is carried out in two stages with liquor reflux back to the first stage, hydrogen sulfide and carbon dioxide exit overhead from the first stage, while ammonia is recovered from the second stripper. Two-stage steam stripping provides adequate ammonia-hydrogen sulfide separation only if sufficient carbon dioxide (alkalinity) is present in the gas liquor.[1,4]

About 98-99% of the ammonia in gas liquors generated from a Lurgi coal-gasification operation can be removed, when the feed quench water contains 11,000-16,000 mg/L of ammonia.[4] Modern ammonia stills at coke-liquor operations are designed[15] to remove 97% to over 99% of influent ammonia and produce residual ammonia levels of less than 50 mg/L.[15] Conventional oil-refinery, single-stage steam strippers remove 90-97% of the ammonia and 98-99% of the hydrogen sulfide from refinery sour waters.[16]

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3 CONTROL TECHNOLOGY NEEDS

A summary tabulation of major wastewater and solid-waste streams from a Lurgi substitute natural gas (SNG) plant, and the applicable pollution control technologies, are presented in Table 8. This tabulation of key process and waste streams lists the pollutant parameters of major concern that are anticipated with an SFB gasification process. A number of the indicated waste streams such as tars, oils, and phenols are confined within the plant or transported for use in other closed-system locations. The hazards associated with these streams are generally related to occupational exposure or stem from accidents and spills during handling and transportation. The characteristics of the waste residues resulting from the treatment of combined plant effluents are determined by the constituents in the three major internal aqueous waste streams; namely, ash-quench slurry, pretreated gas liquor, and waste solvents. The organic compounds in the combined wastewater originate in the gas liquor, and the major inorganic constituents and trace elements, in the ash-quench slurry.

Ash and slag from the gasifier and boiler ash-quench systems constitute the solid waste stream of largest volume in the Lurgi SNG plant. A facility of 250 MMSCF per stream day, using a coal containing 13% ash and employing onsite coal combustion for steam and power generation, would be expected to generate an estimated 3000-4000 tpd of dry ash and slag. As with the utility industry, the disposal of such a quantity of waste can create a major solid waste management problem. These wastes, which usually are disposed of in landfills, contain constituents that may be mobilized in leachate from a disposal site. Such constituents as the soluble inorganic components of the ash, or organic/inorganic materials that become associated with the ash when process gas liquors are used for ash quenching, are of primary concern. Spent catalysts, although of relatively small quantity, are of special concern due to their content of potentially toxic metals; namely, nickel, molybdenum, and cobalt, as well as coal-derived organic compounds and trace elements.

Figure 3 shows the various treatment process options for wastewater pollution control in Lurgi coal-gasification facilities. This schematic corresponds with the tabulated information presented in Table 9 for appropriate effluent controls for the wastewaters generated from an SFB gasification process. Similar information for treatment process options associated with solid waste management in Lurgi coal-gasification facilities is shown in Fig. 4. The appropriate solid waste control options for Lurgi SNG plants are given in Table 10.

Control technologies for management of wastewaters and solid wastes from a Lurgi SNG plant fall into two major categories: (1) those used on waste streams from Lurgi and other gasification processes and (2) those used on similar waste streams from other industries. Most of the technologies in both categories are considered to be commercial, although large uncertainties exist concerning their treatment performance and cost when applied to waste streams from commercial-scale Lurgi SNG facilities. These uncertainties are due largely to differences in waste stream characteristics as well as to the general paucity of available data on applied technology.

Control technologies in the first category are injection of organic by-products into the gasifier; recovery of sulfur from concentrated acid gases;

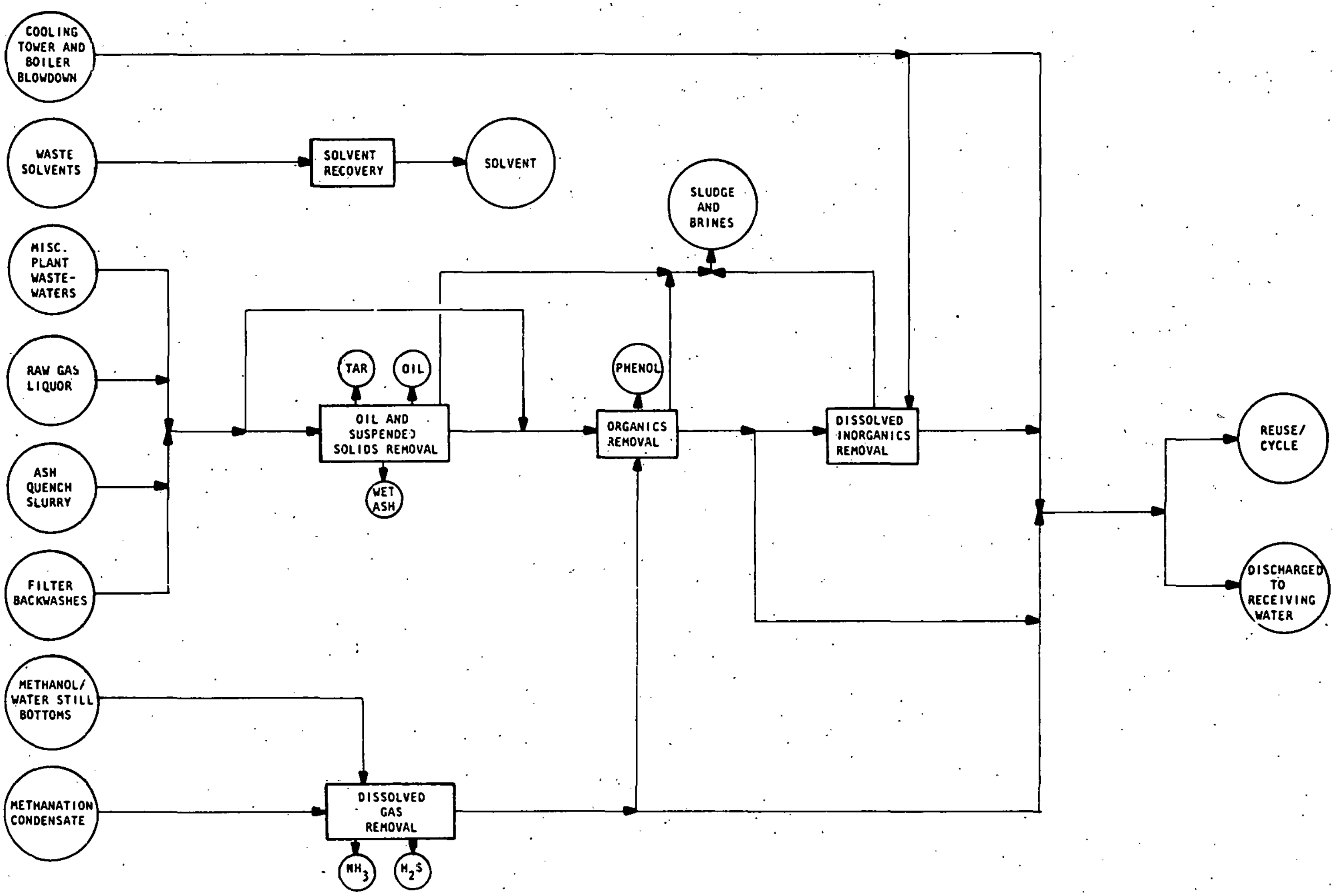

Fig. 3 Treatment Process Option for Wastewater Pollution Control in Lurgi Coal-Gasification Facilities

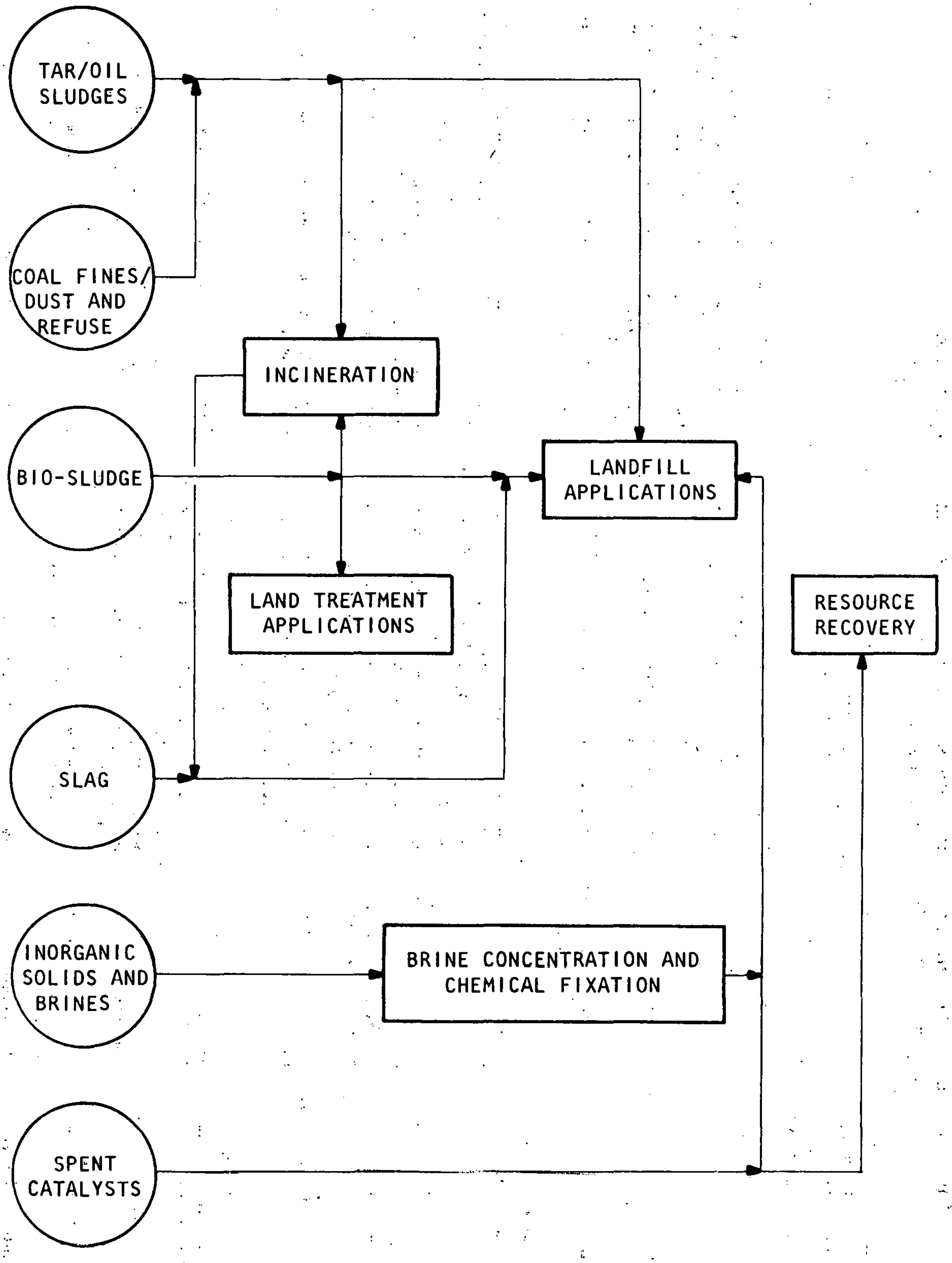

Fig. 4 Treatment Process Options for Solid Waste Management in Lurgi Coal-Gasification Facilities

Table 8 Major Pollutant Constituents in Key Process and Waste Streams from a Slagging, Fixed-Bed Gasification Process

Product, By-Product, Waste Stream	Source	Constituents/Parameters of Major Concern	Applicable Control Technology
Product, by-product			
SNG	Final product	CO, $Ni(CO)_4$	In-plant process control
Tars, oils, and phenols	Raw gas liquor	Aromatic hydrocarbons, polycyclic organics, phenols, trace elements, toxic properties	Prevention of leaks/spills, use of worker protection measures, combustion for steam/power generation, injection into gasifier auxiliary fuel for incineration of biosludges
Naphtha	Rectisol process	Aromatic hydrocarbons, polycyclic organics, toxic properties	Prevention of leaks/spills, use of worker protection measures, combustion for steam/power generation
Ammonia	Gas liquor treatment	Ammonia, trace contaminants	Prevention of leaks/spills, use of worker protection measures
Aqueous waste stream			
Ash quench slurry	Quenching of gasifier ash	Dissolved and suspended solids, alkalinity, trace elements, components of the pretreated gas liquor used for quenching (see below)	Gravity separation, dissolved solids removal, disposal of solids in containment ponds/landfills
Pretreated gas liquor	Ammonia recovery	Sulfide, thiocyanate, ammonia, dissolved organics, BOD, COD, pH	Biooxidation, use as cooling tower or quench water makeup
Waste solvents	Gas cleaning pollution control units	Sulfur compounds, trace elements, dissolved and suspended solids, other constituents (depending on specific source)	Resource recovery, oxidation, dissolved solids removal, use as ash quench
Combined plant effluent	Ash quench and raw water treatment	Dissolved and suspended solids, COD, BOD, alkalinity, trace constituents, toxic properties (bio-assay)	Forced or solar evaporation, discharge to receiving waters
Solid waste streams			
Gasifier slag and ash and boiler ash	Ash and slag quench system	Leachability, compactability, leachate characteristics (including trace elements, organic contents, toxic properties)	Disposal in lined landfills and ponds
Spent catalysts	Shift conversion and methanation	Metallic compounds, accumulated trace elements, organics, leachability, leachate characteristics	Resource recovery, encapsulation, disposal in lined landfills, contract disposal
Tarry/oily sludges and biosludges	By-product storage and wastewater treatment	Aromatic and polycyclic hydrocarbons, trace elements, toxic properties	Energy recovery, disposal in lined landfills
Inorganic solids and sludges	Miscellaneous	Same as for gasifier and boiler ash	Same as for gasifier ash

Sources: See Refs. 1, 2, 4, and 9.

Table 9 Effluent Controls for Wastewaters from a Slagging, Fixed-Bed Gasification Process

Operation/Process	Aqueous Waste Stream	Controls	Comments
Coal pretreatment and handling	Coal pile runoff	Diversion of runoff from adjacent areas, collection of runoff and treatment with other plant wastewaters or alone	---
Coal gasification	Ash and slag quench slurry	Bulk solids settling, fines thickening, storage/settling ponds	Other process wastes such as raw water treatment and air pollution control sludges and brines may be combined with the ash and slag quench slurry for treatment and solids disposal
Gas purification	Raw gas liquor	Use of Lurgi tar/oil separator^a, Phenosolvan process, and ammonia stripping for tar/oil, phenols, and ammonia recovery, respectively	Lurgi tar/oil separator and the Phenosolvan process are Lurgi-licensed and are featured in all designs for proposed commercial facilities
	Methanol/water still bottoms from rectisol process	Addition to dephenolized gas liquor prior to ammonia recovery	---
Gas upgrading	Methanation and dehydration condensates	Depressurization for dissolved gases removal and subsequent use as boiler feedwater	---
Auxiliary processes	Pretreated gas liquor	Use as cooling tower makeup with biological treatment and dissolved solids removal	The need for and effectiveness of biological treatment of pretreated gas liquor was established by this study
	Gas liquor treatment filter backwashes	Addition to ash quench slurry	---
	Waste solvents	Recovery of solvents from gas cleaning processes, addition to ash quench slurry, disposal by deepwell injection	Deepwell injection may not be practical at all sites
	Boiler blowdown	Use as cooling tower makeup	---
	Cooling tower blowdown	Use as ash quench makeup water, discharge to receiving body	---
	Miscellaneous plant wastewaters	Use of treated water and storm water runoff as cooling tower makeup, use of packaged units for the treatment of sanitary wastewaters	---
	Combined plant effluents	Solar or forced evaporation (zero discharge), partial water reuse, total discharge to the receiving body	Depending on the hydrogeological conditions, waste storage ponds may require lining; use of solar evaporation is dependent on local/regional climate

Sources: See Refs. 1 and 9.

[a] Dissolved gas flotation (Lurgi licensed).

Table 10 Solid Waste Control Options for a Slagging, Fixed-Bed Gasification Process

Operation/Process	Solid Waste Stream	Controls	Comments
Coal pretreatment and handling	Coal refuse, coal fines, dust	Use of coal fines as fuel, disposal in settling ponds and landfills	These wastes are not unique to Lurgi gasification plants and the controls are acceptable for other industries
Coal gasification	Wet ash, slag	Disposal in landfills	Quantity of slag accounts for more than 90% of the solid wastes generated at a Lurgi gasification plant; choice and design of disposal system depend on ash content of coal and plant site characteristics
Gas purification	Spent catalyst	Fixation/encapsulation and disposal in landfills, processing for metal recovery, contract disposal	Technical and economic feasibility of resource recovery have not been established
Gas upgrading	Spent shift conversion and methanation catalysts	Processing for material recovery, use of spent methanation catalysts in gas purification, fixation/encapsulation and disposal in landfills, contract disposal	Data on technology for, and economics of, resource recovery have not been established
Auxiliary processes	Tarry/oily sludges	Disposal in landfills with or without fixation/encapsulation, incineration, return to gasifier, landfarming	Because of lack of data on waste characteristics, optimum control(s) cannot be established
	Biosludges	Disposal in landfarms, soil application, incineration	—
	Inorganic solids and brines	Addition to slag/ash quench slurry, direct disposal through evaporation and concentration	Because of lack of data on waste characteristics, optimum control(s) cannot be established
	Fly ash from steam/power generation	Disposal in landfills	

Source: See Ref. 9.

gravity separation of ash-quench slurry; and disposal of gasifier and boiler ash in landfills. Technologies in the second category are combustion of tars for steam/power production in the coke industry; recovery of sulfur from coke-oven gases; treatment of sulfur recovery tail gases in refineries; biological oxidation of petroleum-refinery and coke-plant wastewaters; and disposal of utility ash and sludges in landfills.[15-18]

3.1 TAR AND OIL RECOVERY

The standard approach to treating raw gas liquor in Lurgi SNG facilities is tar/oil/water separation followed by phenol recovery. Separation treatment usually consists of dissolved gas flotation and gravity settling. Tar/oil separators employed in Lurgi SNG facilities operate on the flotation principle in that the reduction in pressure results in the release of dissolved gases that float oil to the surface for recovery. These separators achieve a high removal efficiency, usually up to 99% removal of suspended tar and oil, and are cost-effective because they take advantage of the inherent dissolved gases present in the raw gas liquor. Alternatives to the Lurgi tar/oil/water separation process -- such as separation using API separators, gravity separation enhanced by chemical coagulation and flocculation, and filtration -- do not offer similar design advantages. Nevertheless, the proposed CONOCO design for treatment of raw gas liquors from the SFB coal-gasification process incorporates a relevant filtration unit operation. It would act as a coalescer applied for the removal of residual oil-water emulsions that are not separable under prolonged detention in gravity separators. The filtration unit would precede the Phenosolvan unit.

3.2 PHENOL EXTRACTION AND AMMONIA STRIPPING

The characteristic quality of the gas-liquor wastewater, after implementation of commercial tar and oil pretreatment technologies, was simulated in the laboratory (see appendix) using contaminated quench waters from the GFETC-SFB coal-conversion-process pilot plant. See Table 11 for summary data on these experiments. As these data indicate, the pretreated gas liquor from ammonia recovery would still contain considerable organic material; thus, from this standpoint, it is the most important waste stream in a Lurgi SNG plant in terms of treatment requirements. It should be noted that the batch-scale solvent extraction experiments (appendix) were conducted using methyl isobutyl ketone (MIBK) as the solvent for phenol removal, whereas the commercial Phenosolvan process uses diisopropyl ether. The two solvents should be equivalent in their overall capacity to remove monohydric phenols, whereas the MIBK solvent should be more efficient in the removal of the polyhydric forms. It is generally believed[2,9] that gas liquors generated by the SFB coal-gasification process will have the largest fraction of their component phenols in the monohydric form, and, as a consequence, the residual phenols remaining after solvent extraction with diisopropyl ether should be only slightly higher than the levels obtained by MIBK extraction.

3.3 SOLUBLE ORGANICS REDUCTION

Pretreated gas liquors can be further treated by any of a number of conventional wastewater treatment processes for soluble organics removal.

Table 11 Characteristics during Pretreatment of Gas-Liquor Wastewaters from a Slagging, Fixed-Bed Coal-Gasification Process Using Lignite Feedstock[a] (all units are mg/L except as noted)

Characteristics	Raw Wastewater Run RA-52	Solvent-Extracted Wastewater (MIBK)	Ammonia-Stripped Wastewater
Total organic carbon[b]	11,100	1,950	1,380
Chemical oxygen demand[b]	32,000	3,900	2,980
Biochemical oxygen demand[b]	26,000	2,900	1,820
Phenolics	6,500	5	3
Freon extractable oils	410	-	10
Organic nitrogen	115	51	33
Ammonia-nitrogen	6,300	4,400	30
Nitrate-nitrogen	<5	<5	<5
Cyanides amenable to chlorination	0.1	-	-
Total cyanide	1.8	1.5	1.5
Thiocyanate	120	110	105
Sulfides	100	75	<10
Total sulfur (as S)	380	156	-
Calcium (as $CaCO_3$)	-	10	740
Alkalinity (as $CaCO_3$)	20,700	16,300	850
pH (units)	8.6	8.6	8.8
Conductivity (μmho/cm)	20,000	18,600	1,490
Color (Pt-Co units)	≈500	≈500	≈700

[a] Data obtained from Dr. Richard G. Luthy, Department of Civil Engineering, Carnegie-Mellon University.

[b] Analysis of solvent-extracted samples for TOC, COD, and BOD were performed after gentle heating to expell residual MIBK.

These processes include biological oxidation, chemical oxidation, and activated carbon adsorption. In biological oxidation, the dissolved and/or colloidal organics in the wastewater are converted to the inorganic end-products of metabolism and microbial cells by the action of microorganisms. The residual sludge from the oxidation process is subsequently removed after gravity separation. Although biological treatment can be conducted under anaerobic conditions, aerobic treatment is preferred for most applications because of the higher efficiency and lower costs. Biological wastewater treatment has been employed successfully in the petroleum and petrochemical industries.[16] Moreover, both dephenolated and nondephenolated gas liquors from Lurgi gasification processes have been treated biologically, and data are available on process performance.[19,20] Biological treatment can result in up to 90% removal of the biologically oxidizable compounds in the raw wastewater provided toxic inhibitors are not present in significant amounts. Few data are available in the specific area of biological kinetics of gas liquor treatment, although recent research has emphasized the area of phenol removal and the influences of thiocyanate and cyanide on microbial removal processes.[21] Gas liquors from Lurgi coal gasification processes are usually high in thiocyanate, between 70 and 150 mg/L, but relatively low in cyanide. Generally, the thiocyanate is considered a relatively nontoxic species, and it is easily broken down during biological treatment. A study[20] of the biological treatment of cyanide-spiked gas liquors showed that influent cyanide concentrations of 100 mg/L to the bioreactor did not present a treatment problem. Nevertheless, research indicates[22] that wastewater oxidation in the presence of polysulfide and cyanide should readily form thiocyanate, thus transforming cyanide to a highly biodegradable species.

Several factors affect the applicability and performance of biological oxidation. These factors relate to wastewater constituent biodegradability, toxicity, pH, and nutrient content. Lurgi-process gas liquors tend to be highly aromatic. While certain aromatic compounds such as simple phenols are readily degradable at relatively dilute levels, the more complex and substituted phenols, polycyclic hydrocarbons, and heterocyclic organics are generally less readily degradable, or essentially nondegradable by biological processes. The biodegradability of the organic constituents in coal-gasification wastewaters has been studied extensively[12,13,23] as part of an ongoing research effort to assess the efficiency of activated-sludge treatment when applied to these wastewaters. Results indicate that activated-sludge treatment of gas liquors will remove most of the extractable and chromatographable organic constituents. The experimental data show that phenols, alkylated phenols, anilines, and most alkylated pyridines are removed effectively by activated-sludge treatment. Removals of aromatic hydrocarbons also were fairly satisfactory except for certain alkylated benzenes, polycyclic aromatic hydrocarbons, and cycloalkanes and cycloalkenes, especially at low influent concentrations.

Biological processes are usually most efficient when the pH of the wastewater is in the range of pH 6-8. The pH of the wastewater also affects the relative toxicity of certain wastewater constituents. For instance, toxicity of sulfide to microorganisms increases with decreasing pH, whereas the level of toxicity of free ammonia in the bioreactor increases with increasing pH. A BOD_5:N:P ratio of approximately 100:5:1 is generally necessary for the biological treatment of most industrial wastewaters. When wastewaters are deficient in these essential nutrients, such nutrient concentrations must be adjusted in the raw wastewater before biological treatment. Lurgi-process gas liquor has a sufficient amount of nitrogen, but phosphorus must be added to establish an adequate N:P ratio.

Cooling towers for biological treatment of selected waste streams have been employed successfully in refinery wastewater treatment. Cooling towers provide ideal temperatures and surfaces for biological activity. The oxygen required by microorganisms for biooxidation of organics is provided by the extensive aeration that accompanies the cooling process. In refinery applications, phenolic wastewaters have been used as cooling tower makeup, and more than 98% removal of phenols has been reported.[9] In a demonstration program at the SASOL Lurgi facility, the ammonia stripper bottoms were used as cooling tower makeup. The general level of fouling and corrosion of cooling surfaces was documented, as well as the degree of wastewater foaming during operation. These data provided a basis for the design of a cooling/biooxidation tower system[9] for the proposed El Paso Burnham plant in New Mexico.

In addition to biological treatment, two other types of processes for organic constituent removal are potentially applicable to the treatment of Lurgi gas liquors. They are activated-carbon adsorption and chemical oxidation.

Both granular and powdered activated carbon have been used to treat industrial wastewaters. As a physical treatment process, carbon adsorption is unaffected by the presence of toxic constituents in the wastewater or by fluctuations in wastewater characteristics. Granular activated carbon (GAC) is used in fixed or moving columnar beds with either upward or downward wastewater flow. Powdered activated carbon (PAC) is generally mixed with the wastewater and is subsequently removed by settling or filtration. The use of activated-carbon adsorption for the treatment of soluble organic wastewaters generally would be limited to: (1) the removal of residual organics from biological treatment effluents; (2) the treatment of wastewaters containing high levels of refractory organics or toxic materials; and (3) the recovery of by-products (phenols) from the wastewater. Except when used for by-product recovery, the spent carbon is usually regenerated by thermal treatment and used again. Adsorption by activated carbon can cause a major reduction in wastewater color and complexed metal ions.

A recent development in carbon-adsorption technology applied to the treatment of industrial wastewaters is the addition of PAC to an activated sludge (AS) process. The AS/PAC process may have wider application for the treatment of soluble organic wastewaters, since it has been shown to improve the performance of biological treatment systems with a relatively minor addition of equipment to an existing biological treatment plant. The primary operating parameter that defines the performance of an AS/PAC process is the equilibrium carbon concentration in the aeration basin. This equilibrium carbon concentration is a function of the carbon dosage to the wastewater, the amount of carbon leaving in the final effluent, the quantity of carbon/biological sludge wasted, and the hydraulic retention time. It was estimated[24] that a PAC variation of the AS process can achieve an additional 54% total organic carbon (TOC) removal over conventional, activated-sludge treatment of petroleum refinery wastewaters.

Both GAC and PAC technologies have been demonstrated for the treatment of wastewaters from the petroleum refining industry. The AS/PAC process, however, has some apparent advantages over tertiary GAC adsorption. For example, it permits a more effective use of carbon, dampens organic surges to the bioreactor, prevents biological upset by removal of biotoxic substances, and allows for reduction in excess sludge production.[25,26] In general, the performance of either carbon-adsorption technology is highly dependent on the type of carbon used.

Initial investigations of the application of the AS/PAC process for the treatment of Lurgi-process nondephenolated gas liquors indicated a definite trend in reduction of BOD, COD, color intensity, ammonia-nitrogen, and organic nitrogen of the treated effluents as a function of increasing dosages of PAC (personal communication V. C. Stamoudis, ANL, and R. G. Luthy, Carnegie-Mellon University, April 1980). This study, which is described in the appendix, was conducted using ammonia-stripped quench waters from GFETC's SFB pilot-plant gasifier diluted to about 33% strength, and provides the first experimental application of the AS/PAC process to the treatment of Lurgi-type, slagging-ash gas liquors. The data for GC and GC/MS analyses of the organics present in these treated wastewaters indicated that the number and concentrations of the refractory organics were not significantly altered whether or not PAC was added to the AS reactors. As seen below, this lack of improved removal of organics refractory to the AS process is attributable to the lack of pretreatment of the raw quench water by solvent extraction.

Table 12 presents average performance data for activated sludge and AS/PAC treatments of undiluted, dephenolated (MIBK extracted) gas liquors generated by GFETC's SFB process. These data from the appendix correspond to the operation of biological treatment systems whose physical characteristics are given in Table 13. Hence, it is apparent that the AS/PAC process performed better than the conventional AS process when gas liquors were solvent-extracted prior to the treatment. In general, effluents from the AS/PAC process were lower in TOC, COD, BOD, phenolics, organic nitrogen ammonia-nitrogen, thiocyanate, and color intensity.

Data in the appendix (Tables A.8-A.10) indicate that solvent extraction for phenol recovery removes the major portion of extractable chromatographable organics. Detailed GC and GC/MS analyses also were done for raw, MIBK-extracted, AS-treated, and AS/PAC-treated extracts of the samples. The results (appendix Tables A.8-A.10) show an excellent reduction of extractable and chromatographable organics after MIBK extraction, and also a definite improvement using AS/PAC, as opposed to using AS alone.

The above data indicate that solvent extraction for phenol recovery removes the major portion of extractable/chromatographable organics. The data also suggest that pretreatment by solvent extraction selectively removes a larger fraction of the biodegradable organics, and that the residual organics in the pretreated gas liquor are less readily biodegradable than when phenolics composed the larger fraction of wastewater organics. As a consequence, the AS/PAC process offers an overall advantage for the treatment of SFB Lurgi-process gas liquors because it provides a lower residual organics level (i.e., COD, BOD, TOC) in the effluent than AS treatment alone.

The final treatment technology considered for removal of soluble organics is chemical oxidation. Oxidation by ozone and chlorine has been used by industry to reduce the concentration of cyanide, sulfide, and thiocyanate in wastewater. Under proper conditions, ozonation may cause the destruction of organics refractory to the biological treatment system and may assist in removal of higher-molecular-weight organics by carbon adsorption. The potential for chemical treatment of SFB process gas liquors probably would be limited to wastewater polishing after biological oxidation.

3.4 REMOVAL OF DISSOLVED SOLIDS AND CONCENTRATION OF WASTE BRINES

Biological-oxidation and physicochemical treatment technologies reduce the level of organic-constituent pollution of the SFB process wastewaters. Treated effluents from these processes, however, contain nonbiodegradable organics, dissolved inorganics, residual suspended solids, and trace levels of biodegradable organics. The technologies required to achieve a greater degree

Table 12 Average Performance Data for AS and AS/PAC Treatment of Solvent-Extracted Gas Liquors from a Slagging, Fixed-Bed Coal-Gasification Process Using a Lignite Feedstock[a] (all units are mg/L except as noted)

Wastewater Characteristics	Influent	AS/PAC Effluent	Conventional Activated Sludge Effluent
Total organic carbon	1,380	385	580
Chemical oxygen demand	2,980	640	1,340
Biochemical oxygen demand	1,820	30	32
Phenolics	3	<0.02	≈0.1
Organic nitrogen	33	4	10
Ammonia-nitrogen	30	20	84
Nitrate-nitrogen	<5	100	40
Cyanides amenable to chlorination	≈0.1	<0.1	≈0.1
Total cyanide	1.5	1.3	1.4
Thiocyanide	105	<0.5	4
Sulfate	-	655	1,020
Alkalinity, as $CaCO_3$	850	72	175
Freon extractable	10	<5	<5
Conductivity (μmho/cm)	1,490	2,200	2,230
Color (Pt-Co units)	700	<20	500

[a] Data from appendix.

of pollutant removal to meet operation and discharge standards need the implementation of processes for the removal of dissolved solids. The degree to which water reuse and recycling is incorporated into the design of a commercial SNG facility would determine the extent to which tertiary wastewater treatment technology should be applied to meet specific water quality demands.

The design of coal-gasification facilities that incorporate zero discharge requires technologies that allow maximum reuse and recycling of process wastewaters. Examples of multiple water usage in an SFB process are: (1) the use of boiler blowdown and biologically-treated process wastewaters as cooling-water makeup; (2) the use of methanation condensates for boiler feedwater; (3) the recycling of tar/oil-separated gas liquors to the quench tower; and (4) the treatment of waste brines by distillation and use of the distillate as boiler feedwater. That portion of the wastewater not reused and recycled would be disposed of with waste solids or lost to evaporation in the cooling tower.

Specific treatment technologies for removing dissolved solids from secondary effluents are reverse osmosis, electrodialysis, and forced evaporation (thermal distillation). The application of membrane processes for the removal of dissolved solids is most feasible for the treatment of feedwaters containing 2,000-10,000 mg/L total dissolved solids (TDS). The TDS concentration of SFB Lurgi-process gas liquors lies within this range. Some research[27] has been initiated to study the application of reverse osmosis for

Table 13 System Operating Data for AS and for AS/PAC Treatment of Solvent-Extracted Gas Liquors from a Slagging, Fixed-Bed Coal-Gasification Process Using a Lignite Feedstock[a].

Parameter	AS/PAC	Conventional AS
Mean sludge residence time (days)	20	30
Hydraulic residence time (days)	11.7	12.6
PAC concentration in reactor (mg/L)	5,000	0
MLSS (mg/L)	6,470	1,620
MLVSS (mg/L)	6,110	1,310
Chemical oxygen demand removal rate (mg COD removed/mg MLVSS-day)	-	0.11
5-day biochemical oxygen demand removal rate (mg BOD_5 removed/mg MLVSS-day)	-	0.12
Sludge volume index (mL/g MLSS)	10	65
pH (units)	7.3	7.6
Dissolved oxygen concentration (mg/L)	>4.0	>4.0
Oxygen utilization rate (mg O_2/mg MLVSS-day)	0.02	0.07

[a] Data from appendix.

the treatment of quench waters that have been treated by filtration, phenol extraction, and ammonia stripping. Results indicate a potential for wastewater reuse and recycling within the gasifier although sustained reverse-osmosis flux rates may not be economically acceptable.

3.4.1 Reverse Osmosis

Reverse osmosis is a desalination process that uses a semipermeable membrane and pressure differential to separate relatively pure water from solutions containing salts, dissolved organics, and colloids. Wastewater is driven through the membrane by pressure, leaving behind a concentrated solution of brine. To achieve a separation, the driving pressure of the feedwater must be greater than the osmotic pressure of the concentrate.

Operating pressures for reverse-osmosis membranes and membrane supports are restricted by the type of design. Spiral-wound and hollow-fiber membranes cannot operate at pressures greater than 600-800 psi, whereas tubular membranes are limited to about 1000 psi.[4] Membrane life is limited by the presence of chlorine and other oxidizing agents in the feed water. Reverse-osmosis membranes are classified as either neutral or ion-exchange. Neutral membranes are considered to have the most favorable properties for the removal of trace levels of organics. Two such membrane materials are the cellulose acetate and aromatic polyamide membranes.[28,29]

The economic feasibility of using reverse osmosis for removing dissolved solids depends on the life of the membrane. Rapid deterioration and fouling of the membrane often render the process impractical. Membrane deterioration is the irreparable damage stemming from the hydrolysis of the membrane. The damage can be controlled by adjusting the pH of the feedwater to the range of pH 5 to pH 9 for both cellulose acetate and aromatic polyamide membranes.[30]

Membrane fouling results from the precipitation and deposition of organic and inorganic substances on the membrane surface. Such fouling drastically reduces membrane permeate flux. The organic precipitation and subsequent formation of a slimy layer on the membrane surface is attributed to the presence of biological growth, whereas the inorganic precipitation is caused by calcium carbonate, ferric hydroxide, and other insoluble forms. The fouling of a reverse-osmosis membrane can be controlled by the pretreatment of processed water, addition of antiscaling agents, and periodic cleaning of the membrane surface.

3.4.2 Electrodialysis

Electrodialysis uses a DC electric field and semipermeable membrane to remove ions from wastewater. An electrodialysis desalination process is a series of parallel membranes separated by channels. The membrane types are alternated with respect to each other between cation-permeable membranes and anion-permeable membranes. The electric field causes the ions to migrate toward their oppositely charged electrodes. The ions pass through the adjacent membrane into the next channel where a concentrated brine solution is formed. Desalted product water is produced in every other channel. This series of channels and membranes is referred to as a stack, and there may be as many as 700 channels between a single pair of electrodes.[4]

Practically, electrodialysis is capable of removing only charged ionic particles; therefore, its use should not affect the removal of uncharged dissolved particles and suspended matter. The residual organic solids present in the secondary treated effluents from the SFB process most probably would be quasi-hydrophobic, negatively charged colloids. These colloids would not necessarily be well-defined hydrophobic sols, but they should lend themselves to separation by electrodialysis treatment.

The membranes used in the process are ion-exchange resins made in sheet form, and membrane fouling, particularly with the anion-permeable membrane, is a problem. It should be noted that the electrodialysis process has the advantage of providing semi-permeable membranes with ion exchange properties. One method by which the membranes are manufactured consists of polymerizing styrene and divinylbenzene into a sheet that is then chemically treated to enhance the ion-exchange properties.[31] Exchange resins selective for nitrate removal are available, and special macroreticular polymeric adsorbents such as Amberlite XAD-8 synthetic resin, which have the ability to sorb organics without any substantial inorganic exchange capacity, are promising developments for the treatment of SFB process wastewaters.[9]

3.4.3 Forced Evaporation

Evaporation is appropriate technology for the separation of water and nonvolatile solids. Generally, evaporation finds application in the treatment of boiler-feed water and cooling-tower blowdown.[32] Available forced-evaporation technology includes multistage flash evaporation, multiple-effect evaporation, vapor-compression evaporation, and oil fluidized evaporation.

In a multistage flash evaporator, pressurized water is heated to just below the boiling point. The hot water is then depressured in stages, resulting in vaporization of the water. The product water vapor is condensed in the feed preheat exchanger. Multiple-effect evaporation is a fired evaporation system in which the heat required for evaporation is reused. The vaporized water is condensed against evaporating water that is at a lower pressure. This process continues through multiple effects, causing additional evaporation at each stage. Fouling of heat exchanger surfaces is a major problem with the process but is uncommon in multistage flash evaporators that do not use heat exchanger surfaces in boiling service.

Vapor compression evaporates and recovers water by the use of mechanical energy. The heat required for evaporation is provided by compressing steam formed in the evaporator. The temperature and pressure of the steam formed in the evaporator are increased during compression. This steam is then condensed against water in the evaporator to produce more steam. Vapor-compression distillation, in comparison with other distillation processes, has a relatively low energy requirement and does not require ancillary cooling waters. An important limitation of this evaporator is the fouling of heat exchanger surfaces.

In the process of evaporation, boiling brines cause corrosion, and scale-forming minerals tend to precipitate and coat the evaporator heat-transfer surfaces. As a result, the conventional evaporator design cannot concentrate these supersaturated streams without scaling or fouling. Special evaporators, known as brine concentrators, operate at supersaturated concentrations without scaling. This type of operation eliminates system fouling and allows continuous recovery of pure product water. Brine concentrator corrosion is avoided through the use of titanium and other corrosion-resistant materials. Usually, brine concentrators are vertical, tube-in-shell evaporators designed to concentrate process brines into slurries, and to recover up to 90% of the water from highly saturated brine streams. As a consequence, they greatly reduce the amount of space required for solid waste disposal.

An oil fluidized evaporator is a special type of brine concentration process in which oil of the correct volatility, viscosity, and surface tension is added to the dilute waste brine slurry and the mixture is fed to a multiple-effect evaporator. The mixture passes through the evaporator, leaving the solids suspended in the residual oil as a fluid slurry. The oil is first separated from the dry solids and then recycled back to the process. The dissolved-solids residual emerges in a mixture with a solids content of between 60 and 80% by weight.

The oil maintains fluidity throughout the system, improves heat transfer in the evaporator, and prevents scaling and fouling as the salts become dry. Make-up oil for the process may be available as one of the products or by-products of the SFB process. Choice is governed by such oil properties as specific gravity, viscosity, and vapor pressure. There is apparently no theoretical reason against using recovered phenols as the evaporator oil, provided that caustic is added to the brine to suppress the volatility of phenols.[4] The by-product oil of whatever type, withheld from sale, would be used only for makeup. Most of the oil used by this evaporation process would be returned to the brine concentrator after solids separation for reuse during the evaporation cycle. If viscous impurities contaminate the recycled oil, it can be purged from the system and injected into an incinerator.

Generally, forced-evaporation processes are extremely energy-intensive. Vapor-compression evaporation is the most efficient of the fired evaporation systems because it can produce between 25 and 30 lb of distillate per 1000 Btu of heat input. Multiple-effect evaporators are capable of producing 1 lb per 1000 Btu per effect, whereas multistage flash evaporation can generate only 0.3 lb of distillate per 1000 Btu per stage. Multistage flash systems require larger recirculation rates in order to maintain an efficient use of energy. On the other hand, the multistage flash evaporator will operate more efficiently than the multiple-effect system for high-flow, low-TDS applications, mainly because of reduced chemical precipitation problems during evaporation.

3.5 CLEANUP OF MISCELLANEOUS PLANT WASTEWATERS AND DISPOSAL OF BRINES

Several miscellaneous waste streams that require pollution control are generated in an SFB-process coal-gasification facility. The most important of these streams are (1) storm-generated runoff from within the plant battery limits, (2) coal-pile drainage, (3) sanitary wastes, (4) wastes generated by ion-exchange and demineralization units used for boiler water treatment, and (5) wastewaters accumulated in the various oily-water sewers throughout the plant. Runoff of plant-battery-limits as a rule would be collected by a storm sewer and stored for treatment, entailing the removal of separable oils and other suspended materials prior to reuse or discharge. Coal-pile drainage would require neutralization and chemical treatment for heavy-metal reduction before reuse or discharge.

Gravity separation to remove separable oil and suspended solids is usually the first step in the treatment of wastewaters. Nearly all oily wastewaters have some amount of free, dispersed, and emulsified oil present. Rainfall runoff, which has not been pumped, typically may be contaminated with oils in which 8-10% of the droplets are below 20 microns in size. Contaminated wastewaters will typically have 10-15% or more of the oil in a mechanically emulsified state. Generally, oil droplets of 20 microns and smaller cannot be separated practically with a gravity separator because the net buoyancy force is overcome by the drag force of the continuous water phase. These droplets, traditionally classified as emulsified oils, are so small that random water movement maintains their suspension. Impurities in both the oil and water phases also may affect the separability.

The principal objective of gravity-differential-type oil-water separators, such as the American Petroleum Institute (API) separator and the parallel- or tilted-plate separator, is to establish conditions in which suspended solids are settled coincident with the separation of oil in the influent. The current design principles of the API separator are based on extensive studies of the effect of inlet and outlet arrangements on oil-separator efficiency, and the impact of appurtenances on the hydraulic characteristics in the separation chamber. The principal factors that affect design of oil-water separators are: (1) the specific gravity of the oil; (2) the specific gravity of the wastewater; (3) the wastewater temperature; (4) the percentage of emulsified oils, and (5) the concentration of suspended solids. The specific gravities of both oil and water, which are a function of temperature, determine the rate of oil separation. The aforementioned factors set the allowable hydraulic overflow rate for the particular oil-water separator design.

Flotation oil-water separation is one of the most common oil-refinery wastewater-pretreatment techniques, and its application to the pretreatment of SFB Lurgi-process raw-gas liquors was discussed in a previous section of this report. It is a unit operation specifically designed for the separation of both liquids and solids from wastewater, and it generally includes a chemical coagulation-flocculation step.

The flotation process relies on coupling of gas bubbles with the dispersed-oil phase, resulting in a reduction in the specific gravity of the oil and a subsequent increase in buoyancy. Flotation is strongly influenced by the surface characteristics of the dispersed-oil phase and, to a lesser degree, by the oil-droplet size.

Flotation methods are divided into dispersed-gas and dissolved-gas processes. Dispersed or entrained gas flotation utilizes bubbles generated by one of the following techniques: (1) mechanical shear, (2) gas diffusion through a porous medium, or (3) homogenization of the gas into the wastewater. Dissolved-gas flotation generates gas bubbles by the precipitation of gas from a supersaturated solution. The processes differ in the size of the gas bubbles produced. In dissolved-gas flotation, bubbles average 80 microns in diameter, but are usually an order of magnitude larger in dispersed-gas flotation. The gases commonly used for flotation of dispersed oils are air and nitrogen. Ferrous ion in the wastewater is oxidized by air and may precipitate as ferric hydroxide. The ferric hydroxide, however, may act as a coagulating agent and improve overall oil-removal efficiency.

Dissolved-air flotation (DAF) is the process commonly used in refinery and petrochemical installations to enhance oil and suspended-solids removal. It is typically preceded by a gravity oil-separator that removes gross quantities of free oil and oily suspended solids. The process involves the pressurization of wastewater in the presence of air, thereby creating a supersaturated solution that, when passed into a flotation chamber at atmospheric pressure, precipitates the air from solution in the form of small bubbles. These bubbles unite with the dispersed-oil phase to form a collection of distinct oil droplets and to carry it to the surface. The float is removed to disposal or recovery by mechanical flight scrapers, and the underflow represents the clarified effluent.

The use of chemical agents has historically been an integral part of the flotation process. These chemicals modify the surface properties of one or more phases. For instance, frothers serve to lower the interfacial tension between the air bubble and the wastewater while collectors either reduce the interfacial tension between the dispersed-oil phase and the wastewater or increase the interfacial tension between the air bubbles and the oil phase.

In either case, collectors tend to increase bubble-droplet adhesion. Coagulating chemicals such as aluminum and iron salts often are used to enhance the bubble-capture mechanisms of flotation. These coagulants function to improve the flocculant nature of the dispersed oil phase and enhance the capture of small oil droplets.

Sanitary wastes at coal-gasification facilities could be treated in combination with process wastewaters by biological oxidation, or handled separately in package treatment units as is common practice in many industries. The joint treatment of the sanitary and process wastes is often desirable since the sanitary waste provides some of the nutrients (e.g., phosphorus) required for effective biological treatment.

Waste brines generated from the desalination of demineralization wastes, cooling-tower blowdowns, and treated process wastewaters often are disposed of in evaporation/retention ponds. These ponds are natural or man-made earthen reservoirs into which the waste brines are discharged for onsite retention. The ponds are lined with impermeable materials (plastic, clay, asphalt, etc.) to prevent infiltration and contamination. Although impermeable liners have been used in numerous industrial waste ponds, the ability of a liner to retain its integrity over long periods of time has not been established. The retention of the waste in the pond provides for treatment/disposal by solar evaporation as well as solids deposition, biological decomposition of organics, and the loss of volatile constituents to the atmosphere. Because of solids accumulation, provisions must be made for periodic removal and ultimate disposal of solids from the evaporation pond and/or the ultimate decommissioning of the pond.

Where climatic conditions do not allow for sufficient evaporation, the use of ponds alone is not feasible for ultimate disposal of waste brines. Alternative designs incorporate the use of deep-well injection and chemical fixation/encapsulation for handling waste brines from forced evaporation facilities. Subsurface waste disposal has been used for a number of years in the geothermal and oil fields for reinjection of fluids, and by a number of industries for the disposal of a range of concentrated wastes. Deep-well injection can be practiced only in areas where suitable underground geological formations exist, where there is little possibility for contamination of usable groundwaters, and where injection is not restricted by state or federal law.

A suitable geological formation is one that is sufficiently large in capacity to accommodate the generated waste brines at a reasonable injection pressure. The formation should be located below the lowest groundwater zone and be isolated above and below by impervious layers. The formations should not contain extensive faults or fractures, in order to assure that the injected waters remain within the disposal strata. The wastes to be injected must be physically and chemically compatible with the formation. The primary concern with injecting waste brines into sub-surface disposal stratum is the possible formation of precipitates and the subsequent plugging of pores that would raise reservoir pressures substantially above the allowable operational pressures for injection.

A reservoir considered for injection must have sufficient permeability to allow the fluid to penetrate into the void spaces without the need for unusually high injection pressures. Compacted clays, commonly described as impermeable or impervious, usually have low coefficients of permeability. Waste brines can be injected into clays or shales only at an extremely slow rate; thus these formations are not suitable for waste disposal. Sands, gravels, and vugular or fractured limestones usually have high permeabilities and are given primary consideration as disposal reservoirs.[33]

Well construction should provide adequate protection against groundwater contamination, and should include provisions for continuous monitoring of well performance and movement of the waste underground. In the event of a system failure due to a defective well casing, the casing would have to be replaced or the well sealed (packed and grouted) and abandoned. Provisions must be made for continuous sampling of subsurface potable water courses by the use of monitoring wells.

Chemical fixation, also referred to as cementation, has been used for solidifying highly hazardous industrial wastes prior to disposal by landfilling. The objective of chemical fixation is to reduce the level of solubility and chemical reactivity of the waste, and hence reduce the potential for the contamination of ground and surface waters via leachate formation and storm-water runoff. Both organic and inorganic materials have been used as fixing agents. These fixing agents include asphalt, epoxies, tars, lime-based cements, and proprietary formulations. Chemically fixed brines can be encapsulated in plastic or concrete prior to disposal.

3.6 SOLID WASTE MANAGEMENT

There are essentially five treatment process options for solid waste management in SFB process coal-gasification facilities: (1) incineration, (2) land treatment, (3) landfilling, (4) brine concentration and chemical fixation or deep-well disposal, and (5) resource recovery. These options, as they apply to specific solid wastes and sludges generated during coal gasification, are depicted in Fig. 4. Brine concentration, chemical fixation, and subsurface injection were discussed in a previous section of this report.

The Lurgi gasification operation generates substantial amounts of slag and ash that are quenched with water and then hydraulically transported to thickeners and/or mechanical-dewatering devices. The bulk of the material is recovered as a wet sludge. The most practical disposal method for this material is burial in landfills. This solid waste management option also can be used to handle coal refuse, coal fines and dust, and oil/tarry sludges from the pretreatment of gas liquors. Landfilling also could be employed for the disposal of chemically fixed solid wastes and sludges.

In conventional landfilling, the waste is deposited in layers on land, compacted, and covered with a layer of soil. Provided that adequate measures are taken to reduce the potential for the contamination of ground and surface waters, landfilling can be an environmentally acceptable and cost-effective method for solid waste disposal.[18]

To minimize the potential for the contamination of groundwater, landfills must be located in areas where the subsurface formation is relatively impervious to infiltration of contaminated leachate and where the distance to the groundwater table is significantly large. The landfill area should be properly contoured to divert surface runoff from the site to appropriate impoundment areas for subsequent treatment. When subsurface formations do not provide adequate barriers against leachate infiltration, artificial barriers such as plastic, asphalt, concrete, or clay must be provided as lining for the landfill. The intercepted leachate would be transferred to a surface facility for treatment. Observation wells should be installed in the vicinity of the landfill site to detect leachate migration.

Shift and methanation catalysts eventually become deactivated and require replacement or regeneration. For zinc oxide and most nickel-based methanation catalysts, onsite resource recovery is not practical, and these materials are either sent to metals/catalyst vendors for recovery of metals or disposed of as a solid waste. In the case of the cobalt molybdate shift catalyst, onsite regeneration by air oxidation to remove carbon and sulfur may be possible, and technologies are presently under investigation[9] that specify acceptable unit operations to achieve this goal.

Spent methanation catalysts, although deactivated as far as catalyst activity for methanation is concerned, have a significant capacity for adsorption of sulfur compounds and can be used as gas-cleaning material. Because of the proprietary nature of most catalysts, few data are available on the technical feasibility of metal recovery from spent catalysts.

Because spent catalysts have high concentrations of metals and contain carbonaceous materials (e.g., polycyclic organic material) and sulfur compounds, they are often considered hazardous materials requiring special handling and disposal. Chemical fixation and encapsulation probably would be necessary prior to disposal in landfills. The quantity is usually relatively small and contract disposal of these potentially hazadous materials would be a more likely economical alternative.

Tarry/oily sludges can be disposed of by landfilling alone or in connection with slag and ash disposal. The sludges also may be incinerated, which, when compared to land disposal methods, requires very little space. Experience with refinery oily sludges indicates that a heating value of 30,000 Btu per gallon is the minimum heat capacity that will support combustion without supplemental fuel. Except for potential air pollution problems, which can be controlled with appropriate design, incineration is the most desirable disposal option, especially for the destruction of hazardous organics. The major types of incinerators in commercial use are the rotary kiln, multiple-hearth furnace, and fluidized-bed furnace. These same incinerators can be used for the destruction of waste solids generated by biological-oxidation processes. Incineration has been practiced successfully for the destruction of municipal and industrial biosludges, and is a reasonable alternative where land is not available for sludge disposal.

Waste sludges from biological oxidation also may be disposed of by land treatment applications. When large land areas are available and the climate and hydrogeological conditions are favorable, these organic sludges may be disposed of by application to the soil. The sludge is applied to the soil by spreading and disked under the topsoil. The organic component of the sludge undergoes biodegradation in the soil and eventually becomes part of the soil humus. Sludge disposal by land treatment is sometimes used for the disposal of biosludges from refinery wastewater treatment.

Biosludges often require dewatering prior to ultimate disposal. Sludge dewatering is necessary to enable economic land disposal or incineration. Sludge concentration methods include gravity thickening, centrifugation, vacuum filtration, and the use of filter presses. These methods have been used widely in both municipal and industrial wastewater treatment practice. Chemicals such as lime, ferric salts, and synthetic organic polymers may be added to sludges to improve dewaterability.

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4 CANDIDATE UNIT PROCESSES

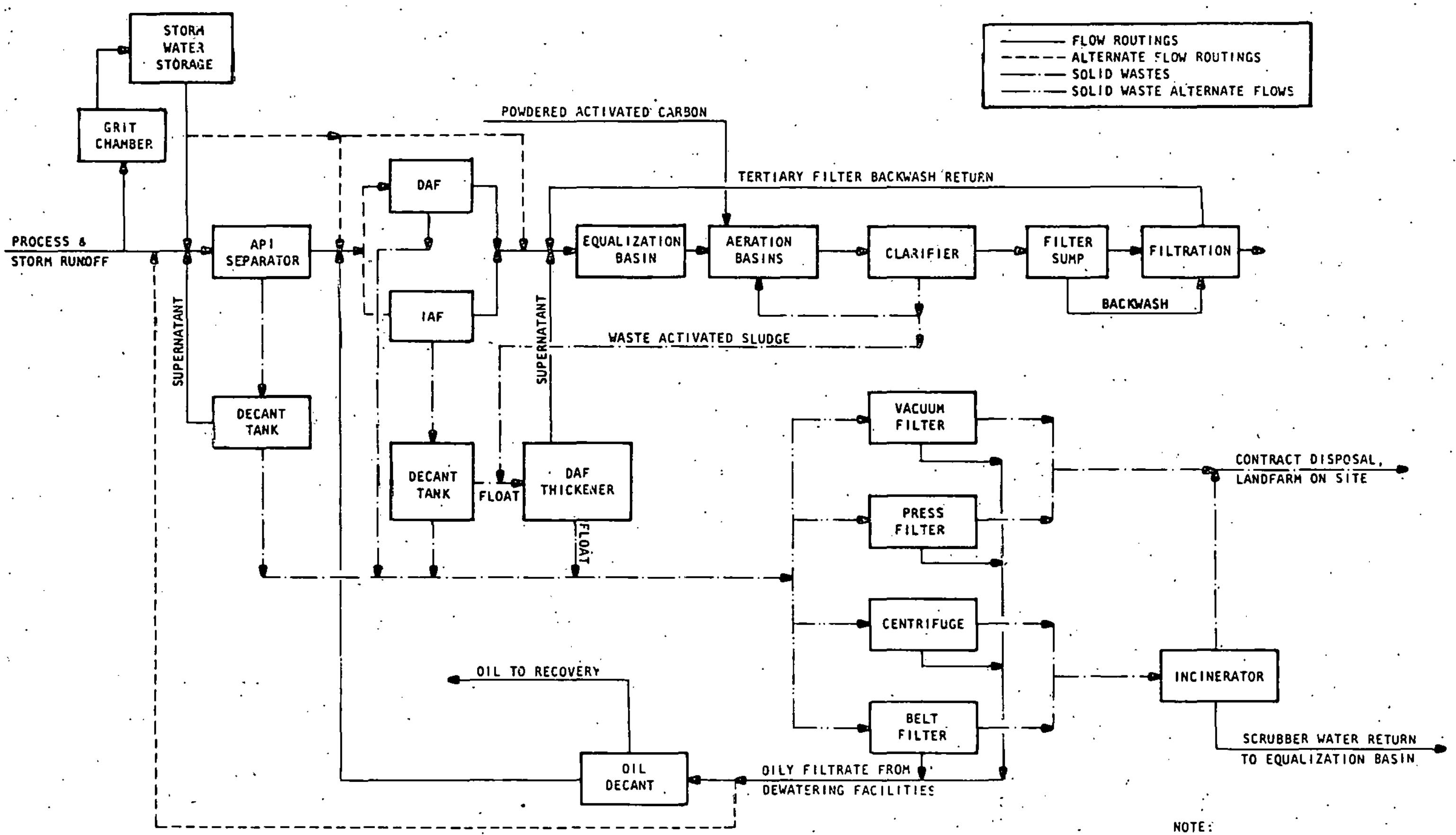
Candidate wastewater treatment, solids handling, and disposal processes are presented schematically in Figs. 5 and 6. These schematic drawings indicate that a multitude of sequential process permutations are possible for the treatment of SFB-process coal-gasification wastewaters. These permutations range from direct contract disposal to a complex system involving primary, secondary, and tertiary wastewater treatment, conditioning, dewatering, incineration, and ultimate disposal of sludges. Selection of the optimum process or system usually is based primarily on economic considerations. Moreover, since the economics of disposal are contingent upon such variable factors as landfill availability and regulatory criteria, the system must be flexible enough for modification. Ideally, the optimum disposal system should provide for a least-cost solution that ultimately allows for the efficient implementation of future expansions as dictated by treatment objectives. In actuality, no such least-cost solution will exist for the coal-conversion industry if there is a government-mandated requirement for zero discharge. There is great uncertainty with respect to the regulatory criteria that will be applied to this industry.

This section addresses the performance levels associated with some of the more appropriate control technologies that apply to the treatment of SFB Lurgi-process coal-gasification wastewaters. The best practicable control technologies were evaluated, and special emphasis was placed on an examination of the activated-sludge/PAC process that may offer the dual promise of cost-effective treatment and reduced pollutant discharges to navigable waters. A more detailed discussion of the activated-sludge/PAC process is presented herein as well as an assessment of how a PAC system compares to a tertiary GAC system when applied to the treatment of SFB Lurgi-process wastewaters.

4.1 OIL-WATER SEPARATOR PERFORMANCE

Although gravity separation does not provide an effluent oil quality satisfactory for direct discharge to biological treatment, it is the most economical and efficient approach to the removal of high concentrations of incoming free oil. The effluent oil concentrations from API separators treating petroleum and petrochemical wastewaters range from 70 to 150 mg/L, although deviations on either side of this range are common due to the great variety of wastewaters treated with this type of oil removal equipment. Nevertheless, under excellent operating conditions, an apparent lower limit of oil in a gravity-separator effluent is usually around 50 mg/L.[34] It should be emphasized that the removal efficiency of all gravity-separation techniques is a function of both temperature and the density difference between oil and water.

The two most significant factors bearing upon separator performance are influent flow rates and oil concentrations. Separators must be protected from flushing during periods of high flow. Bypass and overflow lines generally are used to provide this hydraulic protection. The ideal API separator design seeks to limit the extent to which turbulence and short-circuiting will affect the operation of the separator. The effects of turbulence increase with the magnitude of the ratio of the horizontal velocity to the rate of oil-droplet rise. Theoretically, turbulence can be compensated for only by decreasing the



NOTE:

TREATMENT SYSTEM EXCLUDING GRANULAR CARBON ADSORPTION

Fig. 5 Coal-Gasification Wastewater-Treatment-Plant Schematic

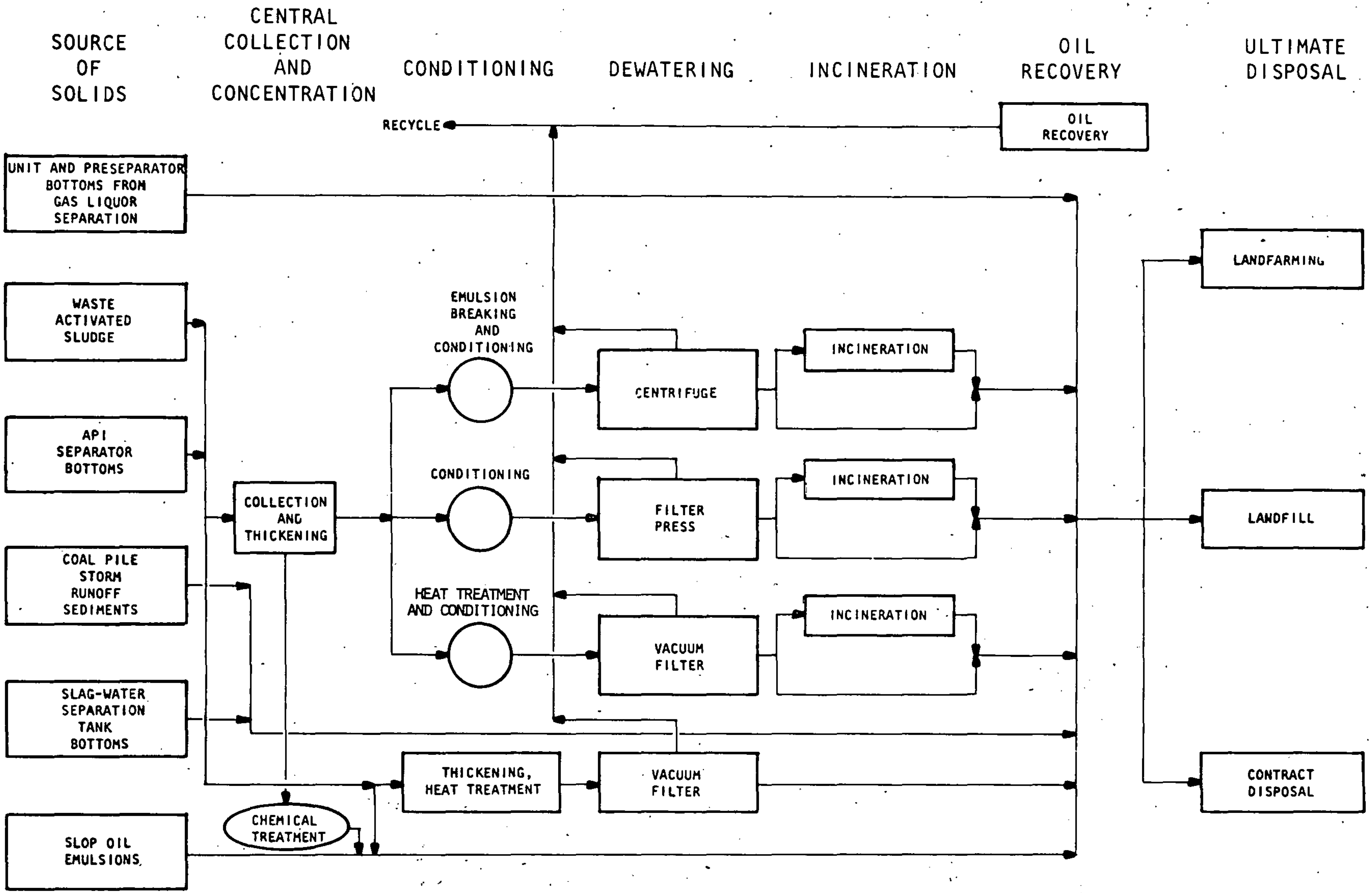


Fig. 6 Schematic of Solids Handling and Disposal Alternatives for Coal-Gasification Wastewater Treatment

overflow rate. Usually, a deterioration of effluent oil quality occurs when hydraulic surges exceed the design maximum. Unfortunately, a theory does not exist that defines the magnitude of a maximum absolute value for the horizontal velocity.

Like API separators, the treatment performance of tilted-plate separator (TPS) units is affected by hydraulic surges, and the suspended solids- and oil-removal efficiency of the unit decreases when the system is operated at 1.5 times the designed average hydraulic load.[34] Data that depicted the variation in the treatment performance of a TPS unit, used for suspended-solids removal from petroleum refinery ballast wastewaters, indicated that the overall removal of suspended solids increased with increased influent-solids concentration. This also was observed for the removal of oil and grease.[34]

Efficiency of oil removal by dissolved-air flotation (DAF) is a function of many factors: overflow rate, retention time, recycle volume, pressurization level, air-to-solids ratio, type and volume of chemical addition, and the concentration and form of the influent oil. As a rule, the DAF unit experiences better oil and grease removal at higher influent concentration levels. This also is the case regarding the separation of influent suspended solids and COD. DAF units designed for oil-water separation of petroleum-refinery wastewaters incorporate coagulation and flocculation, the principal chemical being alum at a dosage of between 100 and 150 mg/L on the average.[34] DAF-unit effluent-oil levels of 10 to 30 mg/L usually can be achieved if the influent oil concentration remains below 200 mg/L. Although it is possible to obtain an effluent-oil quality of 10 mg/L under certain conditions with a DAF unit that incorporates chemical flocculation, consistent performance at a 10 mg/L effluent-oil concentration would be difficult if not impossible to sustain. This aspect is particularly true when considering the fluctuations in influent-oil concentration inherent in most processing operations, and the corresponding effect on gravity and DAF oil-removal systems.

It should be emphasized that air flotation without chemical addition is not widely practiced in petroleum and petrochemical wastewater treatment. The same restraint is anticipated for treatment of oily wastewaters from the SFB Lurgi process. The addition of polyelectrolytes does not increase oil-water separation by air flotation systems enough to warrant its use as anything other than a coagulant aid.

Oil-water separation efficiencies of induced air flotation (IAF) units are essentially equal to those achieved by the DAF units, but operation is more difficult and chemical flocculant requirements are significantly higher. Moreover, the skimmings are much less concentrated and represent a significant waste-solids disposal problem. Suspended solids removal for an IAF is commonly unimpressive, exhibiting greatly decreased efficiency at higher influent solids concentrations. Conversely, effluent-oil concentrations for an IAF unit exhibit increased oil-removal efficiency at higher influent-oil levels. Moreover, the IAF unit will produce a large volume of float material that may be as high as 9% of the throughput volume.[34]

4.2 POWDERED-CARBON ACTIVATED-SLUDGE SYSTEMS

A schematic diagram depicting the PAC modification of AS treatment is presented in Fig. 7. This system, which includes carbon-regeneration facilities, is modeled after the DuPont de Nemours Chambers Works treatment plant in Deepwater, New Jersey. The waste sludge, which contains powdered carbon, is removed from the activated-sludge system and thickened in a gravity thickener. The sludge is then dewatered in a filter press prior to being fed to the regeneration furnace. The regenerated carbon is washed in an acid solution to remove metals as well as other dissolved materials. Fresh carbon is added as makeup to replace the carbon lost in the overflow from the activated-sludge process or in the regeneration system.

The benefits attributed to this system are: (1) improved BOD and COD removal by sorption and improved settling at even lower than optimum temperatures and/or at higher than design flows; (2) sorption of color and toxic agents that cannot be removed by biological oxidation; (3) reduction of bioreactor generated foam; (4) more-uniform plant operation and plant effluent quality during periods of widely varying organic and hydraulic loads; (5) lower sludge-volume index; and (6) denser sludge underflows from the secondary clarifier.[35,36] The improved settling in the secondary clarifier leads to lower suspended solids and residual organics in the effluent. The settling rate of powdered carbon plus biosolids is usually greater than that for biosolids alone.

Longer sludge ages in a powdered-carbon activated-sludge system provide for better bio-oxidation of slowly oxidized organics than would be expected in a conventional AS system. The apparent improvement in effluent quality is the result of a sorption/biodegradation synergism between the powdered carbon and the active biomass that has long been postulated as the principal advantage of operating a bioreactor at longer sludge ages. It should be emphasized that experimental data indicate that this improvement in effluent quality with longer sludge ages is less apparent when carbon is absent.[36] The sorption-desorption phenomenon common to activated-carbon adsorption systems provides a buffer within the bioreactor against the impact of shock organic loads while freeing carbon surface anew for the sorption of more pollutants. The microorganisms continuously degrade residual organics desorbed from the carbon, thereby creating the impression of continuous regeneration of available carbon surface for adsorption. This activity provides the principal advantage of the PAC modification, and this type of treatment, when used as an upgrading of the activated-sludge process, is a viable alternative to tertiary GAC systems.

The regeneration of spent carbon is the major factor in making any activated-carbon adsorption process economically favorable, because provision for reuse of carbon is critical to a cost-effective design. In an AS/PAC process, the regeneration cycle provides the opportunity to simultaneously incinerate the excess biomass from bio-oxidation, whereas a conventional activated-sludge system with tertiary GAC treatment requires separate devices for granular-carbon regeneration and waste-sludge incineration.[7,37]

A multiple-hearth furnace regeneration system is depicted as an integral part of the PAC process presented in Fig. 7, and this type of system has been used extensively for the regeneration of granular activated carbon.

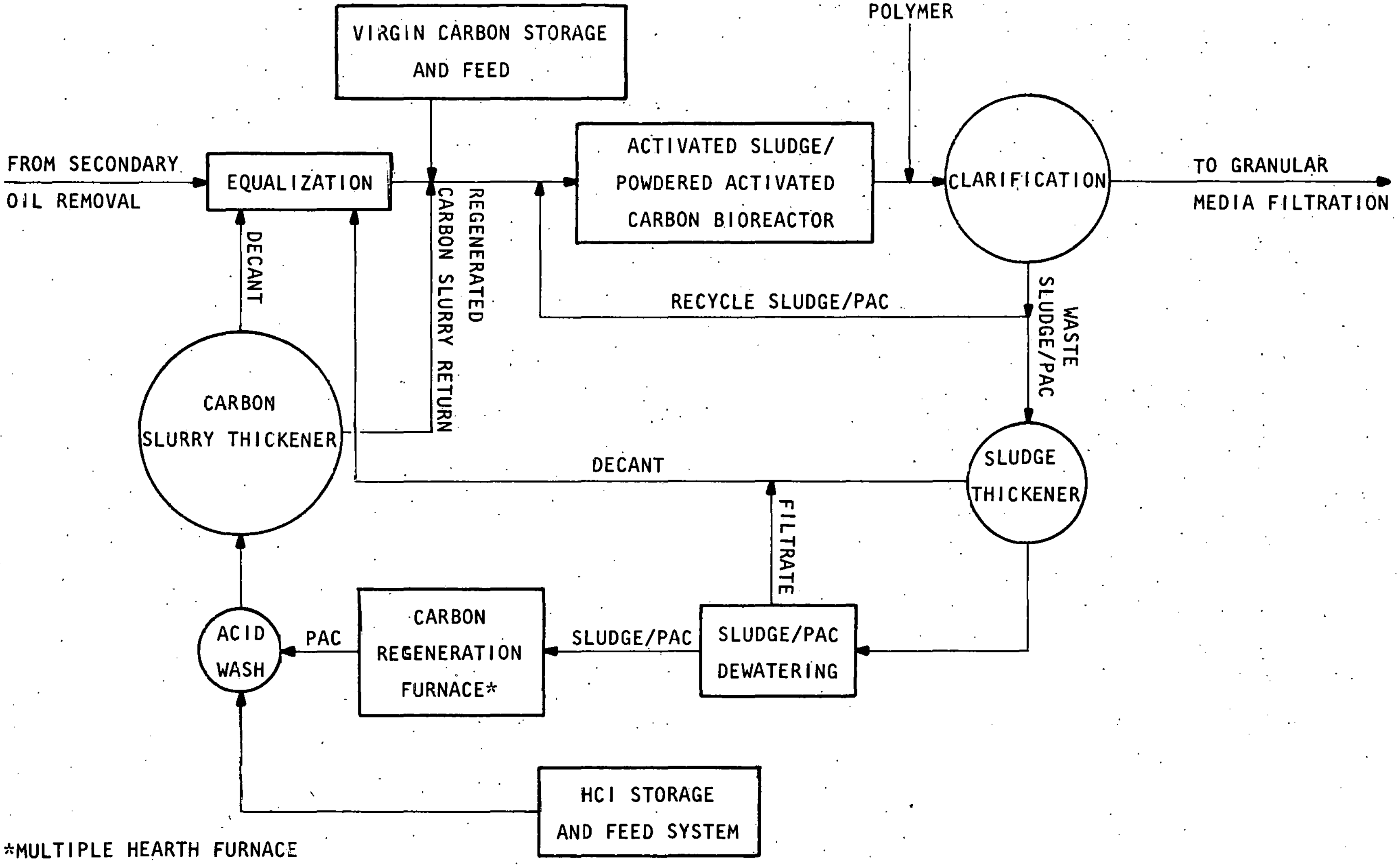


Fig. 7 PAC Modification of Activated-Sludge System

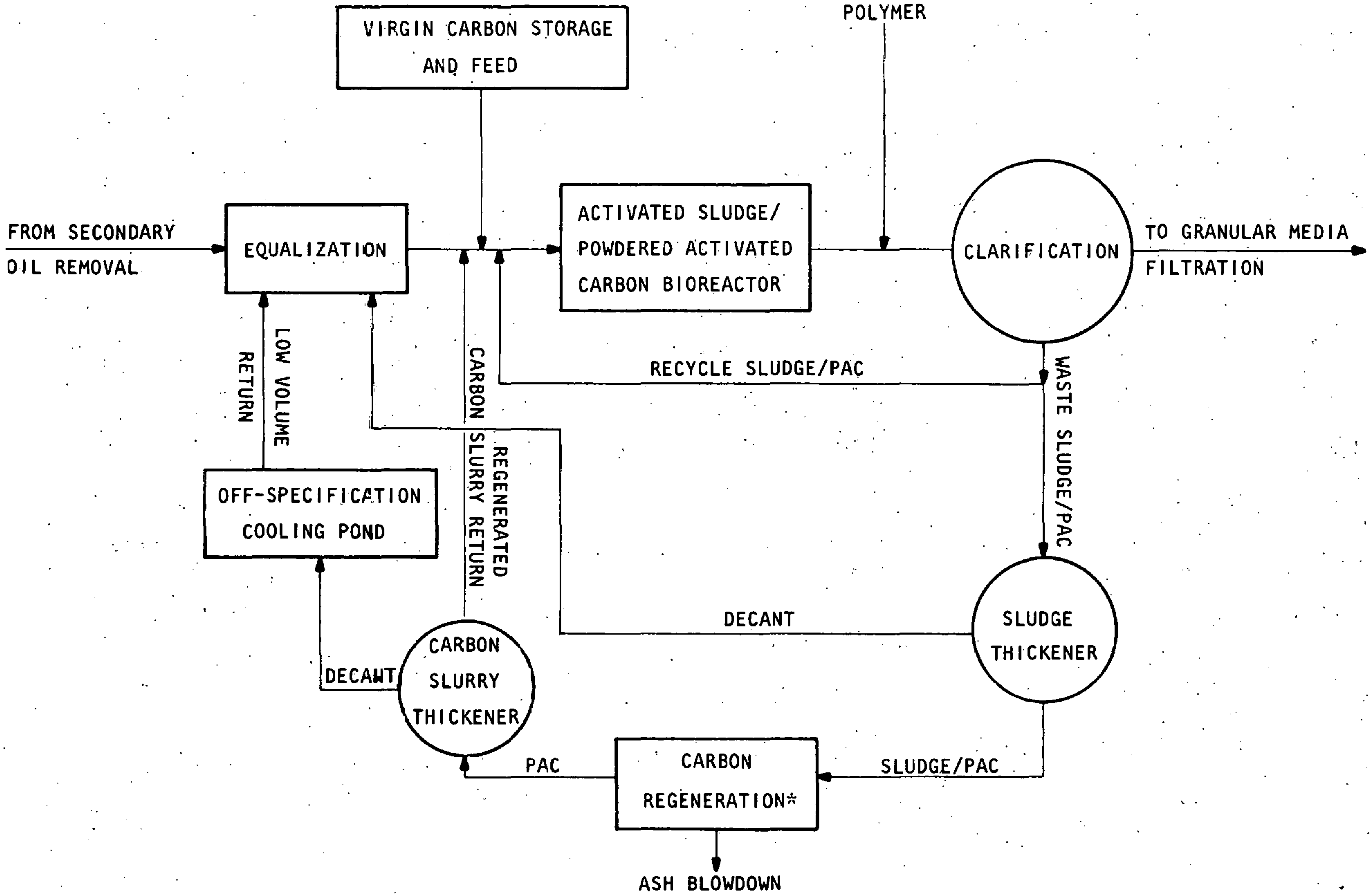
A multiple-hearth furnace regeneration system is used at DuPont's Chambers Works Plant for the regeneration of spent carbon from the operation of their PAC process. DuPont selected this method after detailed study of several alternative regeneration techniques.

Figure 8 shows an alternative powdered-carbon regeneration system for the PAC modification. This carbon regeneration system incorporates wet-air oxidation (WAO), a liquid-phase, high-temperature, high-pressure process for the oxidation of organic sludges. WAO has been used extensively in the pulp and paper industry for energy and chemical recovery from black liquors. For design purposes, the process may be considered to be capable of total oxidation of adsorbed organics on the surface of the powdered carbon as well as the thermal destruction of residual biomass in the waste sludge. A WAO regeneration process does not require a dewatering operation prior to injection into the reactor. The flow scheme presented in Fig. 8 for carbon-sludge regeneration is similar to that used in the wet-air oxidation of sewage sludge and industrial wastes.

In this process sequence, the spent carbon/sludge is withdrawn from the secondary clarifier and concentrated by gravity thickening. The thickened spent carbon/sludge, at approximately 6-8% solids, is pressurized to WAO system pressure, mixed with compressed air and heated to the reaction temperature prior to being conveyed to the reactor where selective oxidation and a consequent temperature rise occurs. Hot spent gases and regenerated carbon slurry continuously pass out of the reactor through the heat exchangers where they are cooled while heating the incoming slurry and air. Cooled gases and regenerated carbon slurry are released to a slurry thickener from which regenerated carbon is returned to the bioreactor. The regeneration system is designed to be thermally self-sustaining so that steam injection from an auxiliary boiler is required only during startup.

Generally speaking, a multiple-hearth-furnace regeneration system will lose between 25 and 35% of the carbon during regeneration. If this were coupled with the probable level of carbon loss associated with conveyance and sludge handling, a maximum of 50% of the regenerated carbon could be lost during the regeneration cycle for this system. On the other hand, it is estimated that the total carbon loss from a WAO regeneration system would not exceed 20% of the mass of powdered carbon regenerated. Moreover, it has been reported that regeneration with a WAO system would successfully recover most of the virgin carbon properties of the spent powdered carbon except for small pore volumes (less than 10 angstroms) not considered essential in the treatment process.[38]

The WAO regeneration system provides a means of purging heavy metals and other residual inorganics from the treatment process because it allows for an ash blowdown from the wet-air reactor. This is not the case with the multiple-hearth-furnace regeneration system, because all residual inorganics would be returned to the treatment train with the decant from the acid wash system. A WAO regeneration system does, however, return high levels of residual organics to the treatment process with the decant from the regenerated carbon slurry thickener, thereby requiring a diversion to off-specification impoundment.



*WET AIR OXIDATION

Fig. 8 PAC Modification of Activated Sludge Incorporating Wet-Air Oxidation for Carbon Regeneration

4.3 TERTIARY CARBON-ADSORPTION SYSTEM

A wastewater-treatment train that incorporates tertiary GAC treatment is shown in Fig. 9. The GAC system consists of one or more trains of carbon-filled columns, each train having three columns operated in series. The carbon columns operate by rotating their positions in the train, so that the newly regenerated carbon is always located in the third adsorption vessel, whereas the vessel with the most spent carbon is the first vessel in the sequence.

Granular-media filtration usually precedes downflow tertiary GAC treatment. Filtration is applied as a treated-effluent polishing process for the treatment of effluents contaminated with suspended and colloidal material discharged from activated-sludge treatment. In concept, all filters operate as three-dimensional strainers. Dual-media and multimedia filters act as multilayer strainers, removing larger flocculated particles in the coarser media and smaller particles in the fine media. A filtration cycle terminates when the amount of particulate matter escaping the filter exceeds the effluent guidelines or when the headloss through the filter caused by solids capture exceeds the limiting value.

Irrespective of their relative efficiency, all filters require the periodic removal of deposited material. Cleaning of a filter at the end of a run cycle commonly is accomplished by high-velocity backwashing, and the overall efficiency of a filtration unit is affected greatly by the amount of backwash water required. In general, the contaminated backwash water can be treated separately or rechanneled back through the biological process.

Characteristics common to most filtration processes used for the treatment of biologically treated secondary effluents are that: (1) the variation in wastewater flow and effluent quality from biological treatment does not adversely affect filter efficiency; (2) most discharge limitations for suspended solids can be met with either deep-bed or shallow-bed filtration units; and (3) filter performance is extremely sensitive to changes in media size and configuration.[34]

The tertiary GAC treatment system evaluated in this analysis includes provisions for onsite carbon regeneration. Such a system is shown in Fig. 10. The spent granular carbon is collected and conveyed to a multiple-hearth regeneration furnace where adsorbed organics are burned off, to produce a reusable carbon that is recycled to the adsorber columns. As with the PAC regeneration system, the furnace off-gas flows through an aqueous scrubber that reduces the concentration of pollutants in the gas to an acceptable level. Scrubber blowdown is recycled to the equalization basin. Storage facilities are provided for regenerated and virgin carbon.

Developed solely as a tertiary treatment process, granular-carbon treatment does not enhance the operating performance of a biological oxidation system, but rather provides supplementary treatment as a polishing step capable of producing a better quality effluent than biological treatment alone. Anaerobic conditions that prevail in granular-carbon reactors have caused difficulty through the proliferation of biological growths in the carbon media and sulfide generation has been particularly troublesome. Full-scale experience[35] has indicated that uncontrolled biological growth in carbon

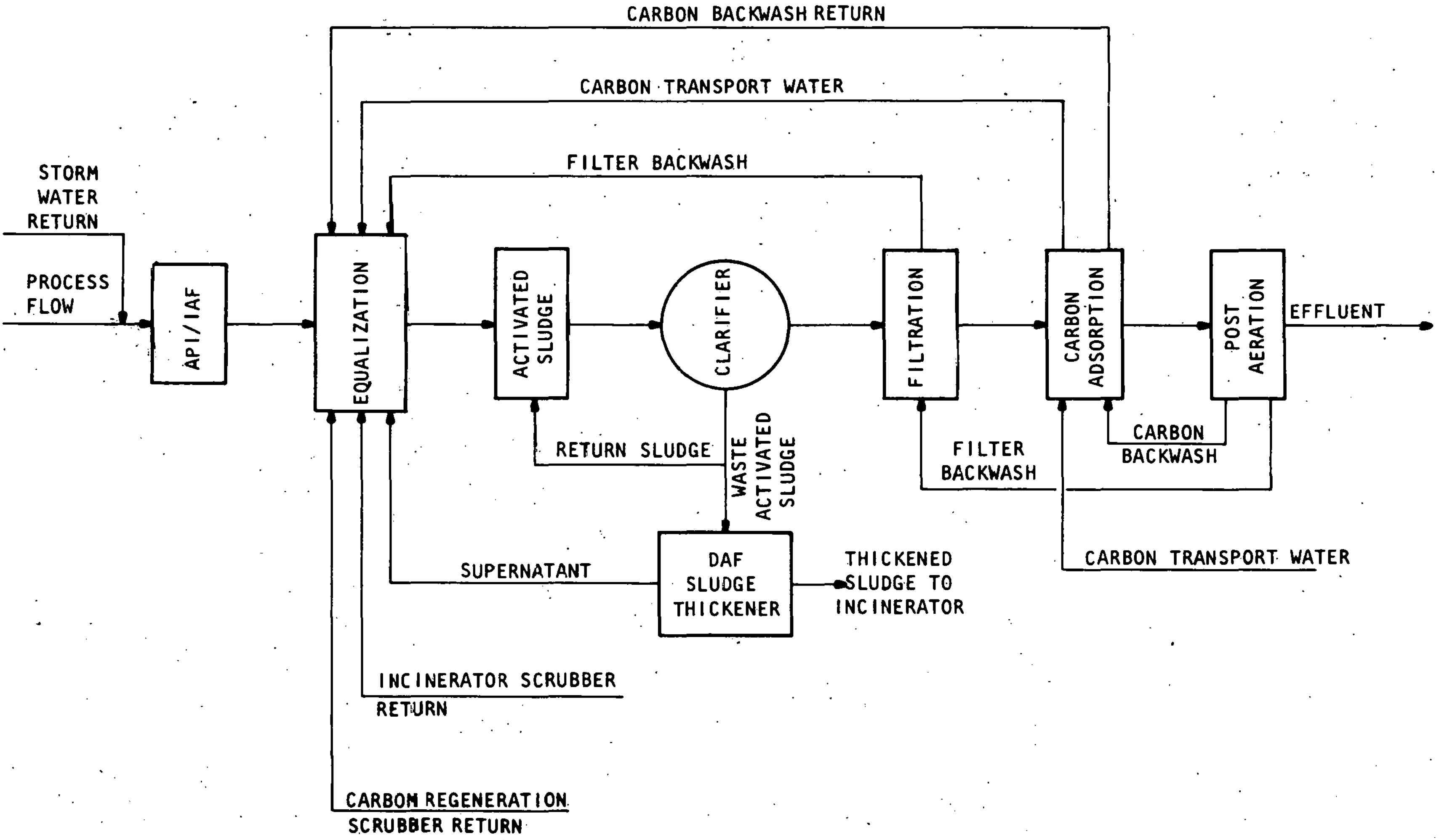
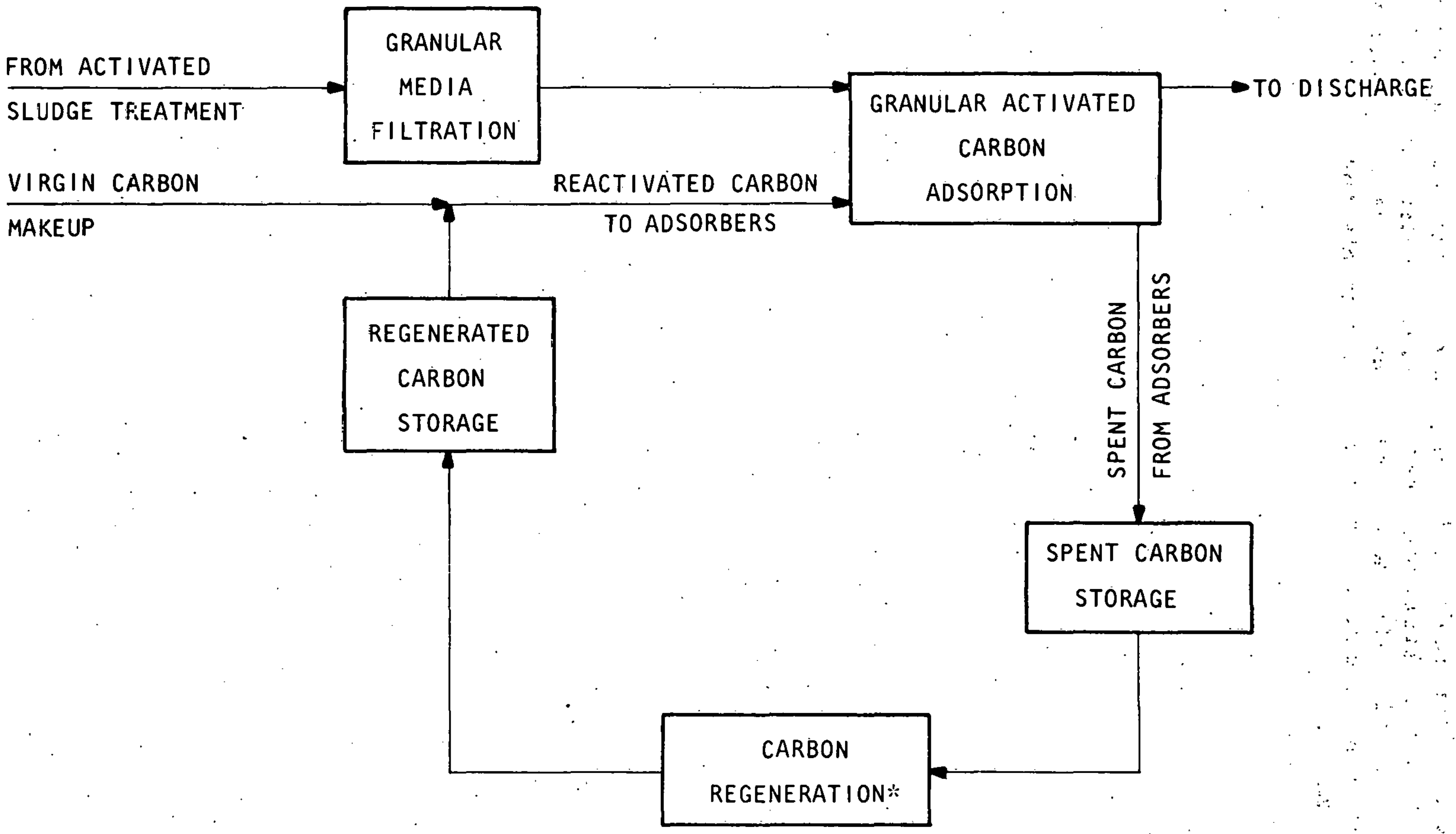


Fig. 9 Tertiary Carbon Adsorption (granulated activated carbon) Addition to Coal-Gasification Wastewater-Treatment Plant



*MULTIPLE HEARTH FURNACE

Fig. 10 Granular-Activated-Carbon Treatment System reactors has more negative features than positive. Carbon capacities used as design criteria for the treatment of industrial wastewaters are usually overstated and have not been realized in full-scale experience. Breakthrough concentrations that force premature regeneration cycles in single-bed adsorbers and the desorption phenomenon that causes low carbon capacity in series-operated polishing columns are partially responsible for poor tertiary GAC treatment performance.

5 SECONDARY-TREATMENT FACILITIES

5.1 CONCEPTUAL DESIGN

The conceptual designs of four possible biological-oxidation process modifications are presented in this section. Each design is based on a projected wastewater composite that most probably characterizes the wastewaters generated from a commercial-scale, SFB Lurgi-process coal-gasification plant designed to manufacture 242 MMSCF per stream day of pipeline-quality substitute natural gas. The principal wastewater streams coming to the secondary treatment facilities are: (1) the pretreated gas liquors from ammonia recovery; (2) the methanol-water column bottoms from the Rectisol process; (3) deoiled wastewaters from the plant oily-water sewer system; (4) tertiary gravity-filter backwash; (5) filtrate from primary sludge dewatering facilities; and (6) waste residuals from secondary oil removal. The estimated pollutant loads associated with each of these streams are presented in Table 14. The estimated COD of the pretreated gas liquors is characteristic of a lignite feedstock to the Lurgi gasifier, and is based on data provided by C-MU for the treatment of GFETC-SFB process quench waters. The estimated average daily flow and heat capacity of each of the principal wastewater streams also are indicated in Table 14.

Equalization of wastewater surges from the coal-gasification processing units is a necessary intermediate step in the treatment system. Experience in the petroleum and petrochemical industries has indicated that highly variable flows and organic mass-loading levels affect the operation and performance of a biological treatment facility. Treatment performance will be enhanced if influent flow and concentration fluctuations to the AS process are minimized. This requires the addition of an equalization basin prior to the biological-oxidation process. This basin should be of sufficient size to adequately absorb wastewater variations caused by production scheduling and to dampen the periodic dump or spill of wastes into plant sewers. Given the probable production schedules that would characterize a Lurgi-type SFB process, the influent-wastewater flows to the equalization basin should remain relatively constant. Therefore, it is anticipated that the organic mass-loading fluctuations will control the design of the equalization basin volume.

An additional factor that must be incorporated into the equalization design is the extent of potential heat loss from influent wastewaters during winter retention in the equalization basin. The winters in the northern portions of the United States, where such commercial-scale gasification facilities are expected to be constructed, are usually severe, having median ambient air temperatures below 20°F. Since the actual operation of an equalization basin closely approaches the model for an ideal, completely mixed basin, significant heat loss may be anticipated, particularly if the basin is mixed with a mechanical surface aerator. Consequently, a short contact time would be the most desirable equalization detention period for heat-conservation purposes.

In general, the design problem consists of determining a functional relationship between the size of the equalization facility and the probable reduction in the fluctuations associated with the pollutant concentration of the wastewater. The approach to the solution of this problem is rather

Table 14 Estimated Pollutant Loads Contributing to Biological Oxidation

Description	Chemical Oxygen Demand (lb/day)	Flow (mgd)	Heat Capacity (10^6 Btu/day)
Pretreated gas liquors from ammonia recovery[a]	76,069	2.606	3,264.015[b]
Methanol-water column bottoms from Rectisol	2,427	0.194	242.985
Deoiled wastewater from oily-water sewer	540	0.144	90.180
Tertiary filter backwash	3,862	0.346	216.683
Filtrate from primary sludge dewatering	3,303	0.079	72.562
Subnatant from float thickener	3,843	0.144	162.324
Total design average	90,044[c]	3.513	4,048.749[d]

[a] Wastewaters cooled from 205°F to 150°F prior to equalization.

[b] Gas liquor after phenol and ammonia removal is estimated to have an average COD ≈ 3,500 mg/L.

[c] Assumes a minimum of 2.5 days of equalization prior to biological treatment; COD ≈ 3,073 mg/L.

[d] Average wastewater temperature at the inlet of the equalization basin is 138°F.

restricted because no data are available regarding the probable nature of organic-pollutant concentration fluctuations associated with Lurgi-type SFB process wastewater. It was, therefore, decided to examine the equalization basin on the basis of its heat-loss characteristics, using the apparently arbitrary design criterion presented in the CONOCO conceptual design[1] for wastewater treatment of Lurgi-type SFB process wastes. Consequently, it was assumed that the average design mass loadings to the biological-oxidation process presented in Table 14 are characteristic of a minimum of 2.5 days of equalization. Therefore, smaller equalization-basin volumes would produce higher organic loadings on the bioreactor. Moreover, the equalization facilities were physically arranged to provide additional storage beyond the normal required volume in order to dampen more-severe variations in the organic loading. Such off-specification impoundment of high organic loads also would provide cooling pond capacity during summer operation.

Mixing is usually provided to ensure adequate pollutant concentration equalization and to prevent settleable solids from depositing in the basin. In order to provide adequate mixing and, at the same time, conserve heat energy during winter operation, subsurface aeration utilizing static mixer aerators was incorporated into the design of the equalization basin. The heat loss characteristic of this aeration system applied to different equalization basin volumes is depicted by the data presented in Fig. 11. These data

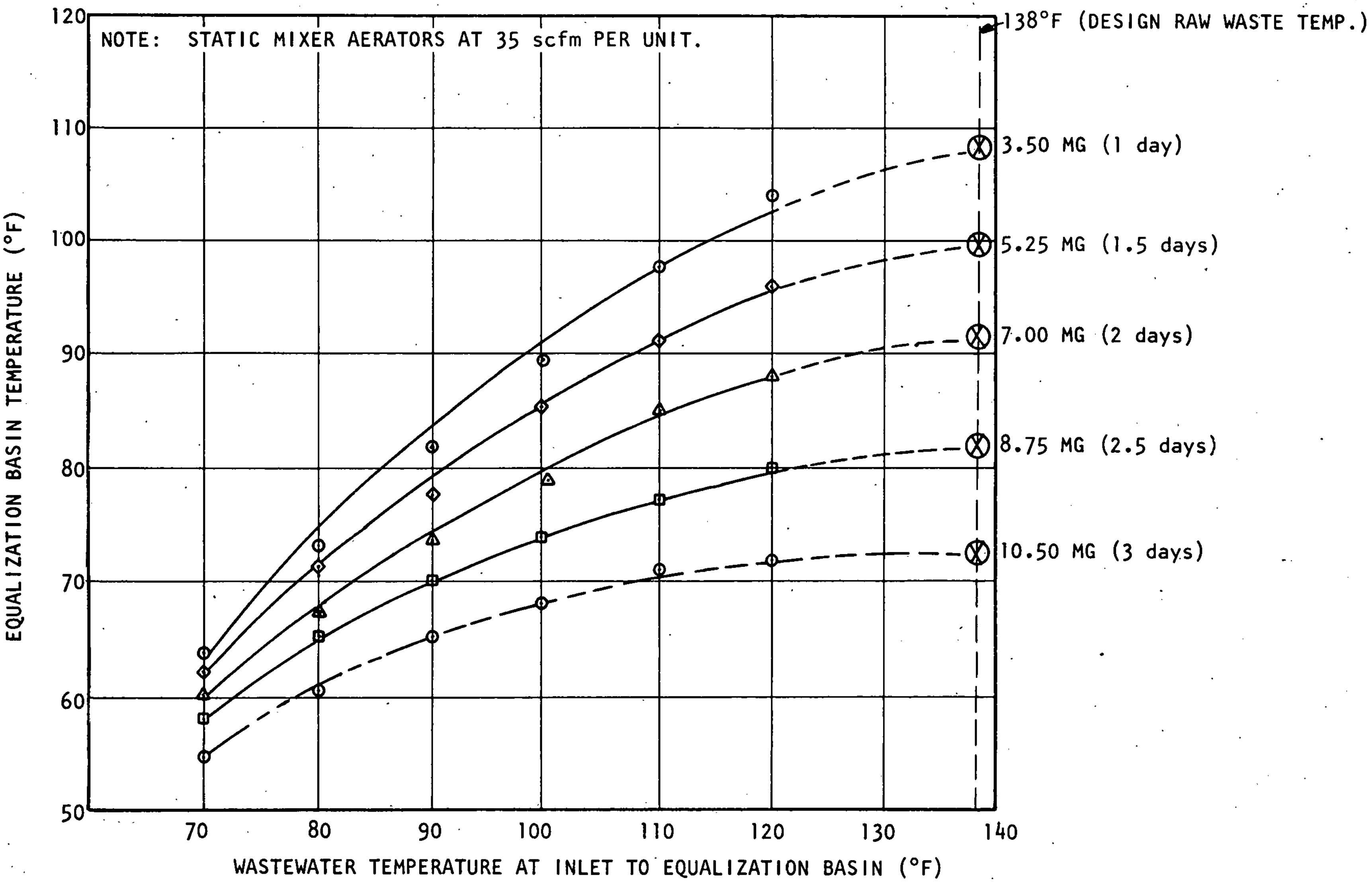


Fig. 11 Inlet vs. Outlet Temperature for Different Equalization-Basin Volumes

indicate the probable effect of equalization-basin mixing on basin wastewater temperature for winter operation. The actual required size and mixing features of the equalization basin depend on the wastewater characteristics, process plant operating schedule, and any unusually severe operational fluctuations such as plant turn-arounds and process facility upsets.

The principal biological-oxidation process that should be most effective in the treatment of Lurgi-type SFB process wastewaters is the activated-sludge system. The basis of the proposed design of an AS system to treat SFB process wastewaters is predicated on maintaining an environment in the bioreactor that is optimal for the growth and activity of selected populations of acclimated microorganisms. The bench-scale treatability study described in the appendix, together with earlier treatability studies[13,14] were conducted: (1) to verify the applicability of biologically stabilizing the organic constituents in the SFB Lurgi-process wastewater; (2) to develop the basic kinetics for process design; (3) to establish the impact of various organic and inorganic wastewater constituents upon biological-oxidation process efficiency; and (4) to predict the treated-effluent quality and evaluate this quality in terms of probable effluent requirements.

The design basis for the four biological-oxidation processes evaluated is presented in Table 15. These data indicate that the candidate biological oxidation processes vary in bioreactor retention time, sludge age, influent COD, and available pretreatment equalization. However, all are designed to provide comparable effluent qualities within the limits of the characteristic biodegradability of the waste. The design basis for the secondary aeration and clarification facilities is presented in Table 16. Three subsurface aeration systems were evaluated, namely: (1) static mixers; (2) submerged turbines with air spargers; and (3) diffusers. It should be recognized that an aerated AS basin is both a cooling pond and a biological reactor, and these subsurface aerators not only oxygenate the mixed liquor but also increase heat transfer from the basins. The degree of heat dissipation dictates the equilibrium basin temperature, which, in turn, influences the efficiency of organic removal by biochemical oxidation.

At the outset, it was assumed that the kinetic parameters developed (appendix) were optimum for the treatment of Lurgi-type SFB process wastewaters, and the bioreactors should be designed to maintain equilibrium basin temperatures in a range that would produce optimum removal of soluble organics. For the completely mixed AS process, the soluble organic content of the treated effluent is equal to that in the bioreactor. Organic removal results from the physical enmeshment of suspended material in the biological floc, the flocculation and absorption of colloidal organics in the biological floc, and the biological oxidation of soluble organics that results in direct cell synthesis. The suspended and colloidal organics present in SFB process wastewaters are essentially removed by the pretreatment processes for primary and secondary oil and solids separation. Therefore, the candidate biological-oxidation process is designed primarily to achieve a reduction in the soluble organics content of SFB Lurgi-process wastewaters.

The impact of any of the candidate subsurface aeration systems on bioreactor basin temperature for winter operation is depicted in Fig. 12. These data indicate that the subsurface diffusers dissipate the greatest amount of heat energy, whereas the static mixer and submerged turbine aerators

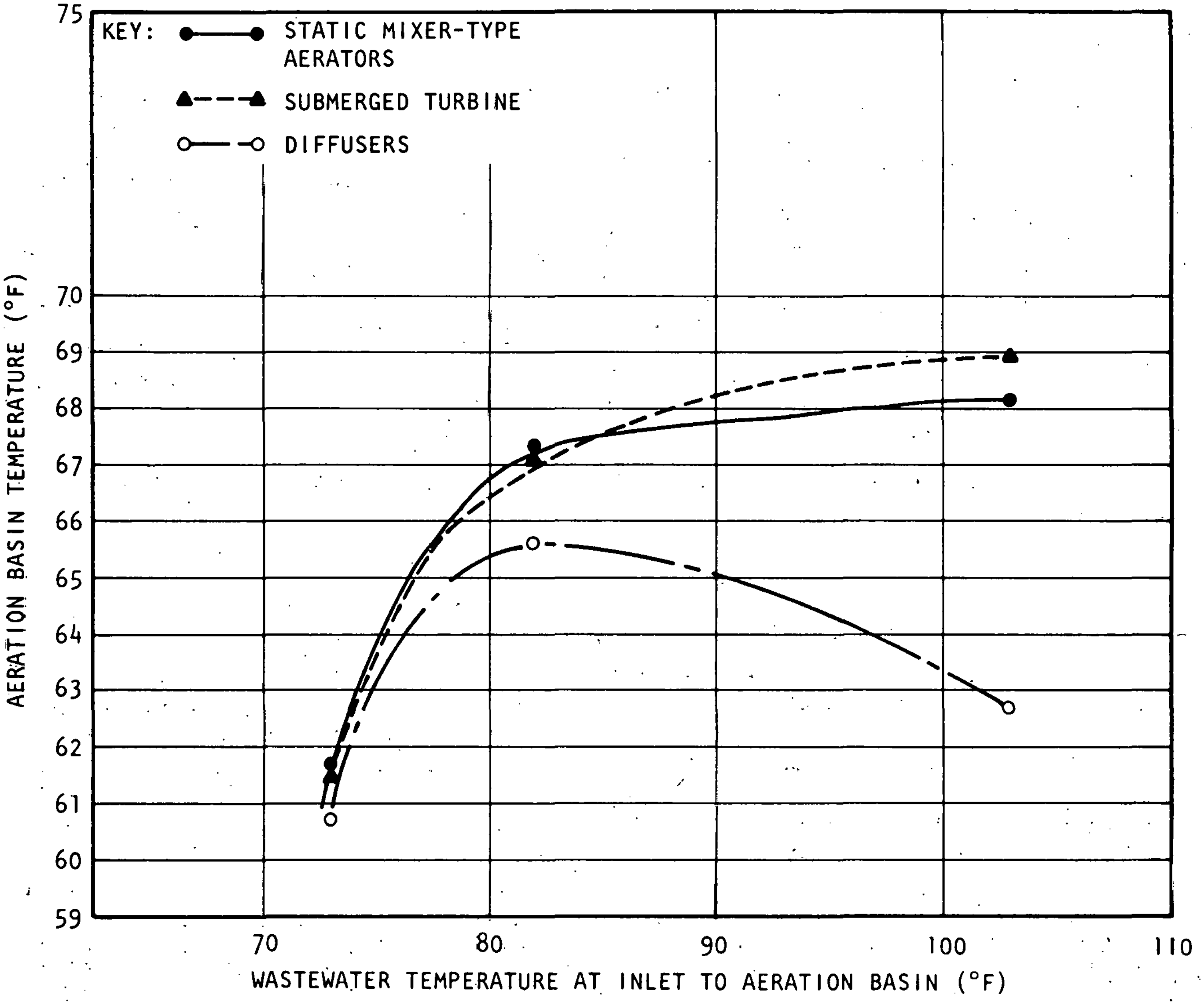


Fig. 12 The Effects of Subsurface Aeration Selection on Bioreactor-Basin Temperatures

Table 15 Design Basis for Biological-Oxidation Processes

Activated Sludge Process	Equalization/ Retention (days)	Bioreactor Retention (days)	Sludge Age (days)	Oxygen Requirements (lb/day)	Sludge Production (lb MLVSS/day)	Influent COD to Bioreactor (mg/L)	Effluent COD[a] (mg/L)
Option A[b]	1	2.43	38	52,700	15,330	3,615	1,340
Option B[b]	2.5	1.85	37	40,150	11,680	3,073	1,340
Option C[b]	3	1.85	37	40,150	11,680	3,073	1,340
With PAC[c]	1	1	50	48,650[d]	11,720[e]	3,615	640

[a] At 77°F with steam addition; PAC at 87°F without steam addition.

[b] MLSS = 10,000 mg/L, MLVSS = 8,500 mg/L, F/M at 25°C = 0.11 lb COD/lb MLVSS-day.

[c] MLSS = 20,000 mg/L, PAC = 12,000 mg/L, F/M = 0.12 lb COD/lb MLVSS-day (estimated).

[d] Based on the oxygen demand associated with biological removal of soluble organics.

[e] Powdered activated carbon comprises 60% of the solid mass.

Table 16 Design Basis for Secondary Aeration and Clarification Facilities

Activated Sludge Process	Static Mixers		Submerged Turbine with Air Sparger		Diffusers		Total Available Clarifier Surface Area (ft^2)	Solids Loading (lb/ft^2-day)	Hydraulic Loading (gpd/ft^2)
	Total Horsepower	Horsepower per 10^3 ft^3[a]	Total Horsepower	Horsepower per 10^3 ft^3[a]	Total Horsepower	Horsepower per 10^3 ft^3[a]			
Option A	1,188	1.04	1,500	1.31	2,170	1.90	20,940	22.75	168
Option B	906	1.04	1,200	1.38	1,650	1.90	16,690	28.71	211
Option C	906	1.04	1,200	1.38	1,650	1.90	16,690	28.71	211
With PAC	900	1.81	900	1.81	-	-	4,760	200[b]	740[b]

[a] Horsepower per 10^3 ft^3 of aeration basin.

[b] Based on data provided by the DuPont de Nemours Central Research and Development Department.

are approximately equivalent in their capacity to dissipate heat. To provide an optimum bioreactor temperature for soluble organics removal, provision was made for steam addition in the design of each of the conventional activated-sludge options. The appropriate design criteria for bioreactor steam addition are presented in Table 17. These data indicate the quantity of steam required to maintain an equilibrium bioreactor basin temperature of 25°C (77°F). Generally speaking, the addition of steam to a bioreactor increases the power levels available for mixing. These data are presented in Table 18 in terms of the power consumed per 1000 gal of wastewater treated. Obviously, the addition of steam to the bioreactor presents a major increase in the level of energy consumption characteristic of the biological-oxidation process.

The sludge settleability and thickening properties of the activated sludges characteristic of the conventional biological-oxidation processes are incorporated among the data presented in Table 16. The data are expressed both in the form of the surface loading rate, which is a basic parameter associated with secondary clarifier operation, and the solids loading, which is the governing parameter for thickening activated sludges. At mixed-liquor suspended-solids (MLSS) concentrations greater than 10,000 mg/L, the activated sludges evaluated in the aforementioned designs are characteristic of flocculent suspensions in the hindered settling zone of the zone settling curve. In this zone, the settling velocities tend to decrease because of the increasing density and viscosity of the suspension surrounding the sludge particles. The stratification and arching action of the settling sludges also tends to retard the settling rate.

The data presented in Table 16 specify surface loadings and solids loadings required to achieve both clarification and thickening of the activated sludges generated during biological oxidation of SFB Lurgi-process wastewaters. The solids loadings required for thickening are based on achieving an underflow concentration from the secondary clarifier of 25 g/L. All the calculated solids loadings for the conventional AS options presented in Table 16 are within an acceptable range of solids-loading rates for mechanical thickeners used for thickening AS solids.

The surface and solids-loading rates required to achieve both clarification and thickening of the carbon bio-sludges that are generated with the PAC modification of the biological-oxidation process also are presented in Table 16. These loading rates are almost an order of magnitude higher than those associated with the thickening of sludges generated in conventional biological-oxidation processes. Obviously, the PAC process shows a definite advantage over conventional AS treatment in the design of secondary clarification facilities obtaining the same solids underflow concentrations. Although, the PAC modification requires higher mixing levels in the aeration basin to maintain the carbon/bio-sludge mixture in suspension, this need is offset by the reduced size of the bioreactor required to maintain the predicted effluent quality.

5.2 COSTS AND ENERGY REQUIREMENTS

This section addresses the costs and energy requirements associated with the secondary-treatment options presented previously. A secondary-treatment process is defined as including equalization, off-specification

Table 17 Required Steam Addition to Aeration Basin to Maintain Equilibrium Basin Temperature of 25°C (77°F)

Activated Sludge Process[a]	Wastewater Temp. at Inlet to Bioreactor (°F)	Aeration System	Enthalpy[b] Before Steam Addition (Btu/lb)	Required Enthalpy Addition as Steam		Required Addition of Saturated Steam[c] (lb/hr)
				Btu/lb	Btu/hr	
Option A	103	Static mixer	36.20 (≈68.1°F)	6.86	8,364,424	7,400
		Submerged turbine	37.01 (≈68.9°F)	6.05	7,376,788	6,530
		Diffusers	30.78 (≈62.7°F)	12.28	14,973,050	13,250
Option B	82	Static mixer	35.35 (≈67.3°F)	7.71	9,400,832	8,320
		Submerged turbine	35.14 (≈67.1°F)	7.92	9,656,886	8,550
		Diffusers	33.65 (≈65.6°F)	9.41	11,473,648	10,150
Option C	73	Static mixer	29.81 (≈61.7°F)	13.25	16,155,774	14,300
		Submerged turbine	29.55 (≈61.5°F)	13.51	16,472,793	14,580
		Diffusers	28.76 (≈60.7°F)	14.30	17,436,044	15,430

[a] See Tables 15 and 16 for design basis.

[b] Required enthalpy equals 43.06 Btu/lb wastewater.

[c] 1,130 Btu/lb steam.

impoundment, biological oxidation, and solids-disposal facilities for waste biological solids and carbon sludge. The cost estimates presented represent the incremental expenditures, beyond primary and secondary oil recovery, required to attain effluent limitations commensurate with the best practicable control technology, if such limitations actually were specified for the treatment of wastewaters from an SFB Lurgi process using a lignite feedstock. In the case of the PAC modification of the biological-oxidation process, effluent quality would achieve levels commensurate with best available technology. The cost estimates do not include land costs, except where land is an integral part of the treatment process (e.g., land application treatment of biosludges).

The cost data presented are based on the specific design information incorporated in the previous section. The following list outlines the cost basis used for calculating the major capital and operating costs given in this report:

1. Concrete at $400.00 per cubic yard
2. Tank steel at $1.50 to $2.00 per pound
3. Powdered carbon at $0.35 per pound
4. Polymer at $1.35 per pound
5. Electricity at $0.025 to $0.04 per kWh
6. Labor at $10-15 per man-hour
7. Steam at $1.00 per 10^6 Btu
8. Fuel oil at $5.17 per 10^6 Btu
9. Capital recovery (amortization) at 10% over 20 years

Table 18 Total Power Consumed in the Aeration Basins during Winter Conditions (horsepower/10^3 gal treated wastewater per day)

System	Activated Sludge Option[a] A	B	C
Static mixer aerator system			
Blower	0.34	0.26	0.26
Steam[b]	0.93	1.05	1.81
Total	1.27	1.31	2.07
Submerged turbine system			
Blower	0.43	0.34	0.34
Steam[b]	0.83	1.08	1.84
Total	1.26	1.42	2.18
Diffusers			
Blower	0.62	0.47	0.47
Steam[b]	1.67	1.28	1.95
Total	2.29	1.75	2.42

[a] Wastewater temperature at inlet to bioreactor: Option A = 103°F, Option B = 82°F, Option C = 73°F. See Tables 15 and 16 for design basis for the three options.

[b] Addition of saturated steam to bioreactor at 110 psig, 344°F.

Capital costs for major equipment items such as clarifiers, blowers, carbon-regeneration furnaces, and solids-dewatering filters were obtained from equipment manufacturers. Operating and maintenance costs and energy requirements were obtained from the references cited in previous sections.

The design basis of an activated-sludge/PAC process for the treatment of wastewaters from a commercial-scale, SFB Lurgi coal-gasification facility is summarized in Table 19. These data supplement the information presented in Tables 15 and 16. Two carbon regeneration options, multiple-hearth regeneration and WAO regeneration, were examined. The PAC modification was designed to maintain substantially higher levels of MLSS under aeration than the conventional AS options. The mixing and recycle capabilities of the PAC modification were designed on the basis of recommendations made by the Central Research and Development Department of DuPont de Nemours. The other design criteria shown in Table 19 are based on the petroleum refining industry's experience with this modification of the AS process as specified by the various references cited in previous sections of this report.

The quantity of waste sludge produced by the various secondary-treatment options is incorporated among the data presented in Table 20. The

Table 19 Design Basis of an AS/PAC Process for the Treatment of Wastewaters from an SFB Coal-Gasification Process Using a Lignite Feedstock

Design Parameter	Quantity
Aeration basin	
Average hydraulic retention (hr)	24
Average sludge age (days)	50
Equilibrium carbon concentration (mg/L)	12,000
Mixed-liquor suspended solids (mg/L)	20,000
PAC feed system	
Maximum daily virgin carbon makeup, 150% avg.	
Multiple-hearth regeneration (lb/day)	5,275
Wet-air oxidation regeneration (lb/day)	2,100
PAC storage capacity, 30-day inventory	
Multiple-hearth regeneration (lb)	158,200
Wet-air oxidation regeneration (lb)	63,500
PAC slurry concentration (lb carbon/gal)	1
Powdered-carbon regeneration	
Furnace capacity (lb carbon/day)	10,550
Furnace capacity (lb sludge/day)	10,890
Regeneration heat requirements (Btu/lb carbon)	5,000
Regeneration steam requirements (lb steam/lb carbon)	1
Estimated carbon loss during regeneration	
Multiple-hearth regeneration (% of carbon regenerated)	50
Wet-air oxidation regeneration (% of carbon regenerated)	20

Table 20 Residuals Produced from Secondary-Treatment Options (lb/day)

Description	Solids Condition[a]		Activated Sludge with PAC
	A	B	
Waste solids from bio-oxidation	13,745	18,035	17,580[b]
Gravity oil-water separator bottoms	600	600	600
Flotation oil-water separator float	3,260	3,260	3,260
Total	17,605	21,895	21,440

[a] Condition A: bioreactor retention time ≃ 1.85 days.
Condition B: bioreactor retention time ≃ 2.43 days.

[b] Carbon sludge (150% average) approximately 10,550 lb/day powdered carbon.

conventional AS treatment options are represented by two solids conditions, each characteristic of different bioreactor retention times. The sludges generated during primary and secondary oil recovery also are included among the residuals produced by secondary treatment.

The capital and operating costs for the alternative secondary-treatment options are presented in Tables 21 and 22, respectively. These costs do not include sludge handling. The uncertainty regarding the peak organic loadings that might be anticipated from the SFB Lurgi process required a conservative interpretation as to the optimum size of the off-specification cooling pond. This basin was designed to provide 10 million gallons of additional storage capacity, and this volume was kept uniform for all the alternative secondary-treatment options.

It is apparent that the PAC modification offers the greatest cost advantage of any of the alternative secondary-treatment options, reflecting the sizing of the bioreactor-clarifier system. Little additional cost advantage appears to be associated with the selection of a specific subsurface aeration system. The principal factors governing the general level of expenditure associated with each of the secondary-treatment options are: (1) the degree to which the waste exhibits the desired level of biodegradability at the temperatures and organic loadings specified by the design and (2) the settleabilities characteristic of the AS suspensions in the bioreactor.

The costs associated with sludge handling for the conventional AS options incorporating both ultimate disposal and land application treatment are presented in Tables 23 and 24, respectively. The ultimate disposal costs include those of thickening, dewatering, and incineration, whereas land application treatment costs incorporate sludge thickening, digestion, and the costs associated with land preparation. It is apparent that land-application treatment of organic sludges is the more cost-effective alternative if land already is available at the site. On the other hand, if additional land must be purchased in order to implement the sludge-handling option, ultimate disposal may become more economical.

The capital costs for carbon sludge handling associated with the PAC modification for both multiple-hearth and WAO regeneration are presented in Tables 25 and 26, respectively; the operation and maintenance costs are presented in Table 27. These data indicate that the WAO regeneration option is the more cost-effective alternative for regenerating powdered carbon.

A summary of the costs and energy requirements associated with the implementation of both conventional biological oxidation and the PAC modification for the control of wastewaters from the SFB Lurgi process are presented in Table 28. An analysis of the data indicates that PAC modification of the AS process, incorporating WAO regeneration, is the most cost-effective secondary-treatment option for SFB Lurgi-process wastewaters. Moreover, the net energy requirements of this secondary treatment option are equivalent to those of conventional biological oxidation with land application of residuals.

Table 21 Capital Costs for Alternative Secondary-Treatment Options[a] (1978 dollars)

Activated Sludge Process[b]	Equalization	Cooling Pond	Sludge Treatment	Total
Option A				
Static mixers	195,300	1,569,000	4,597,800	6,362,100
Submerged turbine	195,300		4,843,300	6,607,600
Diffusers	195,300		4,810,000	6,574,300
Option B				
Static mixers	434,500		4,115,200	6,118,700
Submerged turbine	434,500		4,295,200	6,298,700
Diffusers	434,500		4,175,000	6,178,500
Option C				
Static mixers	516,000		4,124,200	6,209,200
Submerged turbine	516,000		4,304,200	6,389,200
Diffusers	516,000		4,184,000	6,269,000
With PAC				
Static mixers	195,300		1,650,050[c]	3,414,350[c]
Submerged turbine	195,300		1,843,050[c]	3,607,350[c]

[a] Costs do not include sludge handling.

[b] See Tables 15 and 16 for design basis.

[c] Includes initial powdered-activated-carbon charge costs.

Table 22 Operation and Maintenance Costs for Alternative Secondary-Treatment Options[a] (1978 dollars)

Activated Sludge Process[b]	Power Use	Labor	Maintenance Materials	Amortization	Chemicals (polymer)	Total
Option A						
Static mixers	371,100	219,000	57,900	747,290	295,650	1,690,940
Submerged turbine	391,100	226,500	60,400	776,126		1,749,776
Diffusers	491,100	271,500	62,900	772,215		1,893,365
Option B						
Static mixers	356,600	212,250	56,150	718,700		1,639,350
Submerged turbine	382,600	221,250	58,650	739,845		1,697,995
Diffusers	432,600	236,250	61,750	725,725		1,751,975
Option C						
Static mixers	360,600	213,750	57,380	729,330		1,656,710
Submerged turbine	386,600	222,750	59,880	750,475		1,715,355
Diffusers	436,600	237,750	62,980	736,355		1,769,335
With PAC						
Static mixers	343,230	194,625	48,950	401,050	118,260	1,106,115
Submerged turbine	343,230	194,625	48,950	423,720	118,260	1,128,785

[a] Costs do not include sludge handling.

[b] See Tables 15 and 16 for design basis.

Table 23 Costs Associated with Sludge Handling for the Conventional AS Options Incorporating Ultimate Disposal (1978 dollars)

Description	Solids Condition[a] A	Solids Condition[a] B
Capital costs		
Sludge thickener	210,000	210,000
Sludge dewatering	500,000	500,000
Incineration[b]	2,245,000	2,500,000
Subtotal	2,955,000	3,210,000
Piping and pumps	300,000	350,000
Total constructed cost	3,255,000	3,560,000
Engineering and contingency	488,250	534,000
Total	3,743,250	4,094,000
Annual costs		
Power consumption	15,200	17,200
Fuel consumption	139,590	165,440
Labor	86,000	93,000
Maintenance materials	27,100	28,000
Amortization	439,700	480,900
Total	707,590	784,540

[a] Condition A: bioreactor retention time ≃ 1.85 days.
Condition B: bioreactor retention time ≃ 2.43 days.

[b] Multiple-hearth furnace.

Table 24 Costs Associated with Sludge Handling for the Conventional AS Options Incorporating Land Treatment (1978 dollars)

Description	Solids Condition[a]	
	A	B
Capital costs		
Sludge thickener	210,000	210,000
Sludge digestion, thermophilic-oxygen	80,050	102,300
Landfarm, including land preparation	179,650	219,950
Subtotal	469,700	532,250
Piping and pumps	70,455	79,850
Total installation cost	540,155	612,100
Engineering and contingency	110,000	122,500
Total, excluding land cost	650,155	734,600
Land cost[b]	560,000	680,000
Total with land cost	1,210,155	1,414,600
Annual costs		
Power consumption	18,270	21,875
Fuel consumption	4,900	6,350
Labor	48,310	55,790
Maintenance materials	11,850	12,750
Amortization without land	76,370	86,290
Amortization with land	142,145	166,160
Total costs without land	159,700	183,055
Total costs with land	225,475	262,925

[a] Condition A: bioreactor retention time ≃ 1.85 days.
Condition B: bioreactor retention time ≃ 2.43 days.

[b] At $4000/acre, for moderately priced agricultural land.

Table 25 Capital Costs for Carbon Sludge Handling and Regeneration (1978 dollars)

Description	Cost
Equipment	
Powdered-carbon feed system	97,000
Solids dewatering system	425,550
Regenerated-carbon acid wash system	39,500
Subtotal	562,050
Piping and pumps	56,500
Total	618,550
Installation	371,150
Total, constructed cost	989,700
Engineering and contingency	148,500
Subtotal	1,138,200
Carbon regeneration	
System[a]	1,840,000
Engineering and contingency	368,000
Total	3,346,200

[a] Multiple-hearth furnace.

Table 26 Capital Costs for Carbon Sludge Handling and Wet-Air-Oxidation Regeneration (1978 dollars)

Description	Cost
Equipment	
Powdered-carbon feed system	97,000
Solids thickening	112,225
Subtotal	209,225
Piping and pumps	21,000
Total	230,225
Installation	138,135
Total, contructed cost	368,360
Engineering and contingency	55,500
Subtotal	423,860
Carbon regeneration	
System[a]	1,625,000
Engineering and contingency	325,000
Total	2,373,860

[a] Wet-air oxidation.

Table 27 Annual Operation and Maintenance Costs for Carbon Sludge Handling and Regeneration (1978 dollars)

Description	Cost
Multiple-hearth furnace option	
Carbon make-up costs	673,750
Power consumption	29,816
Fuel consumption	90,500
Labor	115,000
Maintenance materials	47,000
Steam addition to regeneration furnace	4,350
Amortization	393,045
Total	1,353,461
Wet-air-oxidation option	
Carbon make-up costs	270,000
Power consumption	35,200
Fuel consumption	5,000
Labor	39,000
Maintenance materials	25,000
Steam addition	4,350
Amortization	278,850
Total	657,400

Table 28 Costs of Alternative Secondary-Treatment Options for the Control of Wastewaters from Coal Gasification

Treatment Option	Capital Cost (1978 \$)	Annual Net Operating Cost (1978 \$)	Net Energy Requirement (equivalent kWh/yr)	Unit Cost (\$/10^3 gal)	Unit Energy Requirement (kWh/10^3 gal)
Biological oxidation[a]					
Incineration of residuals[b]	9,861,950	2,346,940	26,115,400	1.83	20.36
Land treatment of residuals[c]	6,768,855	1,799,050	18,401,500	1.40	14.35
Activated sludge with PAC					
Multiple-hearth-furnace regeneration	6,760,550	2,459,576	23,030,900	1.92	17.96
Wet-air-oxidation regeneration	5,788,210	1,763,515	18,066,920	1.38	14.09

[a] Activated-sludge treatment option B, using static mixers (see Tables 15 and 16).

[b] Multiple-hearth furnace.

[c] Costs exclusive of the cost of land.

6 SECONDARY-EFFLUENT DESALTING FACILITIES

6.1 CONCEPTUAL DESIGN

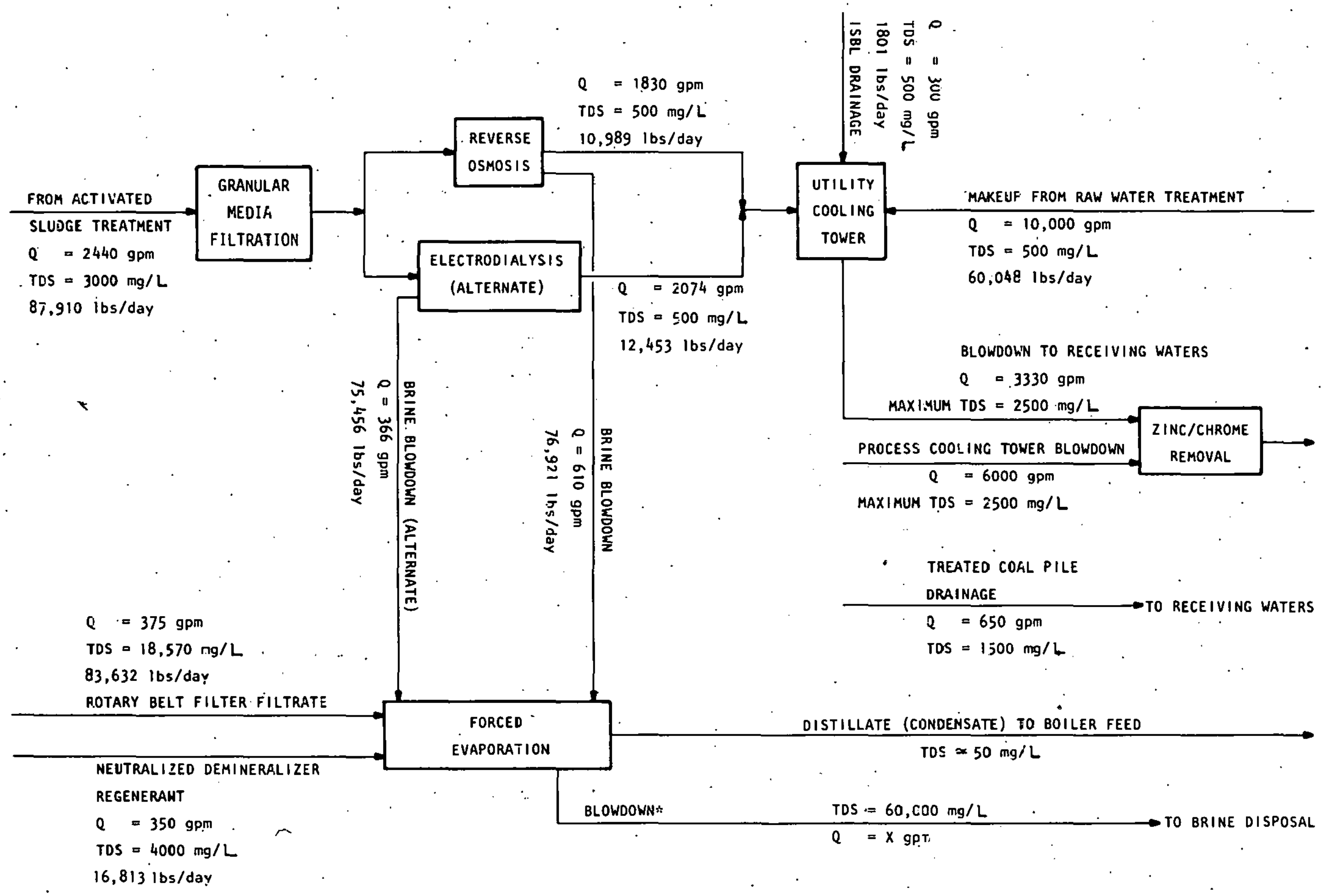
The utilization of secondary effluents for cooling tower makeup can be approached from two different perspectives: the utilization of desalted effluents as makeup to a cooling tower designed to circulate waters at low-to-medium TDS levels or the direct addition of secondary effluents to a cooling tower designed to circulate water at high TDS levels. The former option (Option A) permits the direct discharge of the cooling-tower blowdown to a receiving body, while the latter option (Option B) requires that the blowdown stream be desalted before discharge, recycled to the cooling tower, or reused as boiler-feed water.

A schematic depicting treatment Option A is presented in Fig. 13. Under this option, effluent from the secondary-treatment facility is pumped to a granular-media filtration system for the removal of residual suspended solids. The filtered effluents are passed through a membrane desalination process for removal of dissolved inorganics and nonbiodegradable/nonsorbable organic contaminants. Two membrane processes were examined, namely, reverse osmosis and electrodialysis. The reject brine stream from either membrane desalination process is sent to a forced-evaporation unit for recovery of water. Both multistage flash and vapor-compression distillation processes were evaluated. These units were designed with sufficient capacity to handle such ancillary streams as the filtrate from slag dewatering and spent demineralizer regenerant from raw-water treatment. Desalted effluents from the membrane processes provided make-up water to a low-TDS cooling tower, and condensates from the evaporator provided feed water to the boilers for steam generation. The blowdown from the distillation process either would be concentrated for further recovery of water and chemical fixation of brines, or would be disposed of in solar evaporation ponds or by subsurface injection into a confining reservoir with suitable strata.

A schematic of treatment Option B is presented in Fig. 14. This option incorporates forced evaporation of high-TDS cooling-tower blowdowns, filtrate from slag dewatering, and spent demineralizer regenerant from raw-water treatment. The condensates are used as cooling-tower makeup, and the waste brines are either concentrated for further recovery of water and chemical fixation of residuals, or disposed of in solar evaporation ponds or by subsurface injection. This is essentially a zero-discharge option, for none of the residual streams can be discharged safely to the environment because of the concentrated nature of the residuals.

6.2 COSTS AND ENERGY REQUIREMENTS

A capital cost summary for each of the desalting options discussed in the previous section is presented in Table 29 and the corresponding annual operation and maintenance costs and energy requirements are presented in Tables 30 and 31 for treatment Option A and B, respectively. In the design of the evaporators, a system operating level of 60,000 mg/L TDS in the brine was assumed for efficient operation of the distillation process, using standard materials of construction. This analysis assumes sufficient land area available for solar evaporation waste-brine disposal, and acceptable



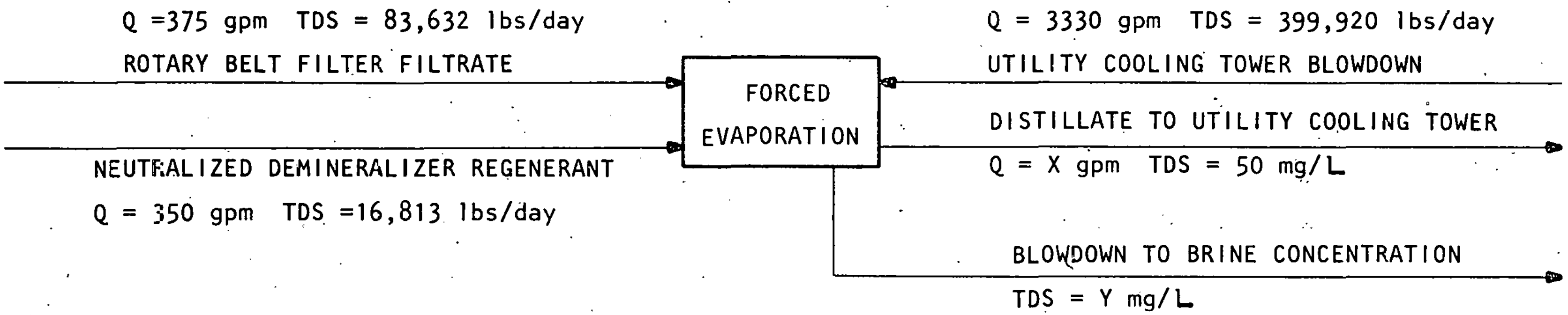
* EVAPORATOR BLOWDOWN

REVERSE OSMOSIS SYSTEM TDS_m = 177,366 lbs/day
Q = 1335 gpm
BPR = 0.225
BRINE DISCHARGE = 300 gpm
CONDENSATE = 1035 gpm

ELECTRODIALYSIS SYSTEM TDS_m = 175,901 lbs/day
Q = 1091 gpm
TDS_c = 13,425 mg/L
BPR = 0.287
BRINE DISCHARGE = 313 gpm
CONDENSATE = 778 gpm

NOTE: BPR = BRINE-TO-PRODUCT RATIO

Fig. 13 Treatment Option A for Desalting Secondary Effluents



EVAPORATOR BLOWDOWN TDS = 30,000 mg/L (2-stage system)

TDS_m = 500,365 lbs/day

Q = 4055 gpm

TDS_c = 10,275 mg/L

1ST STAGE

BPR = 0.52

CONDENSATE	2670 gpm	TDS = 50 mg/L
BRINE	1385 gpm	TDS = 30,000 mg/L

2ND STAGE

BPR = 0.998

CONDENSATE	693 gpm	TDS = 50 mg/L
BRINE	692 gpm	TDS = 60,000 mg/L

NOTE: BPR = BRINE-TO-PRODUCT RATIO

EVAPORATOR BLOWDOWN TDS = 60,000 mg/L (1-stage system)

BPR= 0.21

CONDENSATE	3,363 gpm	TDS = 50 mg/L
BRINE	692 gpm	TDS = 60,000 mg/L

Fig. 14 Treatment Option B (zero discharge) for Desalting Secondary Effluents

Table 29 Capital Cost Summary for Alternative Desalting Processes (1978 dollars)

Description	Cost
Option A	
Desalting of secondary effluents	
Electrodialysis process	3,724,380
Reverse osmosis process	4,249,380
Concentration of waste brines and desalting of ancillary streams	
Multistage flash distillation[a]	
Electrodialysis waste brines	8,720,780
Reverse osmosis waste brines	10,222,620
Vapor compression - vertical tube evaporator	
Electrodialysis waste brines	4,309,350
Reverse osmosis waste brines	5,675,730
Pumping and appurtenance	
Electrodialysis/distillation process	504,570
Reverse osmosis/distillation process	536,100
Waste brine treatment/disposal	
Evaporation lagoons[b]	
Electrodialysis/distillation process	3,615,650
Reverse osmosis/distillation process	3,447,480
Subsurface Injection	578,000
Option B	
Desalting of secondary effluents and ancillary streams	
Two-stage evaporation	
Multistage flash distillation[a]	23,916,045
Vapor compression - vertical tube evaporator	12,612,728
One-stage evaporation	
Multistage flash distillation[a]	21,151,845
Vapor compression - vertical tube evaporator	11,246,348
Pumping and appurtenance	567,600
Waste brine treatment/disposal	
Evaporation lagoons[b]	6,810,875
Subsurface injection	810,000

Description	Cost
Totals	
Option A	
Electrodialysis/distillation process	
Multistage flash distillation	
Evaporation lagoon	16,565,380
Subsurface injection	13,527,730
Vapor compression evaporator	
Evaporation lagoon	12,153,950
Subsurface injection	9,116,300
Reverse osmosis/distillation process	
Multistage flash distillation	
Evaporation lagoon	18,455,580
Subsurface injection	15,586,100
Vapor compression evaporator	
Evaporation lagoon	13,908,690
Subsurface injection	11,039,210
Option B	
Two-stage evaporation	
Multistage flash distillation	
Evaporation lagoon	31,294,520
Subsurface injection	25,293,645
Vapor compression evaporator	
Evaporation lagoon	19,991,203
Subsurface injection	13,990,328
One-stage evaporation	
Multistage flash distillation	
Evaporation lagoon	28,530,320
Subsurface injection	22,529,445
Vapor compression evaporator	
Evaporation lagoon	18,624,823
Subsurface injection	12,623,948

[a] Includes the incremental costs for additional steam generating capacity and cooling water.

[b] Excludes the cost of land.

subsurface strata for deep-well injection. Both of these waste-brine disposal techniques are subject to all the necessary environmental restrictions associated with their implementation for the ultimate disposal of desalination residuals. Nevertheless, these data were presented for comparative purposes in order to evaluate the level of expenditures associated with either of the two secondary-effluent desalting options.

It is apparent upon analysis of the data that the electrodialysis-vapor-compression distillation process with subsurface injection of waste brines offers the most cost-effective alternative approach to Option A. These data also indicate that single-stage vapor-compression distillation with subsurface injection of waste brines is the most cost-effective approach for implementation of Option B. Nevertheless, it should be noted that both water-reuse options have a cost per 1000 gal of product that is between four and five times the equivalent cost for raw-water treatment. The implementation, therefore, of either of these two desalting options could not be justified on the basis of cost alone. Any justification for the implementation of either Option A or B would have to be made on the basis of environmental considerations.

Should subsurface injection of waste brines generated by either of the two desalting options be considered unacceptable, a brine-concentration system would have to be incorporated into the proposed designs. The treatment costs for implementation of such a waste-brine-concentration system for both desalting options are presented in Table 32. This system is designed to produce a concentrated-brine slurry, at approximately 60% by weight, which then could be chemically stabilized and solidified before final disposal in a landfill along with other solid wastes.

Table 30 Annual Operation and Maintenance Costs for Alternative Desalting Processes Treatment Option A[a]

Description	Annual Cost (1978 $)										Unit Costs ($/$10^3$ gal of product)	Energy Demand (equivalent kWh/yr)
	Labor	General and Administrative	Maintenance Materials	Replacement Equipment	Chemicals	Electric Power	Fuel	Feedwater Conditioning	Amortization	Total		
Desalting of secondary effluents												
Electrodialysis process	124,150	37,000	31,500	165,000	81,760	316,495	-	57,440	437,465	1,250,810	1.15	15,824,575
Reverse osmosis process	128,850	38,655	36,750	240,000	72,100	211,900	-	57,440	499,130	1,284,825	1.34	10,579,525
Concentration of waste brines and desalting of ancillary streams												
Multistage flash distillation												
Electrodialysis waste brines	210,240	63,075	43,600	69,800	24,500	107,925	316,200	-	1,024,340	1,859,680	4.55	96,100,654
Reverse osmosis waste brines	259,970	77,995	51,150	81,800	32,650	135,420	420,360	-	1,200,745	2,260,360	4.16	127,673,248
Vapor compression-vertical tube evaporator												
Electrodialysis waste brines	185,400	55,600	21,550	21,550	24,500	-	216,300	-	506,175	1,031,075	2.52	63,332,640
Reverse osmosis waste brines	205,600	61,700	28,380	28,380	32,600	-	287,800	-	666,670	1,311,130	2.41	84,267,840
Pumping and appurtenance												
Electrodialysis/distillation process	51,950	-	-	-	-	29,670	-	-	59,267	140,887	0.08	742,118
Reverse osmosis/distillation process	54,430	-	-	-	-	31,715	-	-	62,970	149,115	0.08	793,218
Waste brine treatment/disposal												
Evaporation lagoons												
Electrodialysis/distillation process	27,120	-	-	-	-	-	-	-	424,695	451,815	2.75	-
Reverse osmosis/distillation process	25,860	-	-	-	-	-	-	-	404,940	430,800	2.73	-
Subsurface injection												
Electrodialysis/distillation process	NA	-	NA	NA	-	46,215	-	-	67,900	142,290	0.90	1,540,440
Reverse osmosis/distillation process	NA	-	NA	NA	-	44,300	-	-	67,900	142,290	0.90	1,476,460
Totals												
Electrodialysis/distillation process												
Multistage flash distillation												
Evaporation lagoon	413,460	100,075	75,100	234,800	106,260	454,090	316,200	57,440	1,945,767	3,703,192	2.47	112,747,347
Subsurface injection	-	-	-	-	-	500,305	-	-	1,588,972	3,393,667	2.26	114,287,787
Vapor compression evaporator												
Evaporation lagoon	388,620	92,600	53,050	186,550	106,260	346,165	216,300	57,440	1,427,602	2,874,587	1.92	79,899,333
Subsurface injection	-	-	-	-	-	392,380	-	-	1,070,807	2,565,062	1.71	81,439,773
Reverse osmosis/distillation process												
Multistage flash distillation												
Evaporation lagoon	469,110	116,650	87,900	321,000	104,750	379,035	420,630	57,440	2,167,785	4,125,100	2.74	139,045,991
Subsurface injection	-	-	-	-	-	423,335	-	-	1,830,745	3,836,590	2.56	140,522,451
Vapor compression evaporator												
Evaporation lagoon	414,740	100,355	65,130	268,380	104,700	243,615	287,800	57,440	1,633,710	3,175,870	2.11	95,640,583
Subsurface injection	-	-	-	-	-	287,915	-	-	1,296,670	2,887,360	1.93	97,117,043

[a] NA = data are not available.

Table 31 Annual Operation and Maintenance Costs for Alternative Desalting Processes Treatment Option B[a]

Description	Annual Cost (1978 $)									Unit Costs ($/$10^3$ gal of product)	Energy Demand (equivalent kWh/yr)
	Labor	General and Administrative	Maintenance Materials	Replacement Equipment	Chemicals	Electric Power	Fuel	Amortization	Total		
Desalting of secondary effluents and ancillary streams											
Two-stage evaporation											
Multistage flash distillation											
First stage	316,500	95,000	88,815	142,105	84,300	199,500	1,086,865	2,086,430	4,099,515	2.92	328,221,620
Second stage	180,900	54,300	30,765	49,225	21,900	114,975	282,300	722,745	1,457,110	3.99	85,942,440
Vapor compression evaporator											
First stage	316,480	94,945	46,247	46,247	84,315	-	743,642	1,086,425	2,418,301	1.72	217,737,790
Second stage	180,850	54,255	16,820	16,820	21,900	-	193,155	395,065	878,865	2.41	56,568,960
One-stage evaporation											
Multistage flash distillation	339,200	101,800	105,760	169,215	132,770	240,800	1,369,200	2,484,490	4,943,235	2.79	412,880,900
Vapor compression evaporator	372,996	111,900	56,232	56,232	106,215	-	936,796	1,320,995	2,961,366	1.67	274,295,040
Pumping and appurtenance	58,700	-	-	-	-	34,100	-	66,700	159,500	0.08	852,640
Waste brine treatment/disposal											
Evaporation lagoons	51,085	-	-	-	-	-	-	800,000	851,085	2.33	-
Subsurface injection	NA	-	NA	NA	-	95,360	-	95,065	241,565	0.66	3,405,705
Totals											
Two-stage evaporation											
Multistage flash distillation											
Evaporation lagoon	607,185	149,300	119,580	191,330	106,200	348,575	1,369,165	3,675,875	6,567,210	3.71	415,016,700
Subsurface injection	-	-	-	-	-	443,935	-	2,970,940	5,957,690	3.37	418,422,405
Vapor compression evaporator											
Evaporation lagoon	607,115	149,200	63,067	63,067	106,215	34,100	936,797	2,348,190	4,307,751	2.43	275,159,390
Subsurface injection	-	-	-	-	-	129,460	-	1,643,255	3,698,231	2.09	278,565,095
One-stage evaporation											
Multistage flash distillation											
Evaporation lagoon	448,985	101,800	105,760	169,215	132,770	274,900	1,369,200	3,351,190	5,953,820	3.36	413,733,540
Subsurface injection	-	-	-	-	-	370,260	-	2,646,255	5,344,300	3.02	417,139,245
Vapor compression evaporator											
Evaporation lagoon	482,781	111,900	56,232	56,232	106,215	34,100	936,796	2,187,695	3,971,951	2.24	275,147,680
Subsurface injection	-	-	-	-	-	129,460	-	1,482,760	3,362,431	1.90	278,553,385

[a] NA = data are not available.

Table 32 Treatment Costs for Waste-Brine Concentration (1978 dollars)

Description	Cost[a] Option A	Cost[a] Option B
Capital cost, installed	3,200,000	4,500,000
Annual cost		
Amortization	375,870	528,570
Operation and maintenance labor	113,000	157,000
Payroll extras	16,950	23,550
General and administrative	38,985	54,165
Maintenance materials	16,000	22,500
Replacement equipment	16,000	22,500
Chemicals	5,680	13,100
Power	283,825	654,375
Total	866,310	1,475,760

[a] See Figures 13 and 14 for schematics of the two secondary-effluent desalting options.

7 INTEGRATED WASTEWATER TREATMENT PROCESSES FOR EFFLUENT CONTROL

7.1 CONCEPTUAL DESIGN

This section addresses the costs, energy requirements, and water quality-related environmental impacts associated with three effluent-control options for the treatment of wastewaters from a commercial-scale, SFB Lurgi-process coal-gasification facility. The three effluent-control options are: (1) zero discharge; (2) water reuse with restricted discharge of treated effluents; and (3) unrestricted discharge of treated effluents.

The zero-discharge option is a modified version of the original CONOCO design for the treatment of SFB Lurgi-process wastewaters. A wastewater-treatment process schematic for the zero-discharge option is shown in Fig. 15. In this design, all process wastewaters and storm-water runoff are treated and recycled within the treatment facility. The modified design incorporates neutralization as a preliminary treatment process prior to flotation oil-water separation. Here, the neutralization step will serve the dual function of oil-water emulsion breaking through pH adjustment and neutralization following gravity oil separation, and neutralization prior to biological oxidation. The treatment facility employs conventional biological oxidation, tertiary filtration, and GAC treatment. The effluent-desalting facilities follow the pattern of treatment Option B discussed in the previous section.

A wastewater-treatment process schematic depicting the partial-water-reuse option is presented in Fig. 16. In this design, secondary effluents are desalted and reused for cooling-tower makeup water. The treatment facility employs the PAC modification of the AS process, tertiary granular-media filtration, and the electrodialysis process for secondary-effluent desalting. The PAC process incorporates WAO carbon regeneration, which also provides for the ultimate disposal of organic sludges from preliminary treatment. The effluent-desalting facilities follow the pattern of treatment Option A discussed in the previous section.

The wastewater-treatment process schematic that represents the treated-effluent-discharge option is presented in Fig. 17. This design incorporates the unrestricted discharge of treated effluents, which were treated to attain an effluent quality commensurate with the best available technology economically achievable. The treatment facility employs the PAC modification of the AS process, and incorporates WAO regeneration of spent-carbon sludges. The WAO process also is used to achieve ultimate disposal of organic sludges from primary and secondary oil recovery units. Secondary effluents undergo granular-media filtration before final discharge to the receiving body. This design permits unrestricted discharge of cooling-tower blowdowns and neutralized spent-demineralizer regenerants. The contaminated filtrates from the slag dewatering facilities are treated with the coal-pile drainage prior to discharge.

All treatment options provide oil-water separation of plant-battery-limits storm water, chemical coagulation and precipitation of coal-pile drainage, and neutralization of spent-demineralizer regenerants. The residuals characteristic of the proposed control options for the treatment of

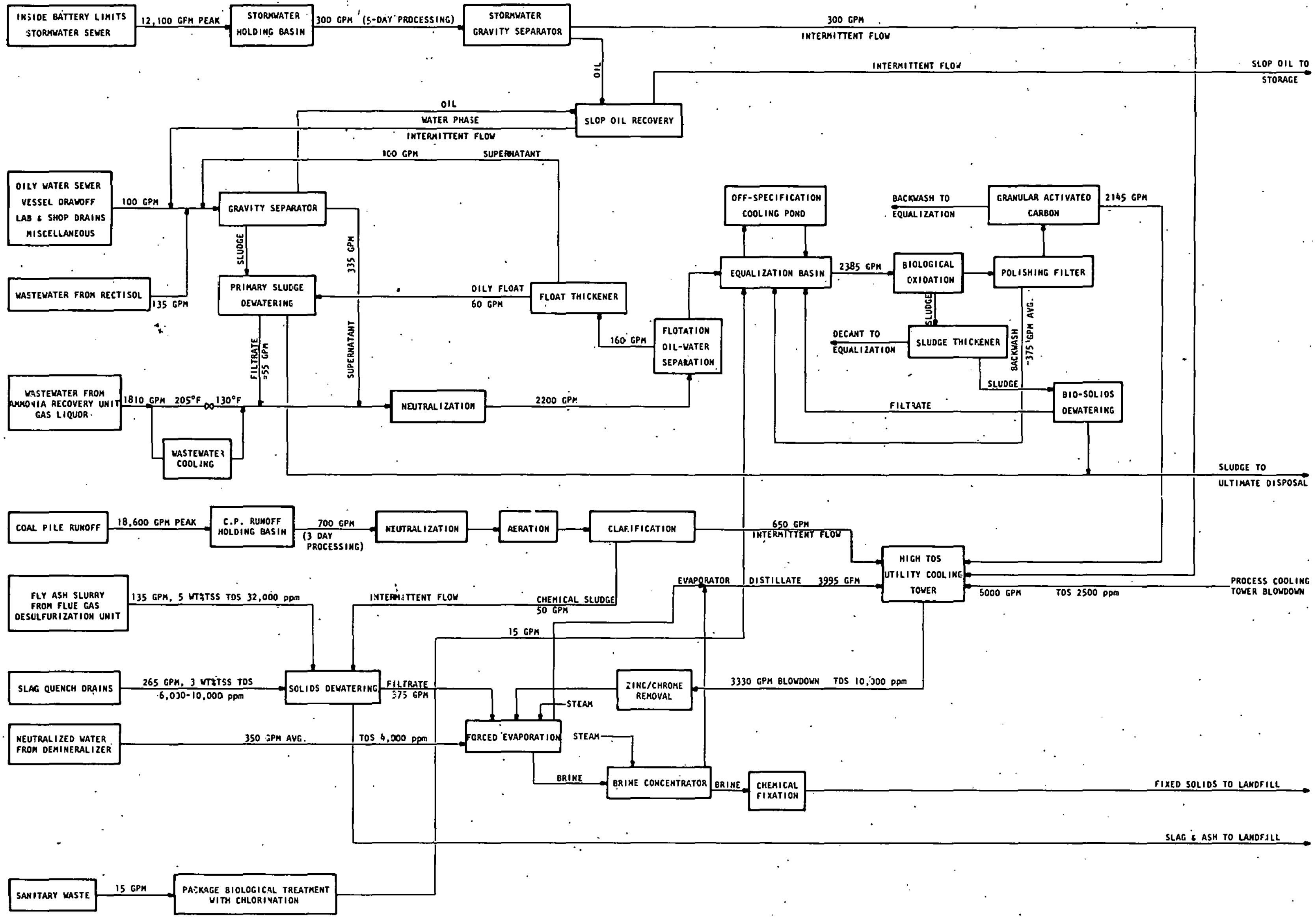


Fig. 15 Wastewater-Treatment Process Schematic, Zero-Discharge Option, Modified CONOCO Design

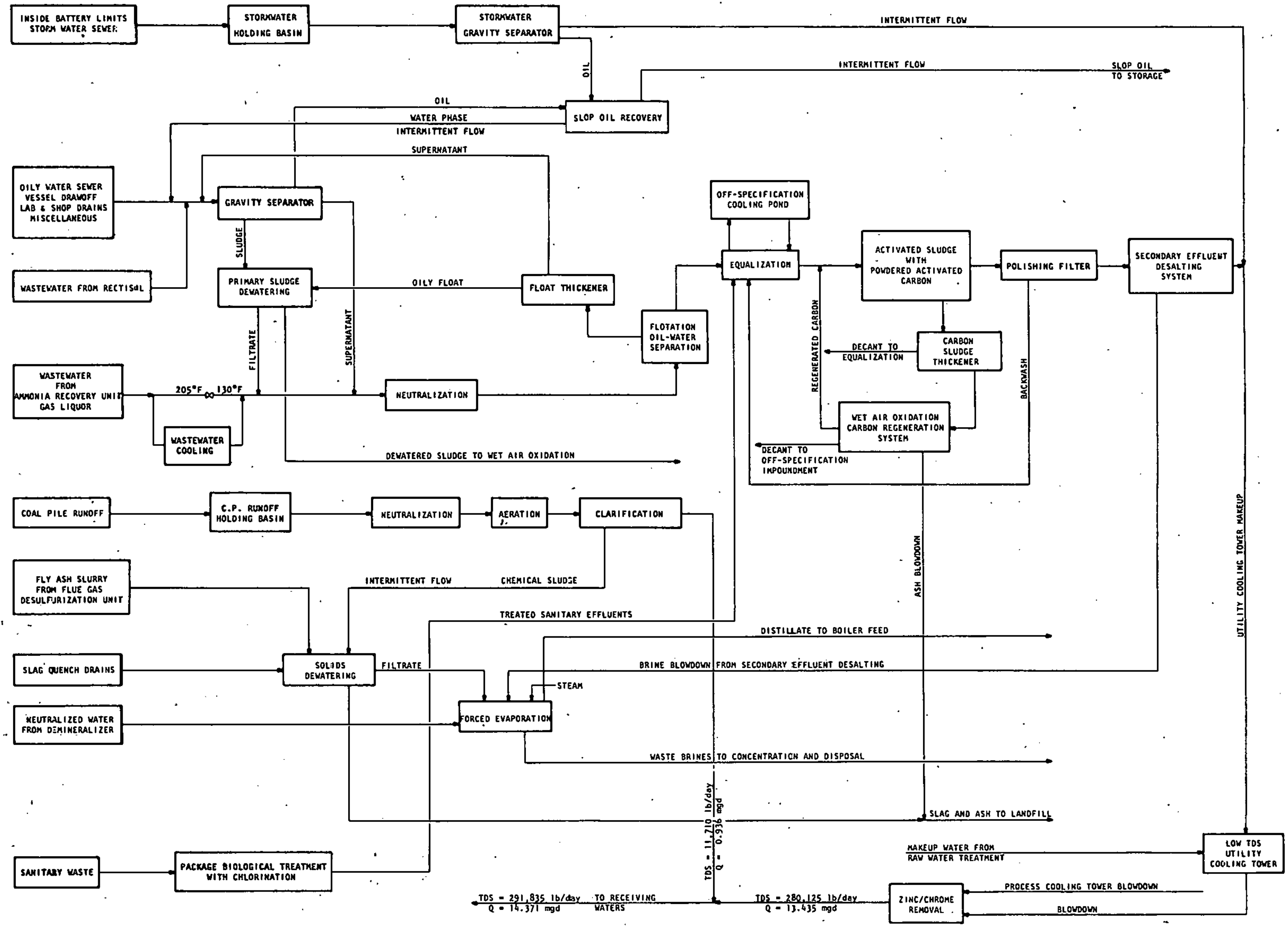


Fig. 16 Wastewater-Treatment Process Schematic, Partial-Water-Reuse Option

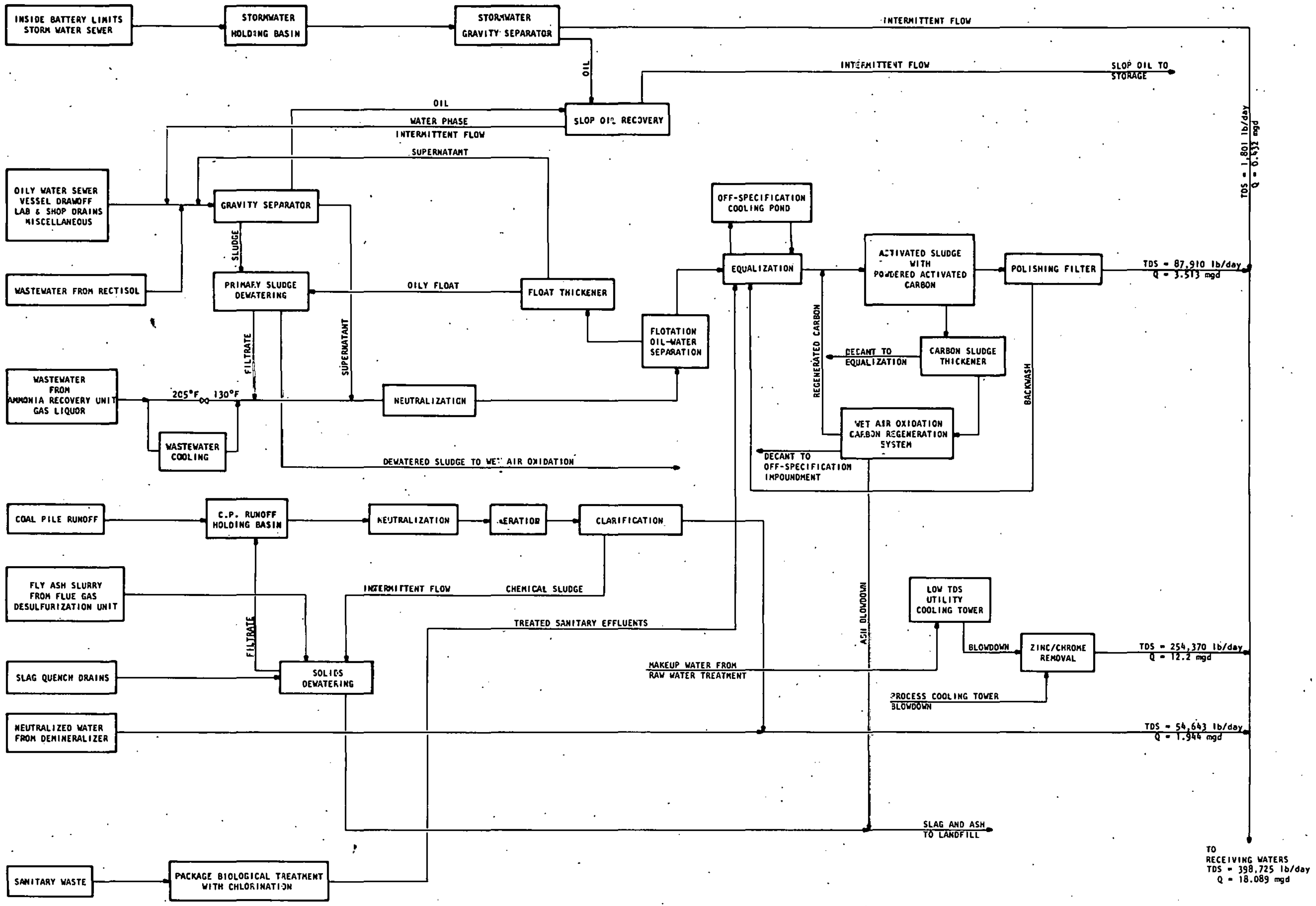


Fig. 17 Wastewater-Treatment Process Schematic, Treated-Effluent-Discharge Option

Table 33 Residuals Characteristics of Proposed Options for Treatment of Coal-Gasification Wastewaters (lb/day)

Treatment Option	Fly Ash from Flue Gas Scrubbing	Slag	Process Wastewater Residuals from Ultimate Disposal	Dissolved Solids from Chemical Treatment of Coal Pile Drainage	Solids to Landfill	Waste Brine to Disposal	Dissolved Solids to Discharge
Zero discharge	81,065	95,475	3,520[a]	27,325	207,385	495,400[b]	0
Partial water reuse	81,065	95,475	3,760[c]	27,325	207,625	203,565[d]	291,835
Treated effluent discharge	81,065	95,475	3,760[c]	124,000[e]	304,300	0	398,725

[a] Ash from the incineration of biological sludges and oil-water separator bottoms.

[b] Chemical fixation of the concentrated waste brines; 60% solids by weight.

[c] Ash from wet air oxidation of carbon sludges and preliminary treatment residuals.

[d] Subsurface injection of concentrated waste brines.

[e] Includes the residuals from the treatment of filtrate from fly ash and slag dewatering facilities.

Lurgi-type SFB process wastewaters are presented in Table 33. These data indicate that the partial-water-reuse option would discharge to the receiving water approximately 145 tons of dissolved solids per day, whereas nearly 200 tons of TDS per day would characterize the unrestricted discharges. The zero-discharge option would require the disposal of about 250 tons per day of waste brine, whereas over 100 tons per day of waste brine would be generated by the partial-water-reuse option.

The wastewater quality data characteristic of the two treated-effluent discharge options are presented in Table 34. These data represent the average treated-effluent quality that would characterize discharges from the PAC modification of the AS process treating wastewaters from an SFB-process coal-gasification facility. Generally speaking, the quantities of nonbiodegradable and nonsorbable organics that characterize the treated-effluent quality associated with the unrestricted-discharge option are substantial. This aspect reflects the apparent level of residual organics in treated effluents from the PAC-modified AS process, which were present in the form of refractory TOC and COD. For instance, more than 20% of the influent COD to the secondary-treatment facilities is neither biodegradable by conventional biological-oxidation processes nor sorbable on PAC. It also is apparent from these data that effluent-desalting processes would substantially reduce the level of residual organic material in the treated-effluent discharges. Moreover, experimental information (appendix) for the residual levels of extractable and chromatographable organics present in biologically treated gas liquors indicate that most of the apparently toxic organic material that can be measured in the SFB process wastewater would be removed down to the submicron-per-milliliter level when powdered carbon was added to the bioreactor. An obvious inference is that the water quality impact associated with submicrogram levels of toxic organics in treated-effluent discharges would be minimal.

The refractory organics should not pose a dissolved-oxygen problem for the receiving waters, since the residual BOD and suspended-solids levels of the treated-effluent discharges (partial-water-reuse and direct-discharge options) would be very low. Moreover, these discharges should meet the minimum water quality conditions applicable to most receiving waters in the United States regarding such pollutants as ammonia, oil and grease, alkalinity, pH, hexavalent chromium, and phenolics. For instance, the residual oil and grease concentration in the combined plant discharge would be less than 1.0 mg/L, while the residual phenolics would be less than 0.01 mg/L. These parameters would not even be detectable in the final plant discharges should the partial-reuse option be implemented.

The only other parameter that might present a water quality problem in the receiving waters is the residual dissolved-solids level in the combined plant discharge. Generally speaking, the TDS of fresh waters should not be changed to the extent that the biological communities characteristic of particular habitats are changed significantly. Usually, the allowable dissolved-solids discharge is set on a case-by-case basis with the permissible discharge level a function of the ambient TDS concentration in the receiving water. For example, a petrochemical complex in Illinois has a maximum-day, treated-effluent-TDS limitation of 3,500 mg/L, which is based on the ambient dissolved-solids levels in the Illinois River at the point of discharge. Placing a limit on the allowable TDS concentration to a receiving water, in

Table 34 Wastewater Quality Characteristics of Treated-Effluent-Discharge Options for the Control of Wastewaters from a Coal-Gasification Process Using a Lignite Feedstock

	Treated Process Wastewater Quality[a]		Quantity of Pollutants to Final Discharge[b]	
Parameter	Secondary Effluent[c] (mg/L)	Desalted Secondary Effluent[d] (mg/L)	Treated-Effluent-Discharge Option (lb/day)	Partial-Water-Reuse Option (lb/day)
Chemical oxygen demand	640	150	22,650	6,000
Total organic carbon	385	90	15,100	2,700
5-day biochemical oxygen demand	30	<5	900	150
Total suspended solids	<10	<0.5	2,500	100
Phenolics	<0.02	<0.005	<1	ND[e]
Oil and grease	<5	<0.5	150	ND[e]
Ammonia as N	20	<5	585	150
Total chromium	-	-	3.5	2.8
Hexavalent chromium	-	-	<0.2	<0.2
Total dissolved solids	3,000[g]	500[g]	2,650[h]	2,435[h]
pH (units)	7.5	7.5	f	f

[a] Average effluent quality characteristic of 30 consecutive days of discharges from an activated-sludge/powdered-activated-carbon treatment process.

[b] Treated process wastewaters mixed with cooling-tower blowdown and treated coal-pile drainage.

[c] Treatment includes tertiary filtration.

[d] Electrodialysis membrane process.

[e] Not detectable.

[f] pH will be maintained in the range from 6.0 to 9.0.

[g] Maximum dissolved solids in treated process wastewaters.

[h] Estimated average daily dissolved solids level in mg/L of treated effluent discharged to the receiving water.

effect, restricts the flexibility associated with cooling-tower operation, inasmuch as these cooling systems must perform system blowdowns at more frequent intervals. Permissible TDS levels are usually not specified for a receiving water, other than to prescribe that ambient dissolved-solids levels shall not change significantly during the discharge of treated effluents. Therefore, the allowable level of permissible TDS discharges is a function of the size of the receiving body and its hydrodynamic characteristics. A commercial-scale, SFB Lurgi-process coal-gasification plant probably would require access to a receiving water with flows in excess of 150 ft^3/s before either the unrestricted-discharge or partial-water-reuse options could be implemented successfully. Most obviously, before treated effluents can be discharged to a receiving water, the proper testing procedures should be followed for estimating any potential hazard that the aforementioned residuals might pose to aquatic life.

7.2 COSTS AND ENERGY REQUIREMENTS

This section evaluates the aforementioned wastewater-treatment process options in terms of the level of capital and operating expenditures required for implementation and the energy demands that would characterize the integrated treatment system. This evaluation makes certain assumptions about the level of expenditure directly attributable to by-product recovery: namely, that the costs associated with the unit processes designed to remove phenolics and ammonia are incorporated in the cost of the production facility, and that these processes are Lurgi-licensed processes that are characteristic of by-product recovery operations, not wastewater treatment. Because the costs associated with phenol and ammonia recovery were included as part of the economic analysis of the product gas, they should not be included again as a wastewater-treatment-related cost.

Because one objective of this study was to evaluate the relative unit costs and energy requirements associated with different wastewater-treatment schemes, the costs that were common to all wastewater-treatment process options were not included in the general treatment cost evaluation. Such items as treatment of plant-battery-limits storm water, along with coal-pile drainage, and slag and ash-handling systems, along with landfilling of residuals, are common to all treatment options and, therefore, would increase the cost of treatment uniformly, but would not contribute to cost differences among the alternative options.

Most of the cost data regarding the various unit processes that encompass the three wastewater-treatment process options were presented in previous sections of this report. Nevertheless, several unit processes were not included in the earlier evaluations and are presented here as supplementary data. These processes are considered ancillary to the secondary-treatment processes, which carry the largest burden of wastewater treatment; nevertheless, they do represent an important part of the integral treatment system. One such process sequence is the preliminary treatment system, namely, gravity oil-water separation, neutralization, and flotation oil-water separation. These unit processes are common to all the wastewater-treatment options, and summary cost data regarding their implementation in a commercial-scale, SFB Lurgi-process wastewater-treatment facility are presented in Table 35. Another process is tertiary GAC treatment, an integral

Table 35 Preliminary Treatment Costs (1978 dollars)

Description	Cost
Capital costs	
Gravity oil separation	92,720
Flotation oil-water separation	280,600
Neutralization	
Rapid mix tank	87,300
Sulfuric acid storage and feed	124,700
Polymer storage and feed	81,100
Subtotal	666,420
Piping and pumps	80,000
Total, constructed cost	746,420
Engineering and contingency	150,000
Total	896,420
Annual operating costs	
Power consumption	40,785
Labor	50,050
Maintenance materials	5,720
Chemicals	
Sulfuric acid	593,125
Polymer (liquid)	59,130
Amortization	105,295
Total	854,105

Table 36 Design Data Base of a Tertiary GAC System for Treatment of Effluents from AS Treated Coal-Gasification Wastewaters

Parameter	Quantity
Average secondary-effluent loadings to tertiary system (lb/day)	
COD	20,515
TOC	5,715
TSS	735
Secondary-effluent filtration, dual-media gravity filter	
Hydraulic loading rate (gpm/ft^2)	2.7
Backwash rate (gpm/ft^2)	20
Minimum backwash duration (min)	15
Minimum filter run (hr)	12
Terminal headloss (ft)	3.5
Solids capture (lb TSS/ft^2-ft headloss)	0.20
Granular-activated-carbon system	
Adsorptive capacity (lb COD/lb carbon)	0.25
Hydraulic loading rate (gpm/ft^2)	6
Empty bed contact time (min)	40
Estimated carbon loss during regeneration (% of carbon regenerated)	10
Multiple-hearth regeneration loading (lb carbon/ft^2-day)	40
Regeneration heat requirements (Btu/lb carbon)	6,000
Regeneration steam requirements (lb steam/lb carbon)	1
Furnace capacity (lb carbon/day)	82,050

part of the CONOCO design for zero discharge, design data for which are presented in Table 36. The tertiary GAC treatment process was designed to provide a level of treatment in conjunction with conventional biological oxidation that would be equivalent to that attained with the PAC modification of the AS process.

The costs associated with tertiary gravity filtration are presented in Table 37. These costs are common to all the wastewater-treatment process options. Finally, the incremental costs associated with GAC treatment are presented in Table 38. These additional cost data provide the information needed to complete the economic evaluation of the different unit processes that characterize the three wastewater-treatment process options.

Summary data for the costs and energy requirements associated with the three wastewater-treatment process options for control of wastewaters from an SFB Lurgi-process coal-gasification facility are presented in Table 39. These data depict the total capital and annual operating costs and annual net energy requirements for each treatment option. The data include all the elements of the process designs presented in previous sections of this report.

It is apparent from these data that the zero-discharge option is the most expensive approach, while the unrestricted discharge of treated effluents is the most cost-effective. The zero-discharge option, costing \$8.84/1000 gal treated, is nearly four times as expensive as unrestricted discharge of treated effluent. Moreover, its energy demand is over 13 times the equivalent energy requirement associated with the unrestricted-discharge option. The partial-water-reuse option would add approximtely \$1.50/1000 gal to the unit

Table 37 Tertiary Gravity-Filtration Treatment Costs (1978 dollars)

Description	Costs
Capital costs	
Filtration units, installed	1,030,000
Interconnecting piping, installed	125,000
Pumps, installed	154,500
Total, installed cost	1,309,500
Engineering and contingency	265,000
Total	1,574,500
Annual operating costs	
Power consumption	6,720
Labor	38,000
Maintenance materials	6,750
Chemicals (polymer)	14,500
Amortization	185,000
Total	250,970

Table 38 Tertiary Granular-Activated-Carbon Treatment Costs (1978 dollars)

Description	Costs
Capital costs	
Granular-carbon contactors, installed	1,060,000
Carbon adsorption pumping, installed	187,000
Piping, installed	115,000
Total installed cost	1,362,000
Engineering and contingency	345,000
Subtotal	1,707,000
Granular-activated-carbon regeneration system, installed	4,500,000
Engineering and contingency	1,000,000
Initial carbon inventory	255,000
Total	7,462,000
Annual operating costs	
Power consumption	51,200
Fuel consumption	930,000
Labor	129,000
Maintenance materials	22,200
Amortization	876,500
Subtotal	2,008,900
Carbon makeup	1,950,000
Steam addition to regeneration furnace	33,815
Total	3,992,715

cost of treatment associated with unrestricted discharge, and over 50 equivalent kWh of energy consumed per 1000 gal of wastewater treated. When one considers that the unit cost associated with raw-water treatment for process use is less than $0.40/1000 gal, the additional costs associated with partial reuse of treated effluents far exceed the benefit derived. The economic data for both the zero-discharge and partial-water-reuse options indicate that, given the cost for desalination treatment, complete or partial wastewater reuse within an SFB Lurgi-process wastewater-treatment facility would always be more costly than an option where wastewaters are treated to a lesser degree and discharged.

Table 39 Cost of Alternative Treatment Options for the Control of Wastewaters Generated from SFB Gasification of Lignite, Assuming a CONOCO-Type, Demonstration-Plant Design[1]

	Capital Cost (1978 $)	Annual Net Operating Cost (1978 $)	Net Energy Requirement (equivalent kWh/yr)
Zero discharge option			
Preliminary treatment of principal organic wastewaters	896,420	854,105	1,359,500
Secondary treatment of principal organic wastewaters[a]	6,118,700	1,639,350	17,830,000
Tertiary treatment of secondary effluents			
Gravity filtration	1,574,500	250,970	140,000
Granular activated carbon treatment[b]	7,462,000	3,992,715	1,280,000
Effluent desalting: secondary effluents and ancillary streams[c]	11,813,948	3,120,866	275,147,680
Solids handling			
Ultimate disposal of biological sludges[d]	3,743,250	707,590	8,285,400
Concentration of waste brines[e]	4,500,000	1,475,760	32,718,600
Chemical fixation of residuals[f]	[k]	2,665,000	180,675
Total	36,108,818	14,706,356	336,941,855
Unit cost ($\$/10^3$ gal treated)	-	8.84	-
Unit energy requirement (kWh/10^3 gal treated)	-	-	202.55
Partial water reuse option			
Preliminary treatment of principal organic wastewaters	896,420	854,105	1,359,500
Secondary treatment of principal organic wastewaters[g]	3,414,350	1,106,115	17,161,500
Tertiary treatment of secondary effluents: gravity filtration	1,574,500	250,970	140,000
Effluent desalting: membrane/distillation process for secondary effluents[h]	8,538,300	2,422,772	79,899,333
Solids handling			
Carbon sludge disposal and ancillary organic sludges[i]	2,373,860	657,400	905,420
Concentration of waste brines[e]	3,200,000	866,310	14,191,200
Subsurface injection of residuals[j]	110,000	25,510	235,425
Total	20,107,430	6,183,182	113,892,378
Unit cost ($\$/10^3$ gal treated)	-	3.72	-
Unit energy requirement (kWh/10^3 gal treated)	-	-	68.46
Treated effluent discharge option			
Preliminary treatment of principal organic wastewaters	896,420	854,105	1,359,500
Secondary treatment of principal organic wastewaters[g]	3,414,350	1,106,115	17,161,500
Tertiary treatment of secondary effluents: gravity filtration	1,574,500	250,970	140,000
Solids handling: carbon sludge disposal and ancillary organic sludges[i]	2,373,860	657,400	905,420
Total	8,259,130	2,868,590	19,566,420
Unit cost ($\$/10^3$ gal treated)	-	2.24	-
Unit energy requirement (kWh/10^3 gal treated)	-	-	15.26

[a] Biological treatment option B, using static mixers.

[b] Includes the cost of granular carbon regeneration.

[c] Vapor compression - vertical tube evaporator (one-stage system).

[d] Multiple-hearth furnace for solids incineration.

[e] Vapor compression evaporator incorporating titanium, stainless steel, and other special steel alloys for effective service life.

[f] To microencapsulate the salts in the waste slurry prior to disposal in a landfill.

[g] Activated sludge with powdered activated carbon addition using static mixers.

[h] Electrodialysis for secondary effluent desalting with vapor compression evaporation for brine concentration.

[i] Regeneration of powdered activated carbon using wet air oxidation.

[j] Deep well injection costs include wells, well field distribution system, and pumping.

[k] Process owned and operated by vendor providing service on site.

8 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations were reached as a result of this study:

(1) Combined AS/PAC treatment incorporating WAO carbon regeneration is the most cost-effective treatment technology available for the removal of organic constituents in Lurgi-type SFB process wastewaters.

(2) Direct discharge of treated effluents to a receiving body is the most cost-effective approach to the treatment of SFB coal-gasification wastewaters, and requires the lowest level of energy consumption.

(3) Zero discharge, and partial water reuse with restricted discharge of treated effluents, are not economical wastewater-treatment process options since they provide little benefit relative to the costs incurred.

(4) Solid residuals generated by implementation of either the zero-discharge or the partial-water-reuse options are extreme and the cost burden associated with effective solid waste management will be substantial.

(5) The cost of desalinating secondary effluents greatly exceeds the cost associated with the treatment of an equivalent quantity of raw water for use in a similar capacity.

(6) Subsurface injection of waste brines is more cost-effective than chemical fixation and encapsulation of residuals produced by the desalination of process wastewaters. However, implementation of such a waste-brine-disposal process will depend primarily on state and federal statutory considerations.

(7) The full environmental impacts associated with direct discharge of treated effluents are not determinable from the available information; nevertheless, quantities of most residual pollutants (i.e., ammonia, BOD, TSS, phenolics, hexavalent chromium) present in treated Lurgi-type SFB process wastewaters will be such that they should not pose a water-quality problem. Moreover, the direct-discharge option, within the limits of proper environmental constraints, should be considered the most cost effective control-technology option for Lurgi-type SFB process wastewaters.

(8) The environmental impact associated with residual nonbiodegradable/nonsorbable organics and total dissolved solids should be carefully considered in the further evaluations of the direct-discharge option. Although, the discharge of treated effluents that contain these pollutants should not cause adverse environmental impacts in a large receiving water body, their presence warrants the examination of potential aquatic-toxicity problems. This recommendation requires implementation of procedures for assessment of potential hazards of toxic residuals in the treated discharges. Such an assessment must incorporate analyses of the environmental fate of the residual organics and their consequent ecological effects.

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REFERENCES

1. Continental Oil Company, *The Pipeline Gas Demonstration Plant Design and Evaluation of Commercial Plant, Volume 2: Process and Project Engineering Design*, U.S. Department of Commerce, NTIS FE-2542-10 (Vol 2) (1979).

2. Water Purification Associates, *Wastewater Treatment in Coal Conversion*, U.S. Environmental Protection Agency, EPA/600/7-79/133 (June 1979).

3. Battelle-Northwest, *Appraisal of Powdered Activated Carbon Processes for Municipal Wastewater Treatment*, U.S. Department of Commerce, NTIS PB-272-933 (Sept. 1977).

4. Pullman Kellogg, *Coal Conversion Control Technology, Volume 1. Environmental Regulations Liquid Effluents,* U.S. Department of Commerce, NTIS PB80-126469, (Oct. 1979).

5. U.S. Environmental Protection Agency, *Innovative and Alternative Assessment Manual,* EPA 430/9-78-009 (Feb. 1980).

6. Southwest Research Institute, *Desalting Cost Calculation Procedures,* Texas Water Development Board and Office of Saline Water, (Feb. 1970).

7. Hutchins, R.A., *Thermal Regeneration Costs,* Chemical Engineering Progress, 71 (5) (May 1975).

8. Scherer, C.R., and Chan, M.C., *Estimating Short-Run Operating Costs for a Reverse Osmosis Desalting Plant*, Desalination, Vol. 18 (1976).

9. TRW Environmental Engineering Division, *Environmental Assessment Report: Lurgi Coal Gasification Systems for SNG,* U.S. Environmental Protection Agency, EPA/600/7-79/120 (May 1979).

10. Tennessee Valley Authority, *Characterization of Coal Pile Drainage,* U.S. Environmental Protection Agency, EPA/600/7-79/051 (Feb. 1979).

11. University of California, *Processing Needs and Methodology for Wastewaters from the Conversion of Coal, Oil Shale and Biomass to Synfuels,* U.S. Department of Energy, DOE/EV-0081 (May 1980).

12. Stamoudis, V.C., and R.G. Luthy, *Biological Removal of Organic Constituents in Quench Waters from High-BTU Coal-Gasification Pilot Plants,* Argonne National Laboratory, ANL/PAG-2 (Feb. 1980).

13. Stamoudis, V.C., and Luthy, R.G., *Biological Removal of Organic Constituents in Quench Waters from a Slagging, Fixed-Bed Coal-Gasification Pilot Plant,* Argonne National Laboratory, ANL/PAG-1 (Feb. 1980).

14. Stamoudis, V.C., and R.G. Luthy, *Determination of Biological Removal of Organic Constituents in Quench Waters from High-BTU Coal-Gasification Pilot Plants,* Water Research, Vol. 14 (1980).

15. Catalytic, Inc., *Applicability of Coke Plant Control Technologies to Coal Conversion,* U.S. Environmental Protection Agency, EPA/600/7-79/184 (Aug. 1979).

16. TRW, Inc., *Applicability of Petroleum Refinery Control Technologies to Coal Conversion,* U.S. Department of Commerce, NTIS PB-288-630 (Oct. 1978).

17. North Carolina University, *Assessment of Coal Conversion Wastewaters: Characterization and Preliminary Biotreatability,* U.S. Environmental Protection Agency, EPA/600/7-78/181 (Sept. 1978).

18. Pittsburgh University, *Environmentally Acceptable Disposal of Coal Conversion Solid Waste Residuals,* U.S. Department of Energy, DOE/ET/20023-1 (Aug.1979).

19. Cooke, R, and P.W. Graham, *The Biological Purification of the Effluent from a Lurgi Plant Gasifying Bituminous Coals,* Int. J. Air and Water Pollution, Vol. 9 (1965).

20. Luthy, R.G., D.J. Sekel, and J.T. Tallon, *Biological Treatment of Synthetic Fuel Wastewater,* J. of the Environmental Engineering Division, *106*(3) (June 1980).

21. Neufeld, R.D., and Valiknac, T., *Inhibition of Phenol Biodegradation by Thiocyanate,* J. WPCF, *51*(9) (Sept. 1979).

22. Luthy, R.G., *Cyanide and Thiocyanate in Coal Gasification Wastewaters,* WPCF, *51*(9) (Sept. 1979).

23. Stamoudis, V.C., R.G. Luthy, and W. Harrison, *Removal of Organic Constituents in a Coal-Gasification Process Wastewater by Activated Sludge Treatment,* Argonne National Laboratory, ANL/WR-79-1 (June 1979).

24. Harrison, W., R.D. Flotard, and D. Ford, *Assessment of Activated Carbon for Environmental Control of Trace Organics in Petroleum Refinery Wastewaters,* Argonne National Laboratory, ANL/WR-79-3 (Mar. 1979).

25. Ferguson, J.F., et al., *Activated Carbon in Contact Stabilization Activated Sludge,* J. WPCF, 51(9) (Sept. 1979).

26. Grieves, C.G., L.W. Crane, and D.G. Venardos, *Powdered Versus Granular Carbon for Oil Refinery Wastewater Treatment,* J. WPCF, *52*(3) (Mar. 1980).

27. Klemetson, S.L., and M.D. Scharbow, *Filtration of Phenolic Compounds in Coal-Gasification Wastewater,* J. WPCF, *51*(11) (Nov. 1979).

28. Lonsdale, H.K., *Recent Advances in Reverse Osmosis Membranes, Desalination,* Vol. 13 (1973).

29. Chian, E.S.K., and H.H.P. Fang, *Physicochemical Criteria of Removal of Trace Organics by Reverse Osmosis,* Water 1976, AIChe Symposium Series, Vol. 73 (1977).

30. Fang, H.H.P., and E.S.K. Chian, *Removal of Dissolved Solids by Reverse Osmosis, ibid.*

31. Lynch, M.S., and M.S. Mintz, *Membrane and Ion Exchange Processes,* A Review, JAWWA, *64*(11) (Nov. 1972).

32. Awerbuch, L., and A.N. Rogers, *Evaporation of Blowdown Water in Power Plants,* Water 1976, AIChe Symposium Series, Vol 73 (1977).

33. Hill, R., *Subsurface Waste Disposal in Texas,* Agency Publication No. 72-05, Texas Department of Water Resources, Austin (n.d.).

34. Engineering-Science, Inc., *An Evaluation of Existing and Emerging Control Technology for the Treatment of Petroleum Refinery Wastewaters and Sludges,* prepared for the University of Tulsa (Aug. 1979).

35. U.S. Environmental Protection Agency, *Activated Carbon Treatment of Industrial Wastewaters,* EPA/600/2-79-177 (Aug. 1979).

36. Robertaccio, F.L., *Combined Powdered Activated Carbon-Biological Treatment: Theory and Results,* presented at the second open forum on Management of Petroleum Refinery Wastewaters, Tulsa, Okla. (June 1977).

37. Culp, G.L. and A.J. Shuckrow, *What Lies Ahead for PAC?, Water and Wastes Engineering* (Feb. 1977).

38. Gitchel, W.B., J.A. Meidl, and W. Burant, *Carbon Regeneration by Wet Air Oxidation,* Chemical Engineering Progress, *71*(5) (May 1975).

APPENDIX

BENCH-SCALE TREATABILITY AND ORGANICS-REMOVAL STUDY USING GFETC'S RUN RA-52 PROCESS QUENCH WATER

by

Richard G. Luthy, Vassilis C. Stamoudis, and James R. Campbell

A.1 EXPERIMENTAL DESIGN

Figure A.1 shows a schematic representation of the experiments performed in this investigation. This study used slagging, fixed-bed (SFB) pilot-plant quench waters obtained from the Grand Forks Energy Technology Center (GFETC) during a run using lignite for feedstock. The process quench water, hereafter called "wastewater," was processed through three treatment steps, including solvent extraction, steam stripping, and biological oxidation with and without addition of powdered activated carbon (PAC). Analyses were performed on raw wastewater and on sample composites following each treatment step in order to document removal of standard chemical constituents as well as to characterize and assess removal of organic contaminants. High-performance liquid chromatography (HPLC) and combined gas-chromatography/mass-spectrometry (GC/MS) techniques were employed to follow the removal of organic compounds during treatment. Organic analyses on raw and pretreated samples included characterization of organics common to both suspended and aqueous phases.

A.2 EXPERIMENTAL TECHNIQUES

A.2.1 Sample Representiveness and Collection

Process quench water was obtained during Run RA-52 that used Indian Head lignite from North Dakota. A description of pilot-plant effluent distributions and operating conditions at the times sample collections were taken are provided in Ellman et al. (1979). It is recognized that this quench water is not representative in a quantitative sense of wastewater that may be generated in a demonstration or commercial facility due to various process factors that differ between a pilot plant and a larger facility. These factors include: gasifier operating conditions; raw-gas quenching design; and efficiency and differences in flow rates and combinations of various aqueous quench and process streams. Despite these factors, it is envisioned that the pilot-plant water employed in this study is representative in a qualitative fashion of quench water that may be produced in a larger-scale facility gasifying lignite. In this respect, the quench water provides a reasonable matrix of inorganic and organic contaminants and is useful for estimating treatment characteristics of a complex coal-conversion wastewater.

Decanted quench water was collected during steady-state pilot-plant operating conditions. Wastewater was collected in a fashion to minimize contribution of start-up water, and was shipped immediately to Carnegie-Mellon University via freezer truck. Wastewater was shipped and stored in plastic

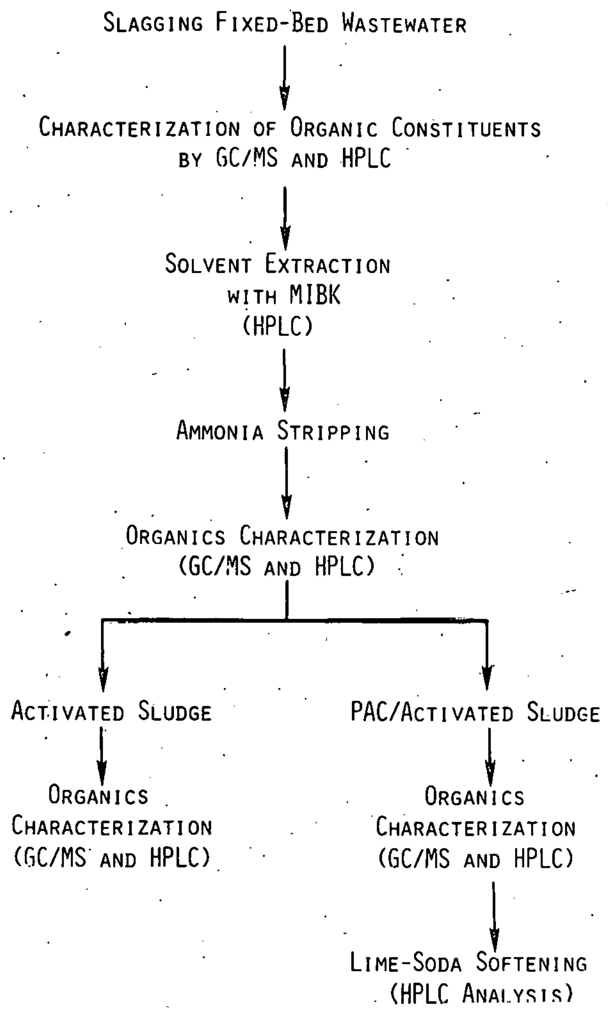

Fig. A.1 Experiments to Evaluate a Coal-Gasification Wastewater-Treatment Train (analytical methods for organic constituents shown in parentheses)

containers owing to the large quantities being handled. Several long-term studies, using this wastewater, have been conducted in which samples have been preserved against degradation by freezing until needed in the experiments.

A.2.2 Wastewater Pretreatment

Wastewater pretreatment included solvent extraction and ammonia stripping. Potential solvents were screened for use in this investigation on the basis of measured phenolic distribution coefficients with raw wastewater. Solvent distribution coefficients were determined by batch extraction, using Teflon separatory funnels, at solvent-to-liquid ratios varying from 0.2 to 1.0 in accordance with procedures recommended by Mayhue (1972).

After selection of the appropriate solvent, wastewater was processed in 16-L batches by mixing and settling. The bench-scale procedure simulated a staged extraction process by contacting wastewater with fresh solvent in five steps at a solvent-to-liquid ratio of 1:15 (V_s/V_w). This technique was chosen by experimental design to reduce phenolics to less than 10 mg/L. Twenty minutes was allowed for each mixing and settling step, after which most of the solvent was decanted by syphoning. The solvent-water interfacial layer was transferred to a separatory funnel to remove the remainder of the solvent. All extraction equipment was cleaned prior to the first and fifth extraction to prevent sample contamination due to handling.

Ammonia removal was performed in a manner that simulated free- and fixed-leg steam stripping. Solvent-extracted wastewater was heated to 85-100°C in a covered container, with condenser, in the presence of a slight nitrogen purge (28.4 L/h). Ammonia was first stripped without chemical addition to release that fraction of ammonium ion that was compensated by deprotonated acid species, *viz* dissolved CO_2 and H_2S. Lime slurry was then added to raise sample pH and the stripping process was continued until NH_3-N was reduced to 30 mg/L. The ammonia stripping process also effectively removed residual dissolved solvent from the water.

A.2.3 Biological Oxidation

The biological reactors employed in this study were complete-mix, air-activated sludge reactors with internal clarifiers. Reactors were supplied wastewater continuously under conditions in which mean hydraulic-residence time, mean sludge-residence time, and PAC reactor equilibrium concentration were held as experimental constants. Mean sludge-residence time was controlled at 30 and 20 days for the activated sludge and the PAC/activated-sludge reactors, respectively, by withdrawing a sample of mixed liquor, filtering, and returning the filtrate to the reactor. Effluent suspended solids were analyzed regularly and these values were used to compute the amounts of sludge to waste on a daily basis according to the following:

$$W = \frac{V\left(\frac{1}{\theta_c}\right)X_1 - QX_2}{X_1}$$

where:

W = sludge-wasting rate, L/d

θ_c = mean sludge-residence time, d

V = reactor volume, L

X_1 = reactor mixed-liquor, volatile suspended solids (MLVSS) mg/L

X_2 = effluent volatile suspended solids (VSS), mg/L

Q = flow rate, L/d

It was observed that biomass and PAC were intimately mixed in the form of bacteria/carbon flocs, hence the sludge wasting procedure for the PAC/activated-sludge reactor assumed a homogeneous suspension. PAC was added to the PAC/activated-sludge reactor on a daily basis to maintain a steady PAC concentration of 5000 mg/L, i.e., with a sludge age of 20 days, 5% of the PAC inventory was removed from the reactor daily and replaced with fresh carbon. The PAC employed in this investigation was Amoco PC-21 at a concentration of 5000 mg/L in the mixed liquor. Selection of this carbon type and dose was guided by prior PAC/activated-sludge studies with nonsolvent-extracted GFETC wastewater (Luthy et al., 1980). Previous adsorption isotherm testing of several representative PACs with raw GFETC wastewater has shown that PX-21 possessed the best adsorption characteristics for phenolics, COD, and color. Physical properties of this PAC are summarized in Table A.1.

Nutrient levels of Fe, K, Mg, and P were added to biological reactor influent. The biological reactors were operated with a relatively long value of hydraulic detention time consistent with the need to conserve a limited amount of wastewater through the duration of the biological-oxidation study. The activated-sludge and PAC/activated-sludge reactors were seeded with sludge obtained from a local coke plant as well as with sludge used in previous biological-oxidation studies with phenolic gasification wastewaters. The reactors were acclimatized to solvent-extracted, ammonia-stripped wastewater over a 30-d period. After this, the reactors were managed under steady conditions for a 60-d balance period. At the end of the 60-d interval, the reactors were operated for an additional period to provide an approximate 10-d sample composite for organic characterization.

Influent feed reservoirs, effluent collection vessels, and biological reactors were covered with aluminum foil to prevent external contamination. All glassware was solvent-rinsed and acid-cleaned prior to use in the experiment. Effluent samples were analyzed and/or preserved on a daily basis in accordance with recommended procedures (APHA, 1975; Luthy, 1978).

Table A.1 Typical Properties of Amoco Powdered Activated Carbon PX-21

Property	Value
Surface area, BET (m^2/g)	2800-3500
Iodine number	2800-3600
Methylene blue adsorption (mg/g)	400-600
Phenol number	13-16
Total organic carbon index[a]	300-800
Total pore volume (cm^3/g)	1.4-2.0
Bulk density (g/cm^3)	0.27-0.32
Screen analysis (wt %)	
Passes 100 mesh	90-99
Passes 200 mesh	70-85
Passes 325 mesh	55-70
Ash (wt %)	2.0 max
Water solubles, inorganic salts (wt %)	1.0 max
pH of carbon	7-9

[a] Municipal wastewater TOC adsorption capacity relative to Aua-Nuchar A or Calgon 300, which are assigned a value of 100.

A.3 ANALYTICAL PROCEDURES

Wet-chemical analytical procedures followed those presented in *Standard Methods*. BOD determinations were performed on settled samples; raw and influent samples were seeded with acclimatized bacteria withdrawn from the biological reactors. Biological-reactor-effluent COD and TOC measurements were performed on filtered samples in order to exclude suspended biomass and PAC. Analyses of solvent extracted samples prior to ammonia stripping for TOC, COD, and BOD were performed after gentle heating to expel residual solvent. Phenolics were determined by distillation and 4-aminoantipyrine color development. Thiocyanate was measured by the ferric nitrate procedure (APHA, 1975) as well as by a technique utilizing copper-pyridine reagents with chloroform extraction (Luthy, 1978).

A.3.1 HPLC Analysis

Determinations for certain polycyclic aromatic hydrocarbons (PAH) were accomplished with a Perkin-Elmer Series 3, high-pressure liquid chromatograph. This included a constant flow·gradient pumping system, a 5-μ ID x 250 mm HC-ODS Sil-X reverse-phase column with guard column, a fixed-wavelength UV detector at 254 nm, a fluorescence detector with variable excitation and emission wavelengths, and compatible strip-chart recorders. Compromise fluorescence wavelengths of excitation and emission were chosen with a solvent program employing acetonitrile and water adapted from Ogan et al. (1979).

Procedures for sample extraction and analysis were modified from the EPA method for the determination of PAH in effluents (Federal Register, 1979). Methylene chloride was chosen as the extraction solvent owing to its excellent solvent properties for PAH, its low boiling point, and its tendency to show less emulsification problems (Acheson et al., 1976). Samples were filtered through 0.45-m glass fiber filters to provide samples for PAH analysis of suspended and aqueous phases. Aqueous- and suspended-phase samples were extracted for twenty-four hours with the suspended-phase sample placed in a pre-cleaned extraction thimble. The presence of phenolics and other hydroxylated compounds interfered during column chromatography cleanup and HPLC analysis of suspended-phase samples. This problem was resolved by use of modified procedures for sample cleanup. The procedure employed aluminum column chromatography (Schiller and Mathiason, 1977) in which the sample extract was precoated on alumina, added to the column, and eluted in succession with hexane, 1:1 hexane and ethyl ether, ethyl ether, and methylene chloride. Eluates were collected and concentrated for HPLC analysis.

All glassware was acid-digested and solvent-rinsed with methanol and methylene chloride; all solvents were high-purity HPLC grade; laboratory water was filtered, deionized, and purified by a carbon-bed system. Analytical standards were obtained from Aldrich Chemical Company.

A.3.2 GC and GC/MS Analysis

Samples were filtered through 0.45-μ glass fiber filters to separate suspended and aqueous phases. Organic constituents in the suspended-phase (suspended solids, SS) were Soxhlet extracted by methylene chloride. The extract was then fractionated into acid, base, and neutral fractions, using generally accepted techniques. The filtered aqueous phase (filtered water, FW) was extracted as done previously (Stamoudis and Luthy, 1980a), using a pH-fractionation method and methylene chloride, into acid, base, and neutral fractions. The extraction scheme is shown in Fig. A.2.

Organics in all fractions were analyzed by both GC and GC/MS. The GC data were used primarily for quantification and the GC/MS data for compound identification. Two GC instruments were used, a Hewlett-Packard (HP) Model 5840 and an HP Model 5880, equipped with HP, Level 4, computer control and reporting capability. Flexible, fused-silica, wall-coated, open-tubular capillary columns were used for chromatographic separation of the organics in the fractions. The columns were purchased from HP and were 50-m long, coated with SP2100 (methyl silicone), and were of either 0.21- or 0.31-mm I.D. The wider bore columns were found to be more durable and suitable for analysis of these fractions. The GC oven temperature was programmed from 20-270°C at 2°C/min with a 2-min hold at 20°C, after injection. The GC/MS system used was an HP Model 5984A equipped with an HP Model 5840 GC and an HP Model 5934A Data System. A Techtronix Model 4631 Hard Copy Unit and a Zeta Model 130-10 Incremental Plotter were also used. All GC instruments were equipped with the HP Model 1883B Grob-type split/splitless capillary inlet system operated in the splitless mode, allowing continuous septum purge except during the first 0.6 min after injection. The carrier gas was VHP He and a flame-ionization detector (FID) was used for all GC analyses. All mass spectra were electron impact (70 eV).

The scope and time frame of this investigation did not permit comparison of all identified compounds with authentic standards. However, representative standards were used to obtain both retention times and mass spectra for direct comparisons. The mass spectra usually were compared to those given in the *Registry of Mass Spectral Data* (Stenhagen et al., 1974) or the *EPA/NIH Mass Spectral Data Base* (Heller and Milne, 1978). The *ASTM Index of Mass Spectral Data* (ASTM Committee E-14, 1969) was also often consulted, but computer searches of mass spectra data banks were not particularly useful in this work. Emphasis was placed upon the identification of compound classes rather than upon differentiating between specific isomers. Therefore, isomers are reported as C_2-, C_3-, . . ., C_n-homologs where n refers to the total number of carbon atoms in saturated alkyl substitutions attached to the parent organic compound.

The scope of this presentation does not allow for a thorough discussion of the accuracy of these analyses. The precision of the chromatographic analysis is typically ±5%. However, due to variations in efficiency of extraction (Stamoudis et al., 1979), and due to differing FID response factors, FID response-factor calibrations were run for only a few representative compounds in each compound class. Considering the varieties of sample handling procedures and the differing nature and concentration levels of chromatographable material contained in each sample, a realistic figure for the absolute accuracy of the analyses reported here is estimated at about ±20%. Percentage removal values were estimated by comparison of influent and effluent total-ion chromatograms of the various compounds. For this reason, percentage-removal values are considered to be more accurate than concentration values, assuming comparable extraction efficiencies of influent and effluent samples.

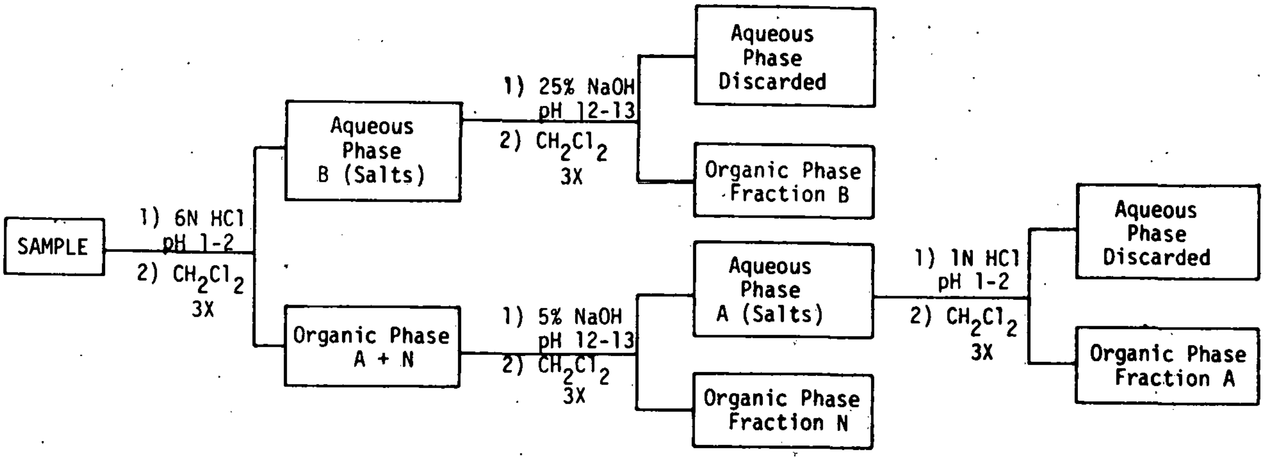

Fig. A.2 Extraction Scheme for Raw Sample and Effluent Samples

A.4 EXPERIMENTAL RESULTS

A.4.1 Solvent Selection

Table A.2 shows equilibrium phenolic distribution coefficients with raw quench water and methyl isobutylketone (MIBK), n-butyl acetate, di-isopropyl ether (DIPE), and toluene where the equilibrium distribution coefficient, K_D, is defined as

$$K_D = \frac{C_s}{C_w} = \frac{\left(W_o - W_1\right)/Vs}{W_1/V_w}$$

where:

C_s = phenolic concentration in solvent

C_w = phenolic concentration in water

W_o = initial phenolic concentration in water, mg

W_1 = final phenolic concentration in water, mg

V_s = solvent volume, L

V_w = quench water volume, L

These values generally agree with those reported in the literature for pure phenol-water-solvent systems (Earhart et al., 1977; and Kiezyk and Mackay, 1971, 1973). MIBK gave the highest distribution coefficient, and additional tests performed with this solvent to evaluate its effectiveness in successive extractions supported the value of $K_D \approx 100$ for phenolics at $V_s/V_w = 0.667$. Since MIBK showed the largest distribution coefficient for wastewater phenolics, this solvent was selected for use in treating the quench water prior to ammonia stripping.

Table A.2 Equilibrium Phenolic Distribution Coefficients with Raw Wastewater

Solute Volume (mL)	Solvent Volume (mL)	K_D			
		MIBK	NBA	DIPE	Toluene
250	50	106	82	31	3.1
250	100	90	77	29	2.7
250	150	103	79	30	2.3
250	200	91	62	30	2.4
250	250	138	73	24	2.5
Avg. value of K_D		106	75	29	2.6

A.4.2 Solvent Extraction

During the course of this investigation, it was necessary to process six batches of quench water through solvent extraction and ammonia stripping. Average raw and treated water characteristics are summarized in Table A.3. Raw wastewater averaged 5500 mg/L in phenolics and 32,000 mg/L in COD, and there were associated high values of TOC and BOD. The water also contained high levels of organic-nitrogen, NH_3-N, SCN^-, S^{2-}, and alkalinity. Most of the cyanide was present as a complexed species not amenable to chlorination. These raw wastewater characteristics are similar to those reported for previous investigations with GFETC wastewater (Stamoudis and Luthy, 1980a, 1980b; Luthy et al., 1980).

Batchwise solvent extraction was performed in five steps with clean solvent at each step at a constant water-to-solvent ratio of 15:1 (V_w/V_s). Final phenolic concentration ranged from 1 to 10 mg/L with an average value of 5 mg/L. Solvent extraction resulted in reductions of TOC, COD, and BOD of 82, 88, and 89%, respectively. The reduction in TOC and COD is significantly greater than that which can be accounted for by reduction of phenolics alone. This fact indicated that solvent extraction with MIBK removed a variety of other compounds in addition to phenolics. Data in Table A.3 can be used to calculate approximate distribution coefficients for COD and BOD both equal to 8 and a value for TOC of 6 according to

$$\frac{W_n}{W_o} = \left(\frac{V_w}{KV_s + V_w}\right)^n$$

where:

n = the number of successive extractions with clean solvent, i.e. 5.

Table A.3 Slagging Fixed-Bed Wastewater Characteristics during Pretreatment[a] (all units are mg/L unless otherwise stated)

Wastewater Parameters	Raw Wastewater Run RA-52	Solvent Extracted Wastewater (MIBK)	Ammonia Stripped Wastewater
TOC	11,100	1,950	1,380
COD	32,000	3,900	2,980
BOD	26,000	2,900	1,820
Phenolics	5,500	5	3
Freon extractable	410	-	10
Org-N	115	51	33
NH_3-N	6,300	4,400	30
NO_3^--N	<5	<5	<5
SCN^-	120	110	105
CN^-_{TOT}	1.8	1.5	1.5
CN^-_{Amn}	0.1	-	-
S^{2-}	100	75	<10
Total S (as S)	380	156	-
Ca^{2+} (as $CaCO_3$)	-	10	740
Alkalinity (as $CaCO_3$)	20,700	16,300	850
pH (units)	8.6	8.6	8.8
Conductivity (μmho/cm)	20,000	18,600	1,490
Color (Pt-Co units)	≈500	≈500	≈700

[a] Analyses of solvent extracted samples for TOC, COD, and BOD were performed after gentle heating to expel residual MIBK.

A.4.3 Ammonia Stripping

Raw wastewater after solvent extraction contained an average total ammonia concentration of 4400 mg/L with alkalinity of 16,300 mg/L as $CaCO_3$ at pH = 8.6. The fraction of ammonia that can be liberated by steam stripping without chemical addition may be estimated as about 80%:

$$\text{fraction of free ammonia} = \frac{\text{alkalinity} - (NH_3\text{-N})}{NH_3\text{-N} + NH_4^+\text{-N}}$$

where all concentrations are expressed as equivalents per liter and the dissociation constant for NH_4^+, $pK_a = 9.3$, is used to compute the proportion of NH_4^+ and NH_3. Stripping tests showed in fact that 80-90% of the total ammonia could be removed readily by stripping. During the bench-scale tests, lime was added when residual ammonia was in the range of 600-800 mg/L in order to accelerate the stripping operation.

Average wastewater characteristics before and after ammonia stripping are summarized in Table A.3. The stripping operation reduced ammonia, alkalinity, and sulfide to low levels. There was also additional removal of quench water organic compounds as a result of stripping and liming. Stripping effectively removed residual MIBK from solvent-extracted water. The increase in calcium hardness is consistent with addition of lime to release residual ammonia.

A.4.4 Biological Treatment

Average operational and performance data are summarized in Table A.4 for activated-sludge and PAC/activated-sludge treatment of solvent-extracted ammonia-stripped wastewater. It was found that solvent-extracted wastewater was easier to treat via activated sludge than water that had not been pretreated for reduction of phenolics. A previous study with GFETC wastewater pretreated only by ammonia stripping had shown that wastewater must be diluted to about 33% strength in order to achieve successful activated-sludge treatment (Stamoudis and Luthy, 1980a). In the present study it was shown that solvent extraction eliminated the need for dilution prior to biological oxidation. Furthermore, solvent-extracted wastewater did not show a tendency to foam excessively as in previous investigations.

The biological reactors were operated under extended aeration conditions with relatively long mean sludge-residence times and corresponding low values of BOD and COD removal rates. These conditions produced effluents with low values of BOD. COD removal efficiency for the activated-sludge reactor was 55%, which was lower than previously observed values in the range of 75-84% with nonsolvent-extracted GFETC wastewater. This result suggests that solvent extraction yields a product wastewater with a greater proportion of residual material not amenable to biological oxidation. However, this did not impair activated-sludge treatment.

PAC/activated-sludge treatment with 5000 mg/L PAC in the mixed liquor under aeration gave better removal efficiencies than activated-sludge

Table A.4 Average Performance Data for Activated Sludge and PAC-Activated Sludge Treatment of Solvent Extracted Slagging Fixed-Bed Wastewater

Operating Data	PAC Activated Sludge	Conventional Activated Sludge
Mean sludge residence time (d)	20	30
Hydraulic residence time (d)	11.7	12.6
PAC conc. in reactor (mg/L)	5000	0
MLSS (mg/L)	6470	1620
MLVSS (mg/L)	6110	1310
COD removal rate (d^{-1})	-	0.11
BOD removal rate (d^{-1})	-	0.12
SVI (mL/g MLSS)	10	65
pH (units)	7.3	7.6
Dissolved oxygen (mg/L)	>4.0	>4.0
O_2 util. rate (mg O_2/mg MLVSS-d)	0.02	0.07

Wastewater Characteristics (mg/L except as noted)	Influent	Effluent	
		PAC Activated Sludge	Conventional Activated Sludge
TOC	1380	385	580
COD	2980	640	1340
BOD	1820	30	32
Phenolics	3	<0.02	≈0.1
Org-N	33	4	10
NH_3-N	30	20	84
NO_3-N	<5	100	40
SCN^-	105	<0.5	4
CN^-_{TOT}	1.5	1.3	1.4
CN^-_{Amn}	≈0.1	<0.1	≈0.1
SO_4^{2-}	-	655	1020
Alkalinity, as $CaCO_3$	850	72	175
Freon extractable	10	<5	<5
Conductivity (μmho/cm)	1490	2200	2230
Color (pt-Co units)	700	<20	<5

treatment for TOC, COD, phenolics, organic-N, NH_3-N, SCN^-, and color. PAC/activated-sludge treatment gave a colorless effluent, whereas activated-sludge treatment gave a value of 500 Pt-Co units. These effluent color concentrations are significantly lower than those observed in previous activated-sludge (Stamoudis and Luthy 1980a) or PAC/activated-sludge studies (Luthy et al. 1980) with nonextracted wastewater even considering the one-third strength dilutions employed therein.

A.4.5 Lime-Soda Softening

Lime-soda softening experiments were performed with a composite sample of PAC/activated-sludge reactor effluent in order to evaluate this process for removal of residual wastewater hardness. Most of the wastewater hardness in PAC/activated-sludge effluent existed as noncarbonate hardness and therefore required addition of soda ash. The appropriate lime dose was determined by the amount of stock lime solution required for alkalimetric titration to pH = 10. Soda dose was then computed as

$$\text{Soda dose} = (Ca^{2+}) + (\text{lime dose}) - (\text{alkalinity}).$$

Chemical requirements computed by these techniques were: 720 mg/L lime (as $CaCO_3$) and 1173 mg/L soda (as $CaCO_3$). The validity of this procedure was verified by experimental results reported in Table A.5 where residual Ca and Mg precipitated to very low levels.

Table A.6 reports results of another set of softening experiments in which lime dose was held constant to give a pH of about 10, but soda dose was reduced in increments of 10, 20, and 30% from that used previously. These data show that depending on the specific situation, hardness may be reduced to desired limits by varying soda dose. A soda dose of about 820 mg/L as $CaCO_3$ gave an 86% reduction in total hardness to 80 mg/L as $CaCO_3$ with an increase in TDS of only 13%.

A.4.6 HPLC Analysis of Raw and Treated Samples

Results of analysis of raw wastewater for PAH are summarized in Table A.7. The results for the suspended-phase PAH were expressed as µg per mg of suspended material on the basis of a measured raw-wastewater suspended-solid concentration of 54 mg/L. Results are also expressed as percent of total PAH in the sample associated with the suspended phase. These data show that the raw wastewater contains appreciable quantities of the eleven PAHs for which determinations were performed. They also show that no PAHs of molecular weight greater than 178 were detected in the aqueous phase. Aside from naphthalene, most of the PAHs characterized in the sample were associated with the suspended phase.

Analysis of suspended and aqueous phases following solvent extraction showed no detectable concentrations. Hence, in the process of reducing phenolics to the range of several mg/L, solvent extraction effectively removed all eleven PAHs from the wastewater. Additional HPLC analyses following ammonia stripping and activated-sludge or PAC/activated-sludge processing also showed no PAH in suspended or aqueous phases.

Table A.5 Lime-Soda Softening of PAC/Activated-Sludge Effluent

Characteristic (mg/L except as noted)	Effluent	Softened Effluent[a]
COD, as $CaCO_3$	685	670
Alkalinity, as $CaCO_3$	115	525
Ca^{2+}, as $CaCO_3$	568	11
Mg^{2+}, as $CaCO_3$	5.4	2.5
TDS	2340	3030
Conductivity (µmhos/cm)	2600	3100
pH (units)	7.7	10.5
Turbidity (NTU)	1.6	7.0[b]

[a] Lime dose = 720 mg/L, soda dose = 1173 mg/L, both as $CaCO_3$.

[b] After settling.

Table A.6 Lime-Soda Softening Studies with Various Doses of Soda

Dose (mg/L as $CaCO_3$)		Treated Wastewater Characteristics			
Lime	Soda	Ca^{2+} (mg/L as $CaCO_3$)	Mg^{2+} (mg/L as $CaCO_3$)	TDS (mg/L)	Cond. (µmhos/cm)
780	1211	12	4.2	3150	3100
780	1090	23	3.3	2900	2850
780	970	58	5.0	2750	2700
780	850	74	5.8	2650	2650

A.4.7 GC and GC/MS Analysis of Raw and Treated Samples

The data from GC and GC/MS analyses of the acid, base, and neutral fractions of the raw sample, and of the samples after the various treatments, are presented in Tables A.8–A.10. These tables contain compound-concentration data obtained from GC analysis of extractable/chromatographable organics identified by GC/MS. Also presented are cumulative percent-removal values after each step of the treatment train.

As shown in Table A.8, the acid fraction of the raw sample consists of phenol, hydroxyindans, hydroxyindenes, naphthols, and their alkylated derivatives. Phenol and cresols make up more than 0.4% of the filtered-water

Table A.7 Characterization of PAHs in Raw Wastewater from the GFETC SFB Coal-Gasification Pilct Plant

Compound	Mass Identified (μg fractions)			Sum of Mass Identified (μg/mg)[a]	Sum of Mass Identified (μg/L)[b]	PAH Associated with Aqueous Phase (μg/L)[c]	Percent of Total PAH Associated with Solids
	1	2	3				
Naphthalene	472	8.3	-	33.3	1800	893	66.8
Acenaphthene	762	<0.27	-	52.7	2850	4.5	99.8
Fluorene	203	0.53	-	14.1	760	3.1	99.6
Phenanthrene	492	14.2	-	35.0	1890	11.7	99.4
Anthracene	115	112	-	15.7	848	101	89.3
Fluoranthene	-	6.4	-	0.44	24	<1.7	>93.4
Pyrene	-	6.4	-	0.44	24	<4.1	>85.4
Chrycene	-	93.9	121	14.9	803	<4.5	>99.4
Benz(a)pyrene	-	21.7	52.7	5.1	278	<0.3	>99.9
Dibenz(ah)anthracene	-	33.7	6.69	2.9	151	<0.4	>99.7
Benz(ghi)perylene	-	25.9	40.1	4.6	247	<0.5	>99.8

[a] Mass of each compound normalized on suspended solid concentration of 54 mg/L.

[b] Mass of each compound normalized on total wastewater volume from which solids were filtered (0.267 L).

[c] Mass of each compound normalized on total wastewater volume filtered (1.80 L).

Table A.8 Concentration (µg/L) of Organics Identified in the Acid Fractions of GFETC SFB Quench Waters at the Various Stages of Treatment[a]

Peak Number	Retention Time (min)	Compound Name	Raw		MIBK[b]		MIBK-AS		MIBK-AS/PAC	
			SS	FW	FW	% Removal	FW	% Removal	FW	% Removal
20	32.5	Phenol	15,100	3,080,000	500	99.8	10	99.99	3	99.99
50	36.6	Methylphenol	6,300	427,000	100	99.9	1	99.99	1	99.99
80	39.0	Methylphenol	16,400	494,000	80	99.9	1	99.99	1	99.99
100	41.9	Ethylphenol	960	18,700	30	99.8	NT	100	NT	100
110	42.4	C_2-Phenol	5,370	85,800	50	99.9				
140	44.7	C_2-Phenol	8,890	155,000	50	99.9				
160	46.3	C_2-Phenol	1,130	28,800	40	99.8				
170	47.3	C_3-Phenol	270	1,110	30	97.2				
180	47.5	C_3-Phenol	160	780	20	97.4				
190	48.0	C_3-Phenol	770	3,650	30	99.2				
210	49.8	C_3-Phenol	400	5,100	30	99.4				
220	50.2	C_3-Phenol	1,500	7,900	60	99.2				
230	51.4	C_3-Phenol	190	2,140	20	99.1				
250	53.6	C_4-Phenol	280	3,300	40	98.8				
260	55.1	Hydroxyindan	340	3,820	40	98.9				
270	55.4	C_4-Phenol and hydroxyindan	250	2,140	30	98.6				
280	56.3	Methyl-hydroxyindan and C_4-phenol	230	2,170	30	98.6				
300	58.8	Methyl-hydroxyindan	100	250	30	88.0				
310	61.3	Methyl-hydroxyindan and methyl-hydroxyindene	110	300	40	86.7				
320	62.7	C_2-hydroxyindan and methyl-hydroxyindene	100	280	40	85.7				
330	64	Hydroxybiphenyl and C_2-hydroxyindan	120	320	40	87.5				
340	65.2	C_2-Hydroxyindan	80	200	30	85.0				
350	65.9	C_3-Hydroxyindan	60	150	20	86.7				
360	66.8	2-Naphthol	110	520	20	96.2				
370	67.7	1-Naphthol	250	1,150	40	96.5				
400	72.9	Methylnaphthol	190	300	20	93.3				
410	74.0	Methylnaphthol	100	300	20	93.3				
420	76.8	C_2-Naphthol	90	200	20	90.0				
440	79.1	C_2-Naphthol	80	200	20	90.0				

[a] SS = suspended solids; FW = filtered water; ND = not determinable; NT = not detected.

[b] No suspended solids detected.

Table A.9 Concentration (μg/L) of Organics Identified in the Base Fractions of GFETC SFB Quench Waters at the Various Stages of Treatment[a]

Peak Number	Retention Time (min)	Compound Name	Raw		MIBK[b]		MIBK-AS		MIBK-AS/PAC	
			SS	FW	FW	% Removal	FW	% Removal	FW	% Removal
10	11.0	Pyridine	3.9	14,530	NT	100	NT	100	0.1	100
15	12.1	Toluene	NT	77	NT	100	NT	100	NT	100
17	12.3	Methyl-piperidine	NT	ND	NT	100	5.0	ND	2.3	ND
20	13.3	Methylpyridine	12	7,120	1.0	99.00	NT	100	NT	100
22	13.6	Methyl-imidazole	NT	45	25	44	25	44	1.7	96
38	15.9	Imidazolidinone	NT	ND	7.6	99.8	3.1	ND	1.3	ND
40	16.0	Methylpyridine	37	4,480	NT	100	NT	100	NT	100
44	16.3	C_2-Imidazole or C_2-pyrazole	NT	ND	1.4	ND	5.8	ND	0.5	ND
50	17.7	C_2-Pyridine	19	1,530	NT	100	NT	100	NT	100
54	18.4	C_2-Dihydroimidazole	NT	ND	7.1	ND	4.0	ND	0.2	ND
55	18.5	C_2-Imidazole or C_2-pyrazole	3.0	460	NT	100	NT	100	NT	100
60	19.0	C_2-Pyridine	4.0	280	NT	100	NT	100	NT	100
68	20.7	C_2-Imidazole or C_2-pyrazole	NT	ND	8.6	ND	9.5	ND	0.9	ND
70	20.9	C_2-Pyridine	67	1,160	NT	100	NT	100	NT	100
80	21.7	C_2-Pyridine	22	370	NT	100	NT	100	NT	100
90	22.7	C_2-Pyridine	11	80	NT	100	NT	100	NT	100
100	23.3	C_2-Imidazole	NT	410	240	41	3.3	98	2.4	99.4
105	23.7	C_3-Pyridine and aniline	6.7	70	NT	100	NT	100	NT	100
110	24.3	C_2-Pyridine	10	140	NT	100	NT	100	NT	100
120	24.6	C_2-Pyridine	11	62	NT	100	NT	100	NT	100
125	25.0	C_3-Imidazole or C_3-pyrazole	NT	ND	NT	ND	14	ND	0.2	ND
130	25.8	C_2-Pyridine	44	250	NT	100	NT	100	NT	100
140	26.2	Aniline	27	6,500	NT	100	NT	100	NT	100
150	26.9	C_3-Pyridine	39	150	NT	100	NT	100	NT	100
152	27.1	Indoline	NT	ND	5.7	ND	NT	ND	0.1	ND
160	27.5	C_3-Pyridine	12	70	NT	100	NT	100	NT	100
168	27.6	Methylthiazole	NT	ND	8.5	ND	NT	ND	NT	ND
170	28.4	C_3-Pyridine	10	50	NT	100	NT	100	NT	100
180	28.7	C_3-Pyridine	14	36	NT	100	NT	100	NT	100
182	28.8	C_2-Diazine	NT	ND	4.1	ND	NT	ND	0.4	ND
190	29.6	C_4-Pyridine	NT	ND	NT	100	NT	100	NT	100

Table A.9 (Contd.)

Peak Number	Retention Time (min)	Compound Name	Raw SS	Raw FW	MIBK[b] FW	MIBK[b] % Removal	MIBK-AS FW	MIBK-AS % Removal	MIBK-AS/PAC FW	MIBK-AS/PAC % Removal
195	30.0	Dimethyl-isothiazole?	NT	ND	4.0	ND	5.1	ND	0.6	ND
200	30.5	C_3-Pyridine	26	70	NT	100	NT	100	NT	100
208	31.1	$C_{10}H_{21}N$ (olefinic amine)	NT	ND	6.3	ND	NT	ND	0.2	ND
210	31.3	C_3-Pyridine	33	70	NT	100	NT	100	NT	100
215	31.8	C_2-Thiazole	NT	ND	14	ND	NT	ND	.2	ND
220	31.9	C_4-Pyridine	27	850	NT	100	NT	100	NT	100
230	32.3	C_4-Pyridine	14	310	NT	100	NT	100	NT	100
240	33.2	C_4-Pyridine	40	610	NT	100	NT	100	NT	100
250	33.7	C_4-Pyridine	11	60	NT	100	NT	100	NT	100
270	34.7	C_4-Pyridine and diazaindene	17	32	NT	100	NT	100	NT	100
285	35.3	$C_{11}H_{23}N$ (olefinic amine)	NT	ND	4.7	ND	NT	ND	NT	ND
290	36.2	C_5-Pyridine and C_4-pyridine	25	32	NT	100	NT	100	NT	100
310	37.2	C_4-Pyridine	28	21	NT	100	NT	100	NT	100
320	37.8	C_4-Pyridine	15	95	11	90	NT	100	NT	100
322	38.0	C_2-Triazine	NT	ND	21	ND	NT	ND	0.5	ND
330	38.1	C_5-Pyridine	16	70	↑	↑	↑	↑	↑	↑
340	38.3	C_5-Pyridine and C_4-pyridine	7.0	35						
342	38.4	C_2-Aniline	NT	60						
350	38.8	C_5-Pyridine and C_2-aniline	16	70						
352	38.8	C_2-Aniline	NT	85						
360	39.6	C_5-Pyridine and methyl-azaindan	16	40						
362	39.7	C_2-Aniline	NT	29						
370	41.2	C_5-Pyridine and methyl-azaindan	10	31						
380	42.5	Methyl-azaindan	9.3	13	NT	100	NT	100	NT	100
390	44.0	Azanaphthalene	450	500						
398	45.1	C_5-Pyridine	17	53						
400	45.5	Azanaphthalene	160	150						
420	46.8	C_2-Azaindan	13	ND						
425	48.3	Dimethyl-diazaindan	17	15						
430	48.9	Methyl-azanaphthalene	160	105						
435	49.2	Dimethyl-diazaindan	NT	29						
440	49.4	Methyl-azanaphthalene	42	12	↓	↓	↓	↓	↓	↓

Table A.9 (Contd.)

Peak Number	Retention Time (min)	Compound Name	Raw SS	Raw FW	MIBK[b] FW	MIBK[b] % Removal	MIBK-AS FW	MIBK-AS % Removal	MIBK-AS/PAC FW	MIBK-AS/PAC % Removal
460	50.4	Methyl-azanaphthalene	64	35	↑	↑	↑	↑	↑	↑
470	50.8	Methyl-azanaphthalene	20	13						
480	51.2	Methyl-azanaphthalene	30	36						
490	52.0	Methyl-azanaphthalene	120	31						
500	52.4	Methyl-azanaphthalene	51	25						
510	53.2	Methyl-azanaphthalene	24	50						
520	53.7	C_2-Azanaphthalene	90	50						
530	54.7	C_2-Azanaphthalene	16	23						
540	55.4	C_2-Azanaphthalene	31	37						
545	56.1	C_3-Diazaindan	NT	65						
550	56.6	C_2-Azanaphthalene	60	ND						
560	57.0	C_2-Azanaphthalene	13	26						
570	57.9	C_2-Azanaphthalene	64	ND						
580	58.7	C_2-Azanaphthalene and azabiphenyl	65	6						
590	59.8	C_2-Azanaphthalene and azabiphenyl	16	5	NT	100	NT	100	NT	100
600	60.7	C_2-Azanaphthalene and C_3-azanaphthalene	30	10						
630	62.7	C_2-Azanaphthalene and C_3-azanaphthalene and methylbiphenyl	38	5						
640	63.0	C_2-Azanaphthalene and C_3-azanaphthalene	11	ND						
650	63.9	C_2-Azanaphthalene and azaacenaphthene and methyl-azabiphenyl and C_2-azabiphenyl	13	9						
690	66.0	Methyl-azaacenaphthene	20	11						
710	67.8	C_3-Azanaphthalene and C_4-azanaphthalene and methyl-azaacenaphthene	10	5						
730	69.7	Azafluorene	20	15						
800	77.7	Azaphenanthrene	8.7	5						
810	79.9	Azaanthracene	16	5	↓	↓	↓	↓	↓	↓

[a] SS = suspended solids; FW = filtered water; ND = not determinable; NT = not detected.

[b] No suspended solids detected; for peak 640 presence of suspended solids not determinable.

Table A.10 Concentration (μg/L) of Organics Identified in the Neutral Fractions of GFETC SFB Quench Waters at the Various Stages of Treatment[a]

Peak Number	Retention Time (min)	Compound Name	Raw SS	Raw FW	MIBK[b] FW	MIBK[b] % Removal	MIBK-AS FW	MIBK-AS % Removal	MIBK-AS/PAC FW	MIBK-AS/PAC % Removal
20	17.7	C_2-Benzene	365	ND	NT	100	NT	100	NT	100
21	17.9	Methylcyclohexene or C_2-cyclopentene	ND	7,220	36	99.5	NT	100	NT	100
32	19.4	Methylcyclohexene or C_2-cyclopentene	ND	22,750	4,230	81	NT	100	NT	100
35	21.0	Benzonitrile	ND	2,900	NT	100	NT	100	NT	100
36	21.2	C_8-Alkane	NT	ND	440	ND	NT	100	NT	100
38	21.6	Methylcyclohexene or C_2-cyclopentene	ND	3,130	ND	100	NT	100	NT	100
39	22.1	Methylcyclohexene or C_2-cyclopentene	ND	850	71	92	NT	100	NT	100
40	26.9	C_3-Benzene and indan	330	ND	NT	100	NT	100	NT	100
42	27.2	C_2-Cyclohexene and C_3-cyclopentene	ND	1,160	67	94	NT	100	NT	100
48	28.1	Methylthiazole	ND	ND	15	ND	NT	100	NT	100
50	29.0	C_3-Benzene and C_2-cyclohexene or C_3-cyclopentene	1,130	8,770	87	99	NT	100	NT	100
55	29.8	C_2-Thiazole	ND	ND	ND	ND	3.1	ND	3.0	ND
70	30.4	Indene	2,300	910	NT	100	NT	100	NT	100
78	31.9	C_2-Thiazole	ND	ND	22	ND	0.6	93	0.7	93
80	32.3	C_3-Benzene	860	ND	NT	100	NT	100	NT	100
82	32.6	Acetophenone	ND	3,583	NT	100	NT	100	NT	100
92	33.2	C_3-Cyclohexene or C_4-cyclopentene	ND	1,540	65	96	NT	100	NT	100
95	34.2	C_2-Thiazole	ND	ND	30	ND	NT	100	NT	100
96	34.5	C_2-Thiazole	ND	ND	40	ND	NT	100	NT	100
100	34.6	Methylindan	290	ND	NT	100	NT	100	NT	100
110	34.8	Methylindan	165	ND	NT	100	NT	100	NT	100
115	35.0	Cresol	ND	5,520	NT	100	NT	100	NT	100
120	35.3	Methylindan	470	ND	NT	100	NT	100	NT	100
125	35.5	C_3-Thiazole	ND	ND	31	ND	1.8	94	2.0	94
130	35.6	Methylindan	590	ND	NT	100	NT	100	NT	100

Table A.10 (Contd.)

Peak Number	Retention Time (min)	Compound Name	Raw SS	Raw FW	MIBK[b] FW	MIBK[b] % Removal	MIBK-AS FW	MIBK-AS % Removal	MIBK-AS/PAC FW	MIBK-AS/PAC % Removal
135	35.8	C_3-Thiazole	ND	ND	30	ND	2.5	92	2.1	93
140	36.3	C_3-Cyclohexadiene or C_4-cyclopentadiene	ND	3,000	NT	100	NT	100	NT	100
145	36.4	C_3-Thiazole	ND	ND	27	ND	1.3	95	1.6	94
150	36.5	Cresol	ND	3,180	NT	100	↑	↑	↑	↑
160	38.5	Methylindene and dihydronaphthalene	1,220	ND	NT	100				
170	38.8	Dihydronaphthalene	1,300	ND	NT	100				
172	39.2	C_3-Thiazole	ND	ND	15	ND				
175	40.1	C_2-Phenol	ND	4,580	NT	100				
180	40.8	Naphthalene	16,300	26,600	NT	100				
185	41.9	C_3-Thiazole	ND	ND	17	ND				
189	42.8	C_2-Phenol	ND	6,140	↑	↑				
190	42.9	C_2-Indan	570	-						
191	43.0	C_2-Phenol	ND	7,850						
199	43.4	C_2-Phenol	ND	1,600						
200	43.5	C_2-Indan	1,450	ND						
210	43.7	C_2-Indan and C_2-azaindan	450	ND			NT	100	NT	100
225	44.6	C_2-Phenol	ND	2,670						
242	45.3	C_3-Phenol	ND	1,190						
248	45.9	C_3-Phenol	ND	710						
250	46.1	C_2-Indene	290	ND	NT	100				
251	46.2	C_3-Phenol	ND	3,320						
260	46.3	C_2-Indene	360	ND						
262	46.4	C_3-Phenol	ND	1,450						
270	46.7	C_2-Indene	880	ND						
278	46.9	C_3-Phenol	ND	8,100						
280	47.0	C_2-Indene	120	ND						
285	47.2	C_3-Phenol	ND	2,300						
290	47.7	Hexahydronaphthalene	610	ND						
295	48.3	C_3-Phenol	ND	2,100	↓	↓	↓	↓	↓	↓

Table A.10 (Contd.)

Peak Number	Retention Time (min)	Compound Name	Raw SS	Raw FW	MIBK[b] FW	MIBK[b] % Removal	MIBK-AS FW	MIBK-AS % Removal	MIBK-AS/PAC FW	MIBK-AS/PAC % Removal
300	48.5	2-Methylnaphthalene	6,300	ND						
302	49.0	C_3-Phenol	ND	7,300						
308	49.3	C_3-Phenol	ND	2,900						
310	49.4	1-Methylnaphthalene	3,530	ND						
320	50.0	C_3-Indan	750	ND						
330	51.0	Indole	150	5,000						
340	51.2	C_3-Indan	570	ND						
345	51.4	C_3-Phenol	ND	1,220						
355	51.8	C_4-Phenol	ND	600						
360	52.9	C_{13}-Alkane and C_4-indan	2,340	ND						
370	53.2	C_{13}-Alkane	350	ND						
380	54.0	Biphenyl	1,100	ND						
390	54.9	C_2-Naphthalene	700	ND						
400	55.8	C_2-Naphthalene	1,900	ND						
405	56.3	Methylindole	ND	570						
410	56.8	C_2-Naphthalene	4,200	ND	NT	100	NT	100	NT	100
420	57.8	C_{13}-Alkane	500	ND						
430	58.2	C_2-Naphthalene	4,930	ND						
440	58.7	C_2-Naphthalene	780	ND						
450	59.0	C_2-Naphthalene	280	ND						
460	60.1	Acenaphthene	2,480	ND						
470	60.8	Methylbiphenyl	1,000	ND						
480	61.3	Methylbiphenyl	690	ND						
490	61.6	Methylbiphenyl	320	ND						
500	62.5	Dibenzofuran	3,340	ND						
510	63.0	C_4-Decalin and BHT (antioxidant)	2,910	NT						
520	63.7	C_3-Naphthalene	820	ND						
530	64.5	C_3-Naphthalene	570	ND						
540	65.5	C_3-Naphthalene	650	ND						
550	66.4	Benzoindene	5,000	ND						

Table A.10 (Contd.)

Peak Number	Retention Time (min)	Compound Name	Raw		MIBK[b]		MIBK-AS		MIBK-AS/PAC	
			SS	FW	FW	% Removal	FW	% Removal	FW	% Removal
552	66.6	Plasticizer (phthalate)	ND	ND	NT	ND	6.7	ND	2.6	ND
560	66.8	C_3-Naphthalene	2,100	ND	NT	100	NT	100	NT	100
570	67.3	Methylacenaphthene	600							
580	67.7	Methylacenaphthene and C_2-biphenyl	750							
590	68.2	Benzoindene	300							
600	68.8	Fluorene and C_2-biphenyl	1,700							
610	69.6	C_2-Biphenyl	1,700							
620	78.0	C_2-Biphenyl and C_4-naphthalene	310							
630	70.7	C_2-Biphenyl and C_4-naphthalene	380							
640	71.5	C_4-Naphthalene and C_2-biphenyl	140							
650	72.2	C_5-Naphthalene	530							
660	73.0	Methylfluorene	1,120							
670	73.4	Methylfluorene	540							
680	73.9	Methylfluorene	630							
690	74.4	C_2-Acenaphthene	220							
700	75.2	C_3-Biphenyl	750							
710	77.2	Phenanthrene	4,680							
720	77.7	C_3-Biphenyl and anthracene	1,160							
728	82.4	Plasticizer (phthalate)	ND	ND	NT	ND	NT	ND	12	ND
740	83.6	Methylphenanthrene	410	ND	NT	100	NT	100	NT	100
750	84.2	Methylanthracene	790							
760	84.7	Methylphenanthrene and/or methylanthracene	180							
770	87.0	Phenylnaphthalene	210							
780	90.6	C_2-Phenanthrene or C_2-anthracene	270							
790	91.2	Fluoranthene	1,510							
810	93.5	Pyrene	830							
820	94.1	Methyl-phenylnaphthalene	250							

[a] SS = suspended solids; FW = filtered water; ND = not determinable; NT = not detected.

[b] No suspended solids detected.

(FW) phase and they constitute more than 90% of the total acidic components. The acidic components of the suspended-solids (SS) phase are similar to the FW phase, but their concentration, referred to the original raw-sample volume, is much less (0.5% to 40%) than that of the FW-phase acidic organic compounds. The difference in the concentration of acidic organics between SS-phase and FW-phase decreases with increasing compound molecular weight and decreasing compound polarity. These data indicate that the less polar, higher molecular weight acidic organics are associated with the suspended solids.

Table A.9 shows that the major components of the raw sample base fraction are azabenzenes (pyridines), azanaphthalenes (quinolines), and anilines. Inidazoles or pyrazoles, diazines, thiazoles, azaindans, and some higher nitrogen-PNAs, such as azabiphenyls, acaacenaphthrenes, azafluorenes, azaanthracenes, and azaphenanthrenes, are present. The proportion of base compounds associated with the SS phase rather than the FW phase is greatest for those species that are of relatively higher molecular weight and that are relatively less polar.

Table A.10 shows that a large variety of neutral organic compounds are present in the raw sample. The SS phase of the neutral fraction contains representatives of virtually all one-to-four aromatic ring compounds and their alkylated derivatives. The FW-phase neutral fraction contained the more polar neutral organics; major components were cycloalkanes, cycloalkenes, benzonitrile, acetophenone, indenes, and naphthalene. The higher polynuclear aromatic hydrocarbons (alkylated napthalenes, biphenyls, and three- and four-ring aromatics) were particularly visible in the SS phase. The FW phase of the neutral fraction contained some phenolics that were not completely fractionated to the acid extract.

Tables A.8-A.10 show that MIBK extraction achieved substantial reduction in concentrations of extractable and chromatographable organic constituents. Acidic components (Table A.8) were reduced 85-99.9%, and the most abundant constituents (phenol and cresols) were reduced 99.8-99.9%. The overall reduction of acidic components was 99.6%.

No organics compounds were detected in the SS phase of the MIBK-extracted samples of acid, base, or neutral fractions. The MIBK aqueous-phase base and neutral fractions did show some compounds not determined in the raw sample, particularly inidazoles in the base fraction and thiazoles in the neutral fraction. That these compounds were not readily determined in the raw sample was presumably due to their low concentration in that sample.

Except for phenol and cresol, activated-sludge treatment of solvent-extracted quench water reduced aqueous phase acidic components (Table A.8) to levels below detection (less than 0.1 μg/L). The PAC/activated-sludge treatment enhanced removal of phenol and cresol and also reduced the concentrations of other acidic compounds to levels less than detectable.

None of the organic constituents identified in base or neutral extracts of the raw sample were found in either activated-sludge or PAC/activated-sludge extracts. Thus, the combination of physicochemical and biological treatment provided excellent removal of all the organics in base and neutral fractions that were readily identifiable in the raw-sample extracts.

The PAC/activated-sludge treatment provided better removal than activated sludge for the imidazoles observed in the MIBK aqueous-phase sample (Table A.9, peaks 22, 38, 54, 68, and 100). Both activated-sludge and PAC/activated-sludge treatment provided excellent removals for neutral-fraction organics in the MIBK aqueous phase sample. Excepting contamination by plasticizers, the only identifiable neutral-fraction organics were several thiazoles present at comparable low levels in either activated-sludge or PAC/activated-sludge effluent (Table A.10, peaks 55, 78, 125, 135, and 145).

A.5 SUMMARY

This study provided information on treatment of a raw quench water from a slagging, fixed-bed lignite gasification process by means of a bench-scale treatment train consisting of solvent extraction with MIBK, ammonia stripping, and activated sludge with and without addition of PAC. In general, effluents from the PAC/activated-sludge process were lower in TOC, COD, BOD, phenolics, organic nitrogen, ammonia-nitrogen, thiocyanate, and color intensity than those of the activated-sludge-only treatment. Detailed HPLC and GC/MS analysis of raw water and MIBK-extracted water showed that solvent extraction intended for phenol recovery removed most of the raw-water extractable/chromatographable organics. Organics associated with the raw-water suspended phase were removed completely by solvent extraction. Detailed GC and GC/MS analysis of activated-sludge and PAC/activated-sludge treated water showed excellent reduction of those extractable/chromatographable organics remaining after MIBK extraction. Final activated-sludge or PAC/activated-sludge effluents contained only very low levels of relatively few compounds and, among those few compounds, PAC/activated-sludge gave better removal values than did treatment by activated sludge without addition of PAC.

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A.7 REFERENCES

Acheson, M.A., et al., *Factors Affecting the Extraction and Analysis of PAH in Water,* Water Research *10*:207-212, Pergamon Press (1976).

American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 14th Ed., APHA, Washington, DC (1975).

Amoco Product Bulletin 677.

ASTM Committee E-14 on Mass Spectrometry, *Index of Mass Spectral Data,* American Society for Testing and Materials, Philadelphia, PA (1969).

Earhart, J.P., et al., *Recovery of Organic Pollutants via Solvent Extraction,* Chem. Eng. Prog., *73*(5):67, (1977).

Ellman, R.C., et al., *Slagging Fixed-Bed Gasification Project Status at the Grand Forks Energy Technology Center,* Presented at the 1979 Lignite Symposium, Grand Forks, ND (May 30-31, 1979).

Federal Register, *Polynuclear Aromatic Hydrocarbons-Method 610, 44*(233):69514-69517, Proposed Rules (Dec. 1979).

Heller, S.R., and G.W.A. Milne, EPA/NIH, *Mass Spectral Data Base,* U.S. Government Printing Office, Washington, DC (1978).

Kiezyk, P.R., and D. Mackay, *Wastewater Treatment by Solvent Extraction,* Canadian Journal of Chemical Engineering, *49*:747-752 (Dec 1971).

Kiezyk, P.R., and D. Mackay, *The Screening and Selection of Solvents for the Extraction of Phenol from Water,* Canadian Journal of Chemical Engineering, *51*:741-745 (Dec 1973).

Luthy, R.G., *Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters,* U.S. Department of Energy, NTIS FE-2496-16 (July 1978).

Luthy, R.G., L. McLaughlin, and V.C. Stamoudis, *Evaluation of Powdered Activated Carbon Treatment,* Dept. of Civil Engineering, Carnegie-Mellon University, in press (Dec. 1980).

Mayhue, L.F., *Solvent Extraction Status Report,* EPA-R2-72-073, Robert S. Kerr Env. Res. Lab., U.S. EPA, Ada, OK (Dec. 1972).

Ogan, K., E. Katz, and W. Slavin, *Determination of Polycyclic Aromatic Hydrocarbons in Aqueous Samples by Reversed-Phase Liquid Chromatography,* Analytical Chemistry, *51*(8):1315-1320 (July 1979).

Schiller, J.E., and D.R. Mathiason, *Separation Method for Coal-Derived Solids and Heavy Liquids,* Analytical Chemistry, *49*(6):1225-1228 (July 1977).

Stamoudis, V.C., et al., *Removal of Organic Constituents in a Coal Gasification Process Wastewater by Activated Sludge Treatment,* Argonne National Laboratory Report ANL/WR-79-1 (1979).

Stamoudis, V.C., and R.G. Lüthy, *Biological Removal of Organic Constituents in Quench Water from a Slagging, Fixed-Bed Coal-Gasification Pilot Plant,* Argonne National Laboratory Report ANL/PAG-1 (1980a).

Stamoudis, V.C., and R.G. Luthy, *Determination of Biological Removal of Organic Constituents in Quench Waters from High-Btu Coal-Gasification Pilot Plants,* Water Research, *14*:1143-1156 (1980b)

Stenhagen, E., S. Abrahamsson, and F.W. McLafferty, eds., *Registry of Mass Spectral Data,* John Wiley and Sons, NY (1974).

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