**FOSSIL FUEL PROCESSING
TECHNICAL/PROFESSIONAL SERVICES**

**TECHNICAL ANALYSIS OF ADVANCED
WASTEWATER-TREATMENT SYSTEMS
FOR COAL-GASIFICATION PLANTS**

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UOP INC. AND
SYSTEM DEVELOPMENT CORPORATION**

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EXECUTIVE SUMMARY

This analysis of advanced wastewater treatment systems for coal gasification plants highlights the three coal gasification demonstration plants which were proposed by the U.S. Department of Energy. These are the Memphis Light, Gas and Water Division (MLGWD) Industrial Fuel Gas Demonstration Plant, the Illinois Coal Gasification Group (ICGG) Pipeline Gas Demonstration Plant, and the CONOCO Pipeline Gas Demonstration Plant.

Technical risks exist for coal gasification wastewater treatment systems, in general, and for the three DOE demonstration plants (as designed), in particular, because of key data gaps. The quantities and compositions of coal gasification wastewaters are not well known; the treatability of coal gasification wastewaters by various technologies has not been adequately studied; the dynamic interactions of sequential wastewater treatment processes and upstream wastewater sources has not been tested at demonstration scale.

This report identifies the key data gaps and recommends that demonstration-size and commercial-size plants be used for coal gasification wastewater treatment data base development. While certain advanced treatment technologies can benefit from additional bench-scale studies, bench-scale and pilot plant scale operations are not representative of commercial-size facility operation. It is recommended that coal gasification demonstration plants, and other commercial-size facilities that generate similar wastewaters, be used to test advanced wastewater treatment technologies during operation by using sidestreams or collected wastewater samples in addition to the plant's own primary treatment system.

Advanced wastewater treatment processes are needed to degrade refractory organics and to concentrate and remove dissolved solids to allow for wastewater reuse. Further study of reverse osmosis, evaporation, electrodialysis, ozonation, activated carbon, and ultrafiltration should take place at bench-scale.

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SECTION 1 - INTRODUCTION

UOP/SDC, A Joint Venture, is providing technical analyses of treatment systems for coal gasification wastewaters to the U.S. Department of Energy (DOE). These analyses include identification of what is known and what is unknown about available and emerging treatment technology for gasification wastewaters. Detailed analyses of the technical risks associated with the treatment systems designed for three demonstration plants are provided in this report. These analyses are intended to assist the DOE's assessment and mitigation of the technical risks associated with wastewater treatment for commercial coal gasification plants, in general, and for the three designed DOE demonstration plants (MLGWD, CONOCO, and ICGG), in particular.

Earlier studies by Water Purification Associates included analyses of water conservation and wastewater treatment for a variety of coal conversion technologies.^{1,2} These two studies highlighted the water conservation and wastewater reuse needs of coal conversion plants in the western U.S. The analyses in this UOP/SDC report provide an update and expansion of this earlier data base on wastewater treatment technologies. The principal focus of the report is on the general needs of coal gasification plants and the particular needs of the three proposed DOE gasification demonstration plants.

Wastewater treatment technology for coal gasification plants faces the challenge of increased regulatory attention to potentially hazardous contaminants and to achieving maximum water reuse. Coal gasification wastewaters are for biologically hazardous polynuclear organics and metal ion complexes. At the same time, maximum water reuse is being promoted as a way to avoid pollutant discharges and to conserve water resources. Processes for the destruction or degradation of refractory organics and for the separation (and concentration for disposal) of highly soluble strong electrolytes will be needed for treating coal gasification wastewaters.

A typical coal gasification plant consumes large quantities of water for cooling and steam generation. Both of these operations normally result in some evaporative water loss. Condensate from these operations, along with wastewaters from such other operations as coal preparation and raw gas cleaning, can be treated for reuse or for discharge. The degree of treatment necessary for these wastewaters is influenced by water availability, local discharge regulations, and the costs of equipment and system operation. The design of treatment systems begins with an assessment of the volume and degree of contamination of various process and non-process wastewater streams.

The composition and quantity of process wastewaters are determined by the composition of coal feed and the conditions of the gasification processes. Generally, the higher the temperature of the reactor vessel and the longer the coal is in the reactor, the cleaner the wastewaters are. High-sulfur coals, such as eastern U.S. coals, generally yield more highly contaminated wastewaters. Non-process wastewaters are characterized by coal type, plant layout and design, type of coal storage, and climatic factors. Open coal storage, in particular, is a significant wastewater source during rainstorms.

The design criteria for gasification plant wastewater treatment systems are affected by the degree of wastewater reuse that is desired. In general, the treatment for tars/oils, suspended solids, dissolved organics, and other contaminants such as ammonia does not depend upon wastewater reuse plans. A major difference, however, can occur if individual process wastewater streams are treated independently for particular reuse applications. This would contrast with wastewater treatment systems designed for the discharge of treated wastewater. Systems designed for discharge usually combine most process and stormwater runoff wastewater streams after minimal pretreatment. This single-train treatment of the combined wastewater streams provide the beneficial effects of buffering, dilution, and economy-of-scale.

The most significant challenge facing a treatment system designed for wastewater reuse, as contrasted with one designed for wastewater discharge, is the separation and concentration of dissolved solids. Conventional wastewater

treatment systems precipitate some dissolved contaminants, but the highly soluble strong electrolytes are normally discharged with the treated wastewater effluent. Concentrations of these strong electrolytes will quickly build up to unacceptable levels unless they are removed from reused wastewaters. Removal of highly soluble strong electrolytes requires the use of somewhat unconventional wastewater treatment technologies, such as reverse osmosis, electrodialysis, and evaporation.

The characteristics of the wastewaters generated by various coal gasification plant process sources and stormwater runoff sources are presented in Section 2. The effectiveness of the various wastewater treatment technologies is analyzed in the review of treatability studies in Section 3. Data gaps in wastewater characteristics and treatability are included at the ends of Sections 2 and 3, respectively. Section 4 of this report describes conventional and unconventional technologies available, or potentially available, for treating gasification wastewaters to meet discharge regulations or reuse requirements. A short subsection on approved instrumental methods is included.

The three demonstration plants are the subject of Section 5. The designed MLGWD, CONOCO, and ICGG demonstration plants are described and their wastewater treatment systems are analyzed. Section 6 presents the conclusions of these technical analyses of advanced wastewater treatment systems for coal gasification plants. Recommendations for eliminating data gaps are presented in Section 7.

SECTION 2 - CHARACTERIZATION OF COAL GASIFICATION WASTEWATERS

2.1 INTRODUCTION

Coal gasification facilities generate wastewaters with contaminant levels far exceeding acceptable limits for discharge or direct reuse. The following section describes the major sources and compositions of wastewaters from gasification facilities. This is a general discussion because the level of pollutants will vary, depending on the type of coal being used and the gasification process employed. A discussion of the origin and distribution of the major pollutants associated with gasification wastewaters is presented. The last section summarizes the data from pilot plant operation and discusses the scalability of that data to demonstration-size and commercial-size facilities.

2.2 DESCRIPTION OF COAL GASIFICATION WASTEWATERS

The sources, quantities, and compositions of coal gasification wastewaters vary according to the gasification process used and the type of coal gasified. The variability of coal composition is shown in Table 2.1. The temperatures and pressures at which gasification processes takes place also affect the composition of the product gases evolved. As the product gas is quenched, water carrying soluble components is condensed from the raw gas. Quench condensate is the largest process wastewater stream and has the potential to be the most contaminated.

Increasing the operating pressure of the gasification reaction results in higher methane concentrations, which increases the heating value of the product gas. Carbon monoxide and hydrogen production is decreased with increasing pressure. Organic by-products shift to higher molecular weights as the pressure increases.

Increasing the gasifier reaction temperatures shifts the equilibrium constants and increases the reaction rates of the principal conversion processes. Elevated gasification temperatures result in cleaner wastewaters because of thermal cracking of phenols, oils, tars and other hydrocarbons. Low-temperature gasification

Table 2.1 Classification of Coals According to Rank
(page 1 of 2)

Anthracite								
Class	Location	Seam	Equilibrium Moisture	Volatile Matter	Fixed Carbon	Ash	Sulfur	Btu/lb (MAF)
Anthracite Meta-Anth.	Pa. Schuylkill	-	4.5%	1.7%	84.1%	9.7%	0.77%	12,745
Anthracite	Pa. Lackawanna	-	2.5%	6.2%	79.4%	11.9%	0.6%	12,925
Bituminous								
High Volatile B Bit.	Ill.	#6	5.8%	36.2%	46.3%	11.7%	2.7%	11,910
High Volatile C Bit.	#Ill. Greene Co.	#5	7.2%	41.8%	48.0%	10.2%	3.9%	12,610
	*Ohio	#9	2.5%	35.0%	40.0%	22.5%	6.3%	14,560
	+Ky.	#9	11.0%	35.4%	41.6%	12.0%	2.8%	11,157
High Vol. B Bit.	#Pa. Greene Co.	#8	2.5%	35.4%	54.4%	10.0%	2.6%	13,670

Coal used in ICGG Demonstration Plant Design.
* Coal used in COMOCO Demonstration Plant Design.
+ Coal used in Memphis Fuel Gas Plant Design.

Reference 3 (P 5-15, Table 21)

Table 2.1 Classification of Coals According to Rank
(page 2 of 2)

Sub-Bituminous								
Class	Location	Seam	Equilibrium Moisture	Volatile Matter	Fixed Carbon	Ash	Sulfur	Btu/lb (MAF)
Sub-Bit. A	Musselshell Co., Mont.	-	14.1%	32.2%	46.7%	7.0%	0.43%	11,140
Sub-Bit. B	Sheridan Co., Wyoming	-	25.0%	30.5%	40.8%	3.7%	0.30%	9,345
Sub-Bit. C	Campbell Co., Wyoming	-	31.0%	31.4%	32.8%	4.8%	0.55%	8,320
Lignite								
Lignite A	Mercer Co., No. Dakota	-	37.0%	26.6%	32.2%	4.2%	0.4%	7,255

results in wastewaters higher in hydrocarbons. Dilution of these wastewaters may be required prior to treatment.

High-Btu gas production results in other wastewaters from shift conversion, methanation, and other gas enrichment processes. Other wastewater streams are coal-dependent, both in source and composition. The pretreatment of caking coals contributes wastewaters from quenching the pretreatment off-gases.

The major sources of wastewaters from gasification plants are:

- Coal pile runoff
- Coal preparation
- Coal pretreatment
- Ash quench
- Gas quench
- Shift condensation
- Methanation condensation
- Cooling tower blowdown
- Process area runoff
- Sanitary sewage
- Plant drains

In this section, the identification of wastewater sources and characteristics is based upon a generic demonstration-size facility.

2.2.1 Coal Pile Runoff

Coal storage is necessary to maintain a constant feed of coal to the gasifier and to allow continued operation during interruptions in coal supply. Storage is divided between live storage and dead storage. Live storage is coal used during normal operation. Dead storage is coal which can be used during interruptions in coal supply when live storage is depleted. Storage methods used for coal vary with the type of coal. Higher-rank coals can be stored in larger piles and stored longer because they oxidize more slowly than low-ranking coal. Higher-rank eastern U.S. coals can be stored longer than lower-rank western

U.S. coals because of this reactivity difference. Finer ground coal has a shorter storage life because the higher surface-to-volume ratio increases oxidation rates. Demonstration-size facilities require as much as 125,000 tons of coal for 90-day storage. The area required for this amount of open storage - about 8 to 10 acres - can intercept a large quantity of water during a storm. The stormwater will penetrate the pile and leach the coal unless a crusting material is used to seal the coal pile. Water, being a polar solvent, dissolves oxidized pyritic minerals in the coal and forms sulfuric acid and ferrous sulfate. Many types of metals and other compounds are leached into solution by the secondary reactions of sulfuric acid with the coal.

The amount of sulfuric acid in coal pile runoff is highly dependent upon the sulfur content of the coal being stored. In general, about 50% of the sulfur content of coal is in the form of pyrite, particularly when the sulfur content of coal is high. Eastern U.S. bituminous coals have sulfur contents ranging from 3% to over 6%. Western U.S. sub-bituminous and lignite coals generally have sulfur contents under 0.5%. It is expected that the runoff from piles of eastern U.S. bituminous coal will be of low pH and high in dissolved solids and metals, whereas the western U.S. coal runoff should have a runoff of near neutral pH and low levels of dissolved solids. The actual pH of runoff will also depend on the duration of storage between storms.

The mineral content of the coal determines the composition and concentrations of the elements that leach from the coal. Mineral components of coal include SiO_2 , Al_2O_3 , TiO_2 , Fe_2O_3 , CaO , MgO , Na_2O , and K_2O . Under acidic conditions, a portion of the metals dissolves. Leaching is expected to be slower for low-sulfur coals because of the higher pH of the runoff.

Coals with higher sulfur content will have a higher sulfate content and a lower pH in the runoff for equivalent storage duration and weather conditions. Runoff wastewaters from high-sulfur coals are high in dissolved solids, including Al, Ca, Mg, K, Si, Na, Fe, Mn, and Zn in concentrations above 1.0 mg/l. Runoff from subbituminous or lignite coals has a pH close to neutral and low levels of dissolved solids.

Neutral pH runoff low in dissolved solids can also occur for high sulfur coal that has been treated with crusting materials. Crusting materials are sprayed on the outer surface of coal piles to prevent stormwater from penetrating the pile. The crusting materials form a barrier to water causing stormwater to run off without leaching oxidized pyrites.

All exposed coal storage facilities should have provisions for collection of stormwater runoff. This is usually accomplished by storing coal on an impervious surface. Runoff is intercepted and conveyed to temporary storage. This wastewater, which can be either treated directly or combined with other wastewater streams, is usually neutralized prior to treatment to prevent treatment process upsets and equipment deterioration.

Because they occur only intermittently, storm runoff wastewaters are usually treated in facilities used primarily for other wastewater streams. Initial treatment, after neutralization, includes dilution and softening followed by precipitation or coagulation-flotation. The choice of the treatment process depends upon the intended disposition of this wastewater. Mixing of runoff wastewater with other water may dilute dissolved solids to concentrations suitable for cooling tower makeup water. Direct reuse of runoff wastewaters is not widespread, however, because it is usually necessary to treat the runoff wastewater before it can be recycled to the cooling tower. Furthermore, certain contaminants in the runoff wastewater may not be acceptable in the cooling tower makeup because they will be released into the air with the cooling tower drift.

Chemical treatment of stormwater runoff to increase the pH and decrease suspended and dissolved solids is expected to be the most cost effective. Softening-flotation or softening-sedimentation processes using lime or NaOH and polymer coagulation aids can be used to reduce the concentrations of dissolved and suspended solids. Addition of small amounts of lime (Ca(OH)_2) to the runoff precipitates sulfates as insoluble CaSO_4 . Use of additional lime precipitates insoluble metal hydroxides. At a pH above 6, aluminum is precipitated as Al(OH)_3 . As the addition of lime causes the pH to rise from 6 to 9, iron is precipitated as

$\text{Fe}(\text{OH})_3$, lead is precipitated as $\text{Pb}(\text{OH})_3$, and zinc precipitated as $\text{Zn}(\text{OH})_2$. As the pH rises above 10, nickel, mercury, and magnesium precipitate as $\text{Ni}(\text{OH})_2$, $\text{Hg}(\text{OH})_2$, and $\text{Mg}(\text{OH})_2$, respectively. Calcium originally present in the wastewater and from added lime precipitates as CaCO_3 if the alkalinity is high enough. Na_2CO_3 is added to increase the $\text{CO}_3^{=}$ concentration if the alkalinity is too low.

Removal of dissolved metal cations by the use of lime softening can be 70% to 90% effective. The precipitates formed can be removed to concentrations of 100 to 500 mg/l by sedimentation or flotation. As the pH of the decanted water is adjusted back towards neutral, the precipitates that carry over redissolve. If higher metal removals are desired, filtration of the decanted water prior to neutralization can be used to reduce the concentration of the insoluble precipitates in the water to 5 to 20 mg/l. These concentrations should be suitable for water reuse, but not for discharge. Additional treatment, such as reverse osmosis and/or evaporation, is necessary to purify the water to discharge quality.

The solids precipitated by lime softening are metal hydroxides, sulfates, and carbonates. These materials may require disposal in a sealed landfill under the new Resource Conservation and Recovery Act (RCRA) guidelines. The possibility of these material's leaching into groundwater systems must be minimized.

2.2.2 Coal Preparation

Coal preparation and handling at gasification facilities include all the steps required to transfer coal from live storage to gasifier coal feed systems. Coal preparation involves crushing, sizing, washing, and drying.

Coal preparation and handling can generate substantial amounts of wastewater from coal washing and dust control. Water consumption for coal washing can be as high as 1500 to 2000 gallons per ton of coal processed. Stormwater falling on coal preparation and handling areas will generate a wastewater similar to coal pile runoff.

2.2.3 Coal Pretreatment

Pretreatment to destroy caking tendencies is needed to gasify most eastern U.S. coals in fluidized-bed or fixed-bed reactors. Untreated caking coals in fluidized-bed gasifiers operated above 800°F can form lumps that interrupt the fluidizing gas streams, causing bed collapse. The lumps formed in fixed-bed gasifiers agglomerate into large masses that prevent the proper flow of hot gases through the bed.

Caking coals are normally pretreated in fluidized bed reactors operated at temperatures too low for caking to occur. Steam and oxygen or air are injected into the bed to partially oxidize the coal surface, forming a non-sticky surface. Pretreatment is not required for some mildly caking coals or for coals slurried with water or light product oil for feeding into entrained-flow gasifiers.

Coal pretreater off-gases are scrubbed with water. Because the temperature at which pretreatment takes place is relatively low, the pretreatment gases are high in phenols, tars, aromatics, and other organic pollutants. These materials are scrubbed out of the gas and are thus in the wastewater from the scrubber. Scrubber wastewater composition depends upon coal composition. Typical concentrations are shown in Table 2.2.

Table 2.2 Composition of Pretreatment Scrubber Water

<u>Material</u>	<u>mg/l</u>
TSS	700-1060
TOC	870-1200
NH ₃	23-26
Phenol	1330
TDS	2600-4800
Oil & Grease	159-239
S ⁼	2-3
SCN ⁻	209-316
CN ⁻	.003-.024

Treatment of pretreater wastewater is similar to treatment of the product gas quench condensate, which is discussed in a later section. Pretreatment and gasification are similar processes that produce similar types of wastewaters; the combination of these wastewaters for treatment is not expected to pose any problems in treatability of the wastewater.

2.2.4 Ash Quench Water

Coal gasification ash can be classified into two distinct types, lignite and bituminous. Lignite-type ash characteristically contains more CaO and MgO than Fe₂O₃. This ash is found in most western U.S. coals. Eastern U.S. coals have bituminous-type ash that contains more Fe₂O₃ than MgO and CaO. Most of the minerals present in the coal appear in the ash.

Ash generated during coal gasification exits in two ways. Small particles are entrained in the product gas and recovered in downstream equipment. Most of the ash, however, is removed from the bottom of the reactor. Steps must be taken to preserve the pressure within the reactor during ash withdrawal and to recover sensible heat from the ash being removed. Pressure can be maintained in the reactor during withdrawal through the use of lockhoppers.

Ash can be removed from the gasifier in two forms, dry or as slag. The determining factor is the reaction bed temperature. At temperatures in the bed above 2000°F, the ash exists as molten slag.

As the ash/slag leaves the gasifier and drops into the quench hopper, it is rapidly cooled by contact with water. Slag, as it hits the water, shatters into small fragments. Heat from the ash/slag is recovered from the quench water in heat exchangers. The water is then separated from the ash/slag and recycled back to ash/slag quench. Makeup quench water is required to replace water lost as steam and with the wet solids.

Ash/slag quench water is high in suspended solids and relatively high in dissolved solids and pH. Concentrations of ammonia, sulfides, and organics are low. The presence of CaO, MgO, Na₂O, and K₂O in the ash/slag causes the pH

of the quench water to rise to 8 to 12. Most heavy metals, such as Zn, Cd, Pb, and Cr, have low dissolved concentrations at these pH levels. Some elements, such as Se, As, F, and B, which can exist as anions under alkaline conditions, can be present at significant dissolved concentrations. A sample tabulation of equilibrium element concentrations in coal ash leachate is shown in Table 2.3.

Recycled ash/slag quench water requires blowdown to reduce the dissolved solids to acceptable levels. The blowdown stream is normally mixed with other wastewater streams for treatment. The addition of carbonates to this high TDS wastewater removes some of the dissolved solid through precipitation. At elevated pH, carbonate compounds of many dissolved metals precipitate and can be removed by filtration, flotation, or sedimentation.

Sludges generated by these treatment processes must be tested for leachability by RCRA-mandated extraction procedures. Wastes determined to be hazardous under RCRA regulations will require special disposal.

2.2.5 Raw Gas Quench Water

The hot product gas stream from the gasifier must be cooled before acid gas removal. The gas is quenched to reduce its temperature and to remove entrained particulates and water soluble gaseous impurities. Water is sprayed through the raw gas in the quench operation. A downstream waste heat boiler recovers heat by condensing the steam in the raw gas and the steam from evaporation of the quench water.

Raw gas quench water is the largest and the most contaminated wastewater stream generated in a gasification facility. The composition of the product gas directly influences the composition of the quench water. Many by-products and impurities in the product gas, namely ammonia, phenol, tars and oils, are readily condensed during the quench operation. Some of the acid gases, such as H_2S and CO_2 , are dissolved in the quench water. Steam condensate from the waste heat boilers also contains water-soluble impurities from the product gas.

Table 2.3 Equilibrium Concentrations of Elements
in Typical Coal Ash Leachate

Element	Leachate Concentrations# (mg/l)
Sb	0.017
As	0.036
Ba	0.3
Be	0.001
B	3.65
Cd	0.003
Cr	0.292
Cu	0.031
F	4.88
Ge	0.01
Hg	0.0003
Pb	0.008
Mn	0.002
Mo	0.167
Ni	0.12
Se	0.103
V	0.01
Zn	0.055
pH	10.9

derived from Reference 4 (P27)

Raw gas quench waters from fluidized-bed or entrained-bed gasifiers are highly particulate laden. Fixed-bed processes have lower particulate levels in the quench water.

Gasifiers that operate in the low-temperature, dry-ash mode have a significant amount of organic contaminants in the raw gas quench water. High-temperature gasifiers have quench waters of much lower organic pollutant loads because the elevated temperatures cause the oils, tars, and phenols to crack into simpler compounds.

Raw gas quench water undergoes phenol and ammonia removal before being blended with other wastestreams for further treatment. Phenol removal precedes ammonia removal because the solvents used to extract phenol do not remove ammonia, whereas ammonia removal processes may also remove phenol, thus making it difficult to recover both phenol and ammonia for sale. The reduction of phenols to sub-lethal concentrations is necessary before downstream biological treatment.

Two separate wastewater streams can be generated if a two-stage raw gas quench is employed.⁵ In this case, the strong electrolytes will dissolve in the initial quenchwater, which will be of a lower discharge volume than the second-stage quench. The latter will remove the weak electrolytes, such as phenols and other soluble organics. The greater part of the raw gas temperature drop will also take place on the second-stage quench. The production of two quench water blowdown streams of distinctly different composition would be advantageous only if these two streams were treated separately for reuse in the gasification plant.

2.2.6 Shift Condensate

The product gas from the gasifier typically has only a medium Btu content. Therefore, for a high Btu product, the quenched gas must undergo a shift reaction before methanation to adjust the hydrogen to carbon monoxide ratio to 3:1. Water containing contaminants condenses when the shifted gas cools. Gases present in the condensate include H_2S and CO_2 . The condensate may also contain

contaminants similar to those in the raw gas quench water, but at lower concentrations.

Since treatment of these wastewaters is similar to the treatment of raw gas quench water, these two waste streams can be combined before treatment.

2.2.7 Methanation Condensate

The final upgrading step to produce pipeline quality gas is methanation. Water formed during methanation is free of dissolved and suspended solids and gases and is therefore suitable for direct reuse.

2.2.8 Cooling Tower Blowdown

The blowdown from cooling towers in gasification facilities should be similar in composition to other cooling tower blowdowns. This wastewater will be very high in dissolved solids and other inorganic and organic materials. The exact composition and concentrations will depend upon the tower operation and the quality of the make-up water.

Before treatment, cooling tower blowdown can be diluted with other wastewaters that are much lower in dissolved solids. If treated wastewaters are used for cooling tower makeup, removal of dissolved solids is necessary to prevent a buildup of dissolved solids in the recycled flow. The entire cooling tower blowdown can also be treated separately and reused as makeup water. The processes available for dissolved solids removal include evaporation and reverse osmosis.

The composition of recycled water in cooling towers must be controlled so that the composition of cooling tower drift does not adversely affect downwind air quality. It is especially important that the concentrations of chemicals with known adverse health effects be kept below hazardous levels in the cooling tower drift.

2.2.9 Process Area Runoff

Gasification process area stormwater runoff must be collected and treated before discharge or reuse. The runoff from a gasification facility should be similar to that from such industrial plants as petroleum refineries. Runoff may be fairly high in suspended solids and oils.

Treatment of this wastewater begins with the separation of solids and oils. The separated wastewater effluent can be reused in process areas if TDS and organics levels are not too high. Otherwise, it would normally be blended with other wastewaters for further treatment.

2.2.10 Sanitary Sewage

The sanitary sewage generated by the employees at a gasification facility can be treated separately or mixed with process wastewaters. Mixing is appropriate only if the process wastewaters can be treated by biological oxidation, which is the most efficient and reliable method of treatment of sanitary sewage. Since wastewater is normally disinfected by chlorination, it should not be combined with other wastewater streams for treatment if toxic chlorinated hydrocarbons will be produced from the latter by chlorination.

2.2.11 Plant Drains

There are numerous drains throughout the plant where miscellaneous wastewaters are discharged and collected. The quantity and composition of these wastewaters depends on plant layout and design.

2.3 SOURCES OF WASTEWATER CONTAMINANTS

This section describes the origin of wastewater contaminants formed during gasification. The composition of the coal being gasified is a major factor in the quantity and composition of the wastewaters eventually produced. The operating conditions under which gasification takes place also determine the amount and

forms of contaminants. Table 2.4 gives the composition of the organic portion of different coals; the remaining fraction is ash.

Compounds formed in coal gasification from the elements in Table 2.4 are phenols, ammonia, cyanides, thiocyanates, and hydrogen sulfides. These compounds constitute the majority of the weak electrolytes produced during gasification.

Most inorganics in coal remain as ash or slag when coal is gasified. The elements comprising the ash are those typically found in minerals, namely silicon, aluminum, iron, and calcium, with smaller amounts of sodium, titanium, magnesium, and potassium. The concentrations of the various oxides of these elements in four coal types are shown in Table 2.5.

2.3.1 Phenol, Tar, and Oil

There are two distinct stages in coal carbonization. The first occurs at 750-950°F, when the coal becomes plastic. At temperatures in excess of 1200°F, the coal begins to decompose. As the temperature rises, the volatile components of the coal begin to be released from the coal. As these products pass through the coal or coke, they initiate secondary reactions with the less volatile components and produce tar. Tar is composed of light and heavy hydrocarbons, nitrogen aromatics, and oxygen-containing molecules.

Hydrocarbons produced range from single ring benzene to multiple ring structures. Nitrogen aromatics include pyridines, picalines, and quinolines. The oxygen aromatics are phenol-based compounds, such as phenol, cresol, xylenol, and naphthol. These products account for a large fraction of the organic loading in gasification wastewaters.

The amount and characteristics of the tar removed from the raw gas stream depend upon the coal type and the operating conditions within the gasifier. Any changes in gasifier operating conditions that reduce the organic loading to the quench water also reduce the treatment required for the condensate stream.

Table 2.4 Coal Composition

<u>COAL</u>	<u>CARBON</u>	<u>HYDROGEN</u>	<u>SULFUR</u>	<u>OXYGEN</u>	<u>NITROGEN</u>	<u>ASH</u>
(all values in weight-percent)						
<u>Bituminous</u>						
Ill. #6	63.26	5.37	3.02	13.46	1.35	13.54
Ky. #9	67.36	5.58	4.78	13.68	1.08	7.52
Pitt. #8	72.29	3.45	2.53	8.62	1.95	11.16
<u>Sub-Bituminous</u>						
Montana						
Rosebud	53.95	6.87	0.59	28.53	1.20	8.86
Wyoming	56.8	5.94	0.55	30.02	0.38	6.31
<u>Lignite</u>						
N. Dakota	46.82	9.45	0.56	35.63	0.73	6.81
<u>Peat</u>						
N.C. Humus	30.22	5.34	0.12	59.84	0.81	3.67

Reference 6 (P5, Table 1)

Table 2.5 Inorganic Components of Coal Ash

RANK	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% TiO ₂	% CaO	% MgO	% Na ₂ O	% K ₂ O	% SO ₃
Anthracite	25-68	25-44	2-10	1.0-2.0	0.2-4.0	0.2-1	-	-	0.1-1
Bituminous	7-68	4-39	2-44	0.5-4.0	0.7-36	0.1-4	0.2-3	0.2-4	0.1-32
Sub-Bituminous	17-58	4-35	3-19	0.6-2.0	2.2-52	0.5-8	-	-	3-16
Lignite	6-40	4-27	1-34	0.0-0.8	12.4-52	2.8-14	0.2-28	0.1-13	8.3-32

Reference 7 (P7, Table 2)

Tars, oils, and phenols are also produced during coal pretreatment. The below 800°F conditions of pretreatment do not favor the cracking of organic compounds evolved during the process. At these low temperatures, the evolved gases contain high concentrations of tars, heavier oils, and phenols.

Review of phenol and tar production in different gasification processes reveals that tar and phenol production is reduced at elevated temperatures. This is due to the instability of aromatic rings at temperatures in excess of 1400°F. Thermal cracking converts aromatic molecules to straight chain molecules. This phenomenon is the reason why the higher temperature slagging Lurgi process produces lower amounts of tars and phenols than the cooler dry ash Lurgi process.

Tar and phenol production from gasifiers can also be reduced by altering the physical configuration of the gasifier. For a Synthane gasifier, the tar and phenol production was significantly reduced when the coal was injected deep into the fluidized bed.⁸ The normal method of introducing coal into the gasifier is to allow it to fall through the rising hot gases. Feeding the coal deeper into the bed reduces the production of tars and phenols partially because the bed temperatures exceed the temperature of the hot gases and partially because of the longer reaction time.

It was found⁸ that extending the residence time of the tars or pyrolyzation gases within the gasifier reduced the amount of tars and phenols evolved. Residence time was found to be optimum at between two and four seconds for the gasifier configuration and the reaction conditions of the study.

At a constant residence time in the Synthane gasifier, phenol conversion increased with increasing temperature to a maximum of about 1800°F. At a temperature of 1800°F, the phenol reduction was over 99%. The gasifier that appears to have the least organics production is the Koppers-Totzek, which operates at 2700°F with a gas residence time of a few seconds. In it, the tars, oils, and phenols are converted into smaller compounds.

The influence of the above factors on tar and phenol production is illustrated in Table 2.6, which gives the composition of quench waters from various gasifiers. The CO₂-Acceptor process is one of the cleanest processes shown. The very low tar and phenol production is due to high temperature and long residence time of the product gas in the gasifier. Operation is at 1500°F with at least 25 seconds of residence time in the bed plus another 30 seconds in a disengaging zone above the bed. The combination of these two conditions effectively reduces the production of tars and phenols to very low levels.

As would be expected, low-temperature gasifiers have high tar and phenol production. In the dry ash Lurgi process, the coal is devolatilized above the bed rather than in the bed. This results in the evolution of gases at a temperature of about 900°F. The Cogas process has aqueous effluents that are high in organics. This again is due to the low temperatures in the first pyrolyzers, where the more volatile components are evolved. Under low-temperature conditions, the conversion of tars and phenols does not take place.

The operating conditions of the Hygas gasifier result in negligible production of tars but significant production of oils and phenols. Devolatilization takes place at high temperatures (1200°F) but the residence time in the gasifier is only about one second. In this case, the high temperature in the reactor reduces the heavier tars to lighter oils and phenols. The oils produced in this process are lighter than oils from Lurgi or Synthane gasifiers. Hygas oils are composed primarily of benzene, toluene, and xylene.

Comparison of organics production from a Lurgi and a Hygas gasifier makes it possible to draw some conclusions about the influence of operating conditions on the organics composition in quench condensates. The temperature at which the devolatilization gases exist determines the nature of the organics produced. Raising the temperature causes the heavier compounds to crack into smaller compounds. The conversion of the light oils and phenols cannot be effectively accomplished by high temperatures alone. The gases must exist at the high temperature long enough for the conversion reactions to take place.

Table 2.6 Organics Produced in Gasification Processes
(lb/1000 lb MAF)

Process	Coal	Condensable Organics		TOC	COD	Phenol
		Tar	Oil			
CO ₂ Acceptor	N.D. Lignite	None	None	0.04	0.8	0.003
Hygas	Montana Lignite	None	85	20	NR	7
	Montana Sub-Bitum.	None	125	5	NR	8
	Ill. #6 Bituminous	None	NR	14	NR	6
Lurgi (Dry Ash)	Montana Sub-Bit.	30	30	NR	28	8
	Ill. #6 Bit.	30	5	NR	26	6
	Ill. #5 Bit.	40	7	NR	22	6
	Pitts. #8 Bit.	40	9	NR	15	4
Slagging Gasifier	N.D. Lignite	[37]		8	NR	NR
Cogas	Ill. #6 Bit.	[160]		NR	NR	20
	Ill. #6	[37]		NR	8	1
Synthane (Free Fall)	Montana Sub-Bit.	NR	NR	NR	10	1.3
(Deep Bed Injection)	Montana Sub-Bit.	NR	NR	NR	10	1.3
Koppers Totzek	S. Africa Bit.	None	None	Negligible	16 mg/l	Negligible

NR = Not Reported

[] = combination of tar and oil

Reference 9

2.3.2 Nitrogen Compounds

The nitrogen content of coal is about 1%. Nitrogen released during coal pre-treatment and coal gasification reacts in these reducing atmospheres to form ammonia, cyanides, and thiocyanates, rather than oxides of nitrogen. Table 2.7 shows the nitrogen-containing byproducts formed in different gasifiers.

About 80% of the nitrogen present in coal is converted to gaseous nitrogen, ammonia, cyanide, and other nitrogen-based compounds during gasification. It is believed that ammonia results from reaction of nitrogen with amino side chains within the volatile components of coal. Nitrogen remaining with the char is usually incorporated into multi-ring compounds that are much more refractory than the amino side chains. The presence of hydrogen in gasification results in more ammonia production than under normal carbonization conditions.

The Koppers-Totzek process produces the least ammonia, the Lurgi and Synthane processes produce the most. Other than the fact that the K-T process uses an entrained bed and operates at much higher temperatures, there are not many data that can account for the differences in ammonia production between these gasification processes.

The production of cyanide is caused by secondary reactions and is enhanced by high temperatures. Cyanide has not been observed to be produced from gasifying coal at low temperatures. Cyanide has been formed by pyrolyzing nitrogen-containing organics, notably pyridine. Data necessary to provide more detailed information on cyanide production are not available.

The formation of thiocyanate in coal gasifiers is documented but is not understood. Thiocyanate is present in significant quantities in quench condensates. It is thought that the thiocyanate concentrations in quench waters are a result of aqueous reactions involving cyanide and various sulfur compounds in the presence of oxygen. Quench water has been found to increase in thiocyanate concentrations while decreasing in cyanide concentrations with time.

Table 2.7 Nitrogen-Containing Byproducts of Coal Gasification
(lb/1000 lb MAF coal)

Process	Coal	NH ₃	CN ⁻	SCN ⁻
CO ₂ -Acceptor	N. Dakota Lignite	12	0.014	0.06
Hygas	Montana Lignite	15	0.001	1.2
	Montana Sub-Bit.	7	0.001	0.5
	Ill. #6 Bit.	9	0.001	5
Lurgi (Dry Ash)	Montana Sub. Bit.	6	0.005	0.06
	Ill. #6 Bit.	8	0.02	0.15
	Ill. #5 Bit.	8	0.01	0.18
	Pitts. #8 Bit.	8	0.01	0.26
Slagging Gasifier	No. Dakota Lignite	4	NR	NR
Cogas	Ill. #6 Bit.	NR	NR	NR
Synthane	Ill. #6 Bit.	8	None	0.01
(Free Fall)	Montana Sub-Bit.	1.2	NR	NR
(Deep Bed)	Montana Sub-Bit.	1.8	NR	NR
Koppers Totzek		Negligible	NR	NR

NR = Not Reported

Most nitrogen compounds produced during coal gasification are soluble in water and are removed during raw gas quench. These nitrogen compounds must be reduced to concentrations that are non-lethal to microorganisms prior to biological processes, if these are used to treat the wastewater. Various removal methods can be employed; the final removal of low concentrations may be accomplished by biological oxidation.

2.3.3 Trace and Minor Elements

A great deal of research has been done to identify and quantify the ways that trace elements can be released by the gasification of coal. Almost every element can be found in coal. To simplify this analysis, only those elements that have been recognized as being hazardous are discussed. These elements are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), tin (Sn), and zinc (Zn).

Trace elements are naturally occurring. In fact, most of these elements are necessary for the proper functioning of biological systems. The quantity and chemical form of each element are the controlling factors for determining relative hazards. "Trace" elements occur in concentrations less than 1000 ppm in the earth's crust. "Minor" elements are those that are present in concentrations exceeding 1000 ppm. Table 2.8 shows the ranges in concentrations for various trace elements in coal.

The trace elements shown in Table 2.9 are of particular importance because their presence in a different chemical form or in higher concentrations than found in coal can be hazardous to plant and animal life. These elements can be volatilized and converted to more hazardous forms in coal gasification. Ash and slag produced during gasification also will contain higher concentrations of materials that are not volatilized.

Elements that are volatilized or partially volatilized during gasification are arsenic, cadmium, and mercury. All these elements are at least 50% volatilized. Transition metals, such as iron and nickel, may be volatilized as carbonyls.

Table 2.8 Trace Element Concentrations in Coal

Element	Mean	Max.	Min.	Std. Dev.
(values in ppm)				
As	14.02	93	0.5	17.7
Cd	2.52	65	0.1	7.6
Cr	13.75	54	4.0	7.26
Cu	15.16	61	5.0	8.12
Hg	0.20	1.6	0.02	0.20
Mn	49.4	181.0	6.0	40.15
Ni	21.07	80	3.0	12.35
Pb	34.78	218	4.0	43.69
Sn	4.79	51	1.0	6.15
Zn	272.29	5,350	6	694.23

Reference 10 (P 2-35)

Table 2.9 Distribution of Hazardous Trace Elements in Coal
(ppm)

<u>Element</u>	<u>West Interior</u>	<u>Eastern Interior</u>	<u>Appalachian</u>
Antimony	3.5	1.3	1.2
Arsenic	16	14	18
Beryllium	2	1.8	2.0
Cadmium	20	2.3	0.2
Mercury	0.13	0.19	0.16
Lead	NR	34	12
Selenium	5.7	2.5	5.1
Zinc	NR	250	13

NR = Not Reported

Reference 10 (P 2-34)

Arsenic is found in tar and raw gas quench water; mercury and cadmium are predominantly associated with tar. The percentage of the original volatile elements carried over with the raw gas increases with increasing gasifier temperatures.

The remaining trace elements remain with the ash or slag removed from the gasifier. The solid slag or ash is separated from the ash quench water and disposed in a landfill. The current regulations of the Resource Conservation and Recovery Act (RCRA) provide procedures for determining the degree of hazard due to leaching. Any material that is immersed in water at a pH of 5.0 for 24 hours and shows a concentration of an element that is 100 times that of the drinking water standard is considered hazardous and subject to all RCRA regulations.

Ash from a dry-ash Lurgi gasifier using Mercer County and Dunn County, North Dakota, lignite was leached at the University of North Dakota. The results are shown in Table 2.10. Leaching in this case was done by crushing the ash and refluxing it for 16-24 hours with boiling demineralized water. The leachate obtained is expected to be more concentrated than normal landfill leachate because the crushed ash has more surface area than normal ash and the boiling water should increase the solubilities of the elements. Ashes from a Lurgi gasifier, a Wellman-Galusha gasifier, and a Texaco gasifier were subjected to the RCRA Extraction Procedure test.¹¹ The results are given in Table 2.11. These leachate tests indicate that these ashes would not be classified as hazardous wastes under RCRA.

2.4 PILOT PLANT DATA

Most wastewaters from coal gasification have been obtained from experimental or developmental facilities. These bench and pilot scale facilities are not necessarily representative of commercial-scale facilities. A commercial-scale plant, in general, has wastewater flows that do not have counterparts in the smaller-scale facilities. In some instances, however, a wastewater stream will be generated by the pilot plant that is representative of the commercial scale process.

Table 2.10 Leachate from Lurgi (Dry) Ash

Element	Leachate (ug/l)		RCRA Standards † (ug/l)
	Mercer Co.	Dunn Co.	
Arsenic	3000	45	5000
Cadmium	700	10	1000
Chromium	70	200	5000
Copper	50	300	-
Mercury	NR	2	200
Manganese	6	120	-
Nickel	9	50	-
Lead	7	20	5000
Tin	3	NR	-
Zinc	20	30	-

† 100 times of primary drinking water standards

NR = Not reported

Reference 12 (P5)

Table 2.11 Characteristics of Waste Extracts Using the RCRA Extraction Procedure

	Concentration, ug/l													
	Ag	As	Ba*	Cd	Cr	Hg	Pb	Se	B*	Cu	Mn*	Ni	U*	Zn*
Lurgi-Rosebud														
3/8"-20 mesh	<0.2	<1	0.5	<0.1	<6	<0.4	<0.2	<1	0.55	2.7	3.22	34	<0.5	0.124
20-100 mesh	<0.2	2	1.0	1.1	<6	<0.4	1.0	<1	1.48	5.4	5.83	80	<0.5	0.157
>100 mesh	<0.2	3	2.3	2.0	<6	<0.4	1.8	<1	1.85	13.3	9.25	138	<0.5	0.321
Lurgi-Illinois #5														
3/8"-20 mesh	<0.2	<1	<0.2	52	5	<0.4	0.9	<1	0.28	5.6	0.39	4240	<0.5	37.1
20-100 mesh	<0.2	<1	0.8	32	3	<0.4	3.1	<1	0.77	6.5	1.15	442	<0.5	28.5
>100 mesh	1.6	3	1.0	26	4	<0.4	4.4	3	0.49	5.1	2.50	441	<0.5	9.2
Lurgi-Illinois #6														
3/8"-20 mesh	0.9	4	<0.2	13	3	<0.4	1.3	3	0.04	<2	0.28	49	<0.5	4.27
20-100 mesh	1.4	<1	<0.2	5.1	3	<0.4	1.3	<1	0.25	<2	0.39	56	<0.5	2.84
>100 mesh	<0.2	<1	<0.2	4.3	<2	<0.4	1.6	<1	0.20	<2	0.71	72	<0.5	1.13
Wellman-Galusha, ash	<1	19	1.0	<7	1	<0.6	7	14	--	--	--	--	--	--
Wellman-Galusha, dust	<1	33	1.0	<1	1	<0.3	8	6	--	--	--	--	--	--
Texaco, slag	<2	<2	0.19	37	4	<0.2	<2	<1	--	--	--	--	--	--
Boiler bottom ash	<1	<1	0.28	<0.3	<3	<0.2	<3	<1	--	--	--	--	--	--
Boiler fly ash	2	5	0.44	5.3	16	<0.2	<3	2	--	--	--	--	--	--
100x primary drinking water standard	5000	5000	100	1000	5000	200	5000	1000	--	--	--	--	--	--

*Values in mg/l
Reference 11, 13

The mode of operation of bench and pilot scale plants also makes it difficult to gather samples that are representative of commercial-scale wastewaters. A commercial plant can maintain essentially steady-state operating conditions. However, bench and pilot scale operations are characterized by wide variations as the optimum gasification conditions are determined. The materials and equipment used in these gasifiers have been subject to failures as the process develops. These failures usually cause a process shutdown. The incorrect selection of process parameters for a gasifier run may also result in process failure. When a steady state condition within the gasifier cannot be achieved, wastewater sampling cannot be representative of a commercial-scale facility.

Pilot plants may also be significantly different from commercial plants in matters other than scale. Often they are not complete plants or are comprised of somewhat different process units. Pilot plants may gasify a variety of coals as the process limitations are investigated. The data obtained during these experimental runs may not be representative of a commercial facility because the operating conditions and the coal being gasified are different. These differences can be critical because wastewater constituents are sensitive to coal type and operating conditions.

Data collection to determine and optimize treatment processes for the wastewaters from coal gasifiers is not unlike the development of the process itself. The gasification process and the wastewater treatment system must evolve at the same time. When the process is ready for commercial-scale operation, the wastewater treatment system operating parameters must have been determined.

The data from pilot and commercial gasification plants are discussed below. Scalable wastewater streams found in the pilot plant studies are identified and characterized.

2.4.1 Synthane

The Synthane process, which is presently mothballed, had been studied¹⁴ to determine the characteristics of the largest wastewater stream, the quench

condensate. This condensate is approximately 95% water, with the remainder being mostly ammonia and phenols. Tars also condense out with the steam.

Characteristics of the raw gas quench waters for different coals are shown in Table 2.12. This table shows that the quench wastewater is highly contaminated, regardless of the type of coal gasified. Western U.S. coals (Wyoming and North Dakota) result in the most contaminated quench waters. COD, tar, and phenol concentrations in the Synthane quench water have been significantly reduced by injecting the coal into the fluidized bed rather than having it fall onto the bed. Deep bed injection subjects the initial gasification products to much higher temperatures and provides a longer residence time. As a result, tars are reduced by 60% and phenols by more than half.

2.4.2 Lurgi

The Lurgi process is one of the few gasification processes that is operating worldwide at commercial scale. The commercial plants in operation are primarily the dry ash type. Modifications of the dry ash process to gasify caking American coals are at the pilot stage of development. The most promising type is the fixed bed, slagging type (British Gas). Advantages of the slagging process include increased efficiency, reduction of aqueous pollutants, and ability to use caking U.S. coals. Extensive studies have been done on the effluents from both the dry ash and slagging Lurgi processes.

The largest water stream generated by a dry ash Lurgi gasifier is the raw gas condensate. This stream also contains most of the pollutants associated with the process. Because of these two factors, this stream is the most intensively investigated at the commercial facilities in operation. Gasification of U.S. coals has been investigated at the Lurgi facilities at Westfield, Scotland, and at the SASOL plant in South Africa. Coals tested at Westfield were Montana Rosebud, Illinois #5, Illinois #6, and Pittsburgh #8. Tests performed at SASOL used Texas lignite. The purpose of these tests was to determine the modifications to the Lurgi process necessary for the gasification of predominantly caking U.S. coals.

Table 2.12 Typical Byproduct Wastewater Concentrations From A Synthane Gasifier*

	Coke Plant	Ill. #6	Wyoming	N.D. Lignite	West Ky. Bit.	Pitts. Bit.	Montana Rosebud Sub-Bit.
pH	9	8.6	8.7	9.2	8.9	9.3	9.2
Suspended Solids	50	600	140	64	55	23	68
Phenol	2,000	2,600	6,000	6,600	3,700	1,700	3,000
TOC	-	6,800	-	-	-	4,980	9,090
COD	7,000	15,000	43,000	38,000	19,000	19,000	22,000
Ammonia	5,000	8,100	9,500	7,200	10,000	11,000	9,500
Thiocyanate	1,000	152	23	22	200	188	31
Cyanide	100	0.6	0.23	0.1	0.5	0.6	0.07
Tar	-	71,600	-	27,800	-	-	23,000

* All values in PPM except pH

Reference 15 (P5, Table 1)

The raw wastewater is processed for tar and oil removal, phenol extraction, and ammonia removal. The resulting stream is referred to as processed wastewater. The processed wastewater is usually treated further to reduce organic and inorganic pollutants. Table 2.13 shows the characteristics of the raw and processed wastewaters obtained by Fleeker¹⁶.

Most contaminants in the raw wastewater were removed in the tar and oil removal, phenol extraction, and ammonia removal. It should be noted that the analyses were obtained from single samples of the raw wastewater and the processed wastewater. The ages of the samples were not accurately known, but the raw wastewater was less than six months old and the processed wastewater was less than a month old. Analyses were completed within four months of receipt. Samples were stored after receipt at 4°C. The effects of sample age are unknown. These data are for information purposes only, because of the statistically small data base.

Wastewater data from the gasification of U.S. coals at Westfield, Scotland, have also been collected. The data were collected from each of the two wastewater streams leaving the tar/oil separator. The overflow goes with the oils to additional oil removal, while the bottoms stream is conveyed with the tar for further separation. Table 2.14 gives the values formed for both these streams during gasification of U.S. coals.

A review of the data shows that both streams for all coals are heavily contaminated. Comparing the heavier tar stream to the lighter oil stream reveals that there is usually a slightly higher BOD and COD in the lighter oil fraction and a much higher free-ammonia content. The heavier tar fraction had a higher pH, a higher TDS content, and a lower cyanide and thiocyanate concentration. These two streams undergo separate tar and oil removal and are then combined and treated further for phenol, ammonia, and organics removal.

These data were obtained from a commercial gasifier, making scaleup of various process streams unnecessary. The drawback of the dry ash Lurgi process was that large quantities of excess steam were required to prevent the formation of clinkers within the gasifier. The large amount of steam rendered the process

Table 2.13 Characteristics of SASOL Wastewaters[#]

<u>Parameter</u>	<u>Raw Wastewater</u>	<u>Processed Wastewater</u>
COD	12,500	1,330
TOC	4,190	ND
TDS	2,460	596
pH	8.9	8.2
Fatty Acids	226	194
Phenols	2,360	3.2
Aromatic Amines	219	0.45
Ammonia	11,200	150

[#] all values in mg/l, except pH
 ND = not determined
 Reference 16 (P2, 12-14)

Table 2.14 Characteristics of Lurgi Dry Ash Condensates[#]

Coal	Montana Rosebud Subbituminous		Ill. #6 Bituminous		Ill. #5 Bituminous		Pittsburg #8 Bituminous	
Wastewater Stream	Inlet Tar Separator	Inlet Oil Separator	Inlet Tar Separator	Inlet Oil Separator	Inlet Tar Separator	Inlet Oil Separator	Inlet Tar Separator	Inlet Oil Separator
PH	9.6	8.3	9.8	8.5	9.5	8.3	9.3	8.2
TDS	4030	1765	2770	1570	3180	1120	1550	1240
BOD	9900	13400	3800	4700	6000	6200	4100	5400
COD	22700	20800	10100	12000	9300	10600	650	7500
Phenol	4200	4400	2200	1900	2900	3750	1400	2150
Free Ammonia	3990	14015	1700	17650	1520	13970	1600	14000
Fixed Ammonia	395	525	280	210	410	330	320	250
Fatty Acids	1250	1670	490	280	400	260	275	610
Carbonate	4070	19460	1280	6500	680	9210	1360	10740
Cyanide	2	4	3	11	7	14	1	2
Thiocyanate	6	15	65	160	79	158	70	185

Reference 17 (P 120, Table 3-20)

[#] All values in mg/l, except pH

somewhat thermally inefficient and produced a great deal of condensate. The solution to this problem was to operate the gasifier with much less steam, allowing the bed temperatures to exceed the ash fusion temperature. Under these slagging conditions, the Lurgi process was able to efficiently gasify U.S. coals.

A slagging, fixed-bed gasifier was installed at the Grand Forks Energy Research Center (GFERC), Grand Forks, North Dakota, in 1958-1959. Operation of the plant was resumed in 1976. During 1977 and 1978, wastewaters from the gasification of various western U.S. coals were compared, and the process was modified to reduce the wastewater treatment required. The wastewater streams were analyzed for two runs of the gasifier^{18,19,20}.

Samples from one run were analyzed for pH, TSS, COD, ammonia, phenol, sulfide, sulfate, total sulfur, cyanide, and thiocyanate. The samples were stored and analyzed according to procedures developed specifically for the wastewaters being studied. Difficulties were experienced because of a high concentration of suspended solids and oils in the sample. In addition, interferences were discovered during some analyses that pointed to interactions between the oils and solids. Because of large inconsistencies in values obtained and the inadequacies of some of the testing procedures, the data were not used. What these tests did reveal were the modifications necessary to the analysis procedures for wastewaters from slagging gasifiers.

A composite wastewater sample was collected in July of 1977 (Table 2.15). Equilibrium for the spray wash system for the gas quench was achieved towards the end of the steady state run. It can be seen that the pollutant levels from this slagging gasifier are not significantly less than for the dry ash Lurgi process. The reasons for this unexpected result are not apparent.

2.4.3 Hygas

Hygas process development by the Institute of Gas Technology (IGT) began in 1946. The pilot plant was designed and built to convert 4 tons of coal per

Table 2.15 End of Run Composition of Quench Water
from GFERC Run RA-21*

Total Phenol	4378
NH ₃	9110
COD	25410
TSS	440
pH	8.1
TDS	10650
Alk. as CaCO ₃	17130
Cyanide	94
Thiocyanate	296
Sulfide	358
Total Sulfur	421

Reference 20 (P 95, Table 18)

* All values in mg/l, except pH

hour to 1.5 million cubic feet of gas per day. During 1973, pipeline quality gas was first produced in sustained steady-state conditions. At various times in the continued development and refinement of process operating conditions, steady-state conditions have been achieved. The longest continuous, steady-state Hygas test (7 days), using Illinois #6 coal, was completed in 1979.

The Hygas pilot plant has some scalable wastewater streams, the two most important being ash slurry and product gas quench condensate. A significant difference between pilot plant operation and proposed commercial operation is in the treatment of pretreater off-gases. In pilot plant operation, gases evolved from the pretreater are quenched, and the condensate is combined with the product gas quench condensate. The low-temperature pretreater liberates high levels of phenols, which results in lower levels in the product gas condensate. In the proposed commercial operation, the pretreater off-gases will not be quenched but, instead, will be used as a fuel in the plant boilers. Pilot plant data in which the pretreater was used are not representative of commercial operation. The use of a pretreater results in reduced phenols in the raw gas quench water.

Compositions of wastewaters from the Hygas raw gas cyclone (operated dry in commercial operation) and the downstream raw gas quench are presented in Table 2.16. It should be noted that the values in this table are without pretreater operation. A review of these data shows that even though some phenol, ammonia, and other volatiles are removed in the pilot plant cyclone, most of these volatiles are removed in the quench section. Most suspended solids are removed in the cyclone. Wastewater contaminants from the Hygas process are less than from either the Synthane or the Lurgi processes.

The effect of pretreater operation is shown in Table 2.17. As shown, phenol levels and corresponding TOC levels are substantially reduced by pretreatment of the coal feed. Higher levels of suspended solids are a result of the coal type and not process variation. It is interesting to note that ammonia and cyanide levels were unaffected by pretreatment. Increased sulfur concentrations are a result of using high-sulfur coals.

Table 2.16 Composition of Hygas Wastewaters During Tests
Without Coal Pretreatment*

Component	Test 37 Lignite		Test 52 Sub-Bituminous		Test 58 Sub-Bituminous	
	Raw Gas Quench Condensate	Cyclone Slurry Water	Raw Gas Quench Condensate	Cyclone Slurry Water	Raw Gas Quench Condensate	Cyclone Slurry Water
Phenol	2055	ND	3772	1969	4390	2455
TOC	4294	ND	7240	2714	3324	1518
TDS	1782	ND	1293	913	2089	669
TSS	36	ND	67	2642	1011	26,000
pH	7.2	ND	7.3	7.5	7.4	7.1
Ammonia	3045	ND	4000	518	6048	257
Cyanide	Negligible	ND	0.0006	0.003	0.01	0.01
Thiocyanate	510	ND	385	211	214	198
Sulfate	126	ND	104	39	195	34

ND = Not Determined

* All values in mg/l except pH

Reference 21 (P5, Table 1)

Table 2.17 Composition of Hygas Wastewaters During Tests
with Pretreater Operation*

<u>Component</u>	<u>Test No. 46 Bituminous</u>		<u>Test No. 54 Bituminous</u>	
	<u>Product Gas Quench Condensate</u>	<u>Cyclone Slurry Water</u>	<u>Product Gas Quench Condensate</u>	<u>Cyclone Slurry Water</u>
Phenol	244	552	1227	394
TOC	321	721	1008	509
TDS	720	875	1090	432
TSS	27,500	17,500	36	15,700
pH	7.4	8.1	7.8	8.0
Ammonia	7413	1168	6552	439
Cyanide	0.02	0.04	Negligible	Negligible
Thiocyanate	27	64	99	31
Sulfate	333	473	1084	76

* All values in mg/l, except pH

Reference 21 (P6, Table 2)

2.4.4 CO₂-Acceptor

Wastewaters from the CO₂-Acceptor pilot plant have been extensively sampled. The only scalable pilot plant wastewater stream is the raw gas quench condensate. Most sampling was done during Runs 39 and 45. A summary of gasifier quench condensate characteristics is shown in Table 2.18. Contaminant concentrations are much lower than for the gasification processes previously discussed. Differences between runs can be partially attributed to the different coals gasified. Run 39 was fed Glenharold Lignite and Run 45 used Wyodak Subbituminous.

2.4.5 Bi-Gas

The Bi-Gas process has been under development at Bituminous Coal Research, Inc., since December, 1963. The bench-scale unit processed 5 pounds of coal per hour and generated design parameters used to scale up to a 120 ton/day pilot plant. The pilot plant in Holmer City, Pennsylvania, was completed in 1976. The most successful run of the pilot plant was completed in November, 1977, when a 24-hour, steady-state condition was achieved.

The Bi-Gas pilot plant is fairly new, and as a result, numerous mechanical and structural failures have prevented long steady-state operations. Although most pilot plant studies have been process related, some wastewater characterization has been done. The Bi-Gas pilot plant is unique in that all of the wastewater streams are scalable to a commercial-size facility.

Wastewater characteristics for the three most contaminated streams are shown in Table 2.19. The data presented are for information only, because steady-state conditions were not achieved. The recycle gas quench water originates from the coal drying area. The other two wastewater streams are those normally associated with coal gasification operations.

2.4.6 U-Gas

Information on U-Gas process wastewaters, being generated by IGT, is not available outside of the MLGWD Industrial Fuel Gas Demonstration Project.

Table 2.18 Characteristics of CO₂-Acceptor Gasifier Quench Condensate*

<u>Component</u>	<u>Run 39</u>	<u>Run 45</u>	<u>Average</u>
TDS	1520	930	1225
TSS	1780	4090	2935
pH	8.7	8.3	8.5
COD	87	43	65
TOC	2.5	3.2	2.9
Ammonia	2420	1210	1815
Phenol	0.011	0.4	0.2
Alkalinity	6270	4900	5585
Cyanide	7.8	11.1	9.5
Thiocyanate	5.6	2.6	4.1
Chloride	37	7.4	22

* All values in mg/l, except pH

Reference 22 (P 215, Table 6.1)

Table 2.19 Characteristics of Wastewaters from Bi-Gas
Pilot Plant Operation*

<u>Component</u>	<u>Recycle Gas Quench Water</u>	<u>High Pressure Gas Wash Water</u>	<u>Slag Quench Water</u>
TSS	58,425	10,456	2440
TDS	13,145	1594	834
COD	116,700	16,400	ND
BOD	355	214	ND
Phenol	0.37	22	ND
Ammonia	4.7	305	8
Cyanide	0.09	0.57	0.33
Thiocyanate	0.5	0.92	0.5
Sulfide	ND	9	15
Alkalinity	6300	1821	350
pH	7.0	8.4	7.6

ND = Not Determined

* All values in mg/l, except pH

Reference 23 (P 69, Table A-1)

2.4.7 Cogas

The Cogas process consists of two steps. The first step, the pyrolysis of coal to produce gas, oils, and char, is referred to as Char Oil Energy Development (COED). The second step of the process is the gasification of the char to produce a hot gas, which, in addition to being a raw product gas, supplies heat to the COED pyrolysis.

The main wastewater stream from the COED section is the raw gas quench condensate. This wastewater is characterized in Table 2.20. Data from the char gasifier raw gas quench are not available. The condensate associated with the pyrolysis section is scalable. Wastewater treatment for a commercial facility will differ from that of the pilot plant, however. In pilot plant operation, this wastewater is evaporated in the last pyrolysis stage, but it would be sent to a wastewater treatment system in a commercial-scale plant.

2.4.8 Winkler

Although this gasification process has been in operation for over 50 years, information on wastewaters from gasifying U.S. coals is not available.

2.4.9 Koppers-Totzek

The Koppers-Totzek process is operating at commercial scale worldwide at over 13 locations. However, wastewater information from the gasification of U.S. coals is not available.

2.4.10 Wellman Galusha

The Wellman Galusha process has been operated at commercial scale for over 35 years. Over 150 gasifiers have been installed in various industrial applications. There are more than seven Wellman-Galusha gasifiers operating in the United States at large industrial plants. A pressurized version of this gasifier was built for the DOE Morgantown Energy Research Center (METC). Analyses of decanter water produced by the METC gasifier is shown in Table 2.21.

Table 2.20 Characteristics of Cogas (COED Section) Raw Gas Quench Condensate*

<u>Component</u>	<u>Illinois Bituminous</u>	<u>N. Dakota Lignite</u>	<u>Utah Bituminous</u>	<u>W. Kentucky Bituminous</u>	<u>Pittsburgh Bituminous</u>
TDS	0.77	ND	ND	ND	ND
TSS	1.58	0.29	0.39	0.53	1.08
Phenol	0.41	1.04	0.54	0.17	0.2
Oil	ND	0.0	0.48	0.24	0.48
pH	8.8	8.9	8.9	8.7	7.1

ND = Not Determined

* All values in weight percent, except pH

Reference 24 (PA-6D, Table A-22)

Table 2.21 Characteristics of Decanter Water Samples
from METC/DOE Gasifier*

<u>Component</u>	<u>Run 85</u>	<u>Run 86</u>	<u>Run 88</u>	<u>Run 90</u>
TDS	ND	3,876	3,289	5,140
TSS	ND	21	38	36
Phenol	1,230	2,955	2,460	300
Ammonia (Free)	3,242	7,344	3,838	6,426
N (Total)	3,467	7,742	ND	ND
COD	87,251	ND	16,856	74,000
pH	8.7	8.8	8.7	8.5

ND = No Data Available

* All values in mg/l, except pH

Reference 25 (P8, Table 4)

Of interest are the low suspended solids levels and the high COD values. METC attributes the high COD value partially to reduced inorganics, such as sulfides. Further testing by METC will further characterize the wastewaters from this process.

2.4.11 Texaco

The Texaco coal gasifier is a pressurized, entrained-bed, downflow slagging gasifier. Two pilot units operating at 300 to 1,200 psi, respectively, have been gasifying 15 to 20 tons per day of an eastern U.S. coal (Illinois #6) and two western U.S. coals (Kaiparowits). Tables 2.22 and 2.23 presents the compositions of these test coals²⁶.

Tables 2.24, 2.25, 2.26, and 2.27 compare wastewater composition for the two test coals to the input process water. The slag wastewater is blowdown from slag quench settling, and the excess wastewater is a combined raw gas quench and excess gasifier slurry wastewater stream.

Table 2.22 Texaco Coal Analyses

<u>Ultimate analysis, wt % (Dry)</u>	<u>Eastern coal</u>	<u>Western coal</u>
Carbon	65.56	67.80
Hydrogen	4.76	4.72
Nitrogen	1.27	1.17
Sulfur	4.17	0.35
Ash	13.15	11.22
Oxygen (diff)	11.09	14.74
HHV (Btu/lb)	11,736	11,707

Table 2.23 Texaco Analyses Trace Components

<u>Element, ppm</u>	<u>Eastern coal</u>	<u>Western coal</u>
Antimony	1.2	<0.5
Arsenic	8.0	<0.9
Barium	64	320
Beryllium	0.6	<0.2
Boron	NR	15
Chlorine	602	24
Cadmium	1.4	0.2
Chromium	35	34
Cobalt	5	0.9
Copper	19	8
Fluorine	96	65
Lead	23	4.0
Manganese	95	34
Mercury	0.08	0.1
Molybdenum	8	0.3
Nickel	55	3.7
Selenium	2	1.7
Silver	0.2	0.3
Thallium	0.25	0.3
Vanadium	25	14
Zinc	147	7.9

Table 2.24 Texaco Water Quality Data
Eastern Coal

<u>Component</u>	<u>Process water</u>	<u>Slag water</u>	<u>Excess water</u>
pH	NR	8.0	7.7
TDS, ppm	0.0	355	1708
Conductivity	NR	1650	7100
COD, ppm	NR	221	405
TOC, ppm	<1	28	215
Ammonia, ppm	NR	380	1270
Anions, ppm			
Bromide	<1	<1	<1
Chloride	29	146	740
Fluoride	<1	31	175
Cyanide	NR	<1	8
Formate	<1	94	522
Nitrate	<1	3	9
Sulfide	0.3	6	316
Sulfate	25	38	21
Thiocyanate	NR	2	8
Thiosulfate	NR	5	NR
Trace organics, ppb			
Benzene		<0.5	3.0
Toluene		<0.5	2.0
Anthracene		1.0	0.5
Fluoranthene		2.0	0.5
Naphthalene		-	2.0
Pyrene		0.6	0.7
Phenanthrene		0.2	0.02
Phenols		NR	<10

Table 2.25 Texaco Water Quality
Western Coal

<u>Component</u>	<u>Process water in</u>	<u>Slag water out</u>	<u>Excess water out</u>
pH	5.3	8.9	8.8
TDS, ppm	<5	28	420
Conductivity	<10	410	10,800
COD, ppm	<5	48	760
TOC, ppm	0.4	38	360
Ammonia, ppm	<1	130	2700
Anions, ppm			
Bromide	<0.05	<0.05	<0.05
Chloride	<0.1	42	7.5
Fluoride	<0.01	<0.1	28
Cyanide	<0.2	0.4	11
Formate	<0.1	56	1200
Nitrate	<0.5	<0.5	2.0
Sulfide	<0.5	<0.5	61
Sulfate	1.3	5	47
Thiocyanate	<4	<4	29
Trace organics, ppb			
Phenols	NR	1.2	1.2
Unidentified	NR	7.0	2.8

Table 2.26 Texaco Trace Elements in Water Streams
Eastern Coal

<u>Element, ppm</u>	<u>Process water</u>	<u>Slag water</u>	<u>Excess water</u>
Antimony	<0.001	.016	<.001
Arsenic	0.002	.07	.022
Barium	0.003	.10	.54
Beryllium	0.0004	.005	.018
Boron	-	-	-
Cadmium	0.010	.003	.003
Chromium	0.002	.003	.006
Cobalt	0.005	.10	.021
Copper	0.01	0.017	.010
Fluorine	<1	31	175
Lead	0.005	.045	.054
Manganese	0.13	.08	.104
Mercury	<0.0001	<.0001	<.0001
Molybdenum	<0.02	.03	<.02
Nickel	0.03	.07	.03
Selenium	0.005	0.033	0.010
Silver	0.0006	0.002	0.002
Thallium	0.002	.006	.01
Vanadium	<0.04	<.04	<.04
Zinc	0.195	.046	.03

Table 2.27 Texaco Trace Elements in Water Streams
Western Coal

<u>Element, ppm</u>	<u>Process water</u>	<u>Slag water</u>	<u>Excess water</u>
Antimony	<0.001	<0.001	<0.001
Arsenic	<0.001	0.015	0.016
Barium	0.004	0.05	0.90
Beryllium	<0.001	<0.001	0.002
Boron	0.2	0.3	1.4
Cadmium	<0.006	<0.001	<0.001
Chromium	<0.001	<0.001	<0.001
Cobalt	<0.001	<0.001	<0.001
Copper	0.031	0.008	0.005
Fluorine	<0.1	<0.01	29
Lead	<0.005	0.011	<0.005
Manganese	0.002	0.003	0.024
Mercury	0.002	0.002	0.002
Molybdenum	<0.001	0.003	0.015
Nickel	<0.01	<0.01	<0.01
Selenium	<0.001	0.025	0.460
Silver	<0.002	<0.002	<0.002
Thallium	<0.002	<0.002	0.003
Vanadium	<0.01	<0.01	<0.03
Zinc	<0.01	<0.01	<0.01

SECTION 3 - WASTEWATER TREATABILITY STUDIES

3.1 INTRODUCTION

All coal gasification processes will use large quantities of water and produce wastewaters that require treatment prior to discharge or reuse. Current water quality regulations may impose strict constraints on wastewaters discharged from coal gasification facilities. Ultimately, these facilities may face the constraint that no wastewaters are to be discharged from the plant boundaries.

Preliminary wastewater source identification and characterizations from pilot plant operations indicate a need for further treatability studies to identify potential treatment processes. A survey of processes indicated that a major wastewater source in all gasification processes is the raw gas quench condensate. Quench condensates from first-generation processes, such as dry ash Lurgi, are contaminated by high levels of organics, ammonia, and other materials. Second-generation processes, such as Synthane and CO₂-Acceptor, generate less contaminated wastewaters. The quench condensates from most gasifiers are characterized by high concentrations of suspended solids, ammonia, organics (notably phenols), tars, and oils.

3.2 INDUSTRY EXPERIENCE

Wastewater treatment processes used by industries having wastewaters similar to those produced during coal gasification were investigated because the U.S. operating experience in these industries greatly exceeds that for coal gasification. It was found that coking wastewaters have characteristics similar to those produced by coal gasification. Some wastewaters generated during petroleum processing are also similar to those generated from coal gasification. The information obtained from processes used to treat these related wastewaters can then be applied to the analyses of treatment systems for coal gasification wastewaters in the U.S. A review of wastewater treatability information for coking and refinery wastewaters and of treatability studies on gasification wastewaters follows.

3.2.1 Coking Industry

Given the many similarities between coking and coal gasification processes, including the individual process sources of wastewaters, it seems reasonable to assume that the wastewaters from coking and coal gasification will have similar characteristics. Coking wastewater treatment technology should be effective in treating coal gasification wastewaters.

Coke is produced by destructive carbonization of low-sulfur, bituminous coal in the absence of oxygen. Coal used in making coke is usually a blend of high volatile coal with 10 to 50% of low-volatile coal. The blend should not contain over 1.5% sulfur and 9% ash. Coking processes are designed to recover byproduct gases and chemicals. Major unit operations in a coke plant are coal handling and preparation; coking; quenching; primary cooling; tar separation; tar extraction; ammonia removal; final cooling; light oil scrubbing; and sulfur removal. Modern coking plants have refining facilities for the recovery of benzene, toluene, and xylene from the light oils. Cleaned coke gas is often used as a low-Btu fuel source.

Coking takes place at atmospheric pressure and temperatures between 2000°F and 2100°F in 16 to 27 hours. Coking a ton of coal will produce approximately 78 pounds of tar, 5 pounds of anhydrous ammonia, 20 pounds of light oil, and 309 pounds (10,350 scf) of gas. It was found (Table 3.1) that some similarities exist among the effluent gases from coal gasification and coking processes. However, wide variations do exist. The higher CO₂/H₂S ratios for gasification reactions, for instance, will make sulfur removal and recovery more difficult than for gases in the coking industry.

Compositions of raw gas quench wastewaters from gasification and coking are compared in Table 3.2. Ranges and types of contaminants are reasonably close. The concentrations of contaminants in coking wastewaters are usually high enough to make recovery and sale economical. The coking industry uses steam stripping for ammonia removal. If feasible, the stripped ammonia is recovered by using the Phosam W, or similar process. Stripped phenols are most often recovered using a solvent extraction process.

Table 3.1 Compositions of Effluent Gases From Gasifiers and Coke Ovens¹

<u>Component</u>	<u>Lurgi</u> ²	<u>K-T</u> ³	<u>Coke</u> ⁴
H ₂	22.63	26.37	38.22
CO	11.65	51.79	6.18
CO ₂	16.16	8.82	1.33
O ₂	None	None	1.26
N ₂	0.18	0.69	0.45
NH ₃	0.55	0.08	0.70
HCN	0.16	0.02	0.16
H ₂ S	0.20	0.41	0.51
COS	0.007	0.04	0.02
CS ₂	None	None	0.01
Light Oil	0.14	None	0.79
Tar Oil	0.11	None	None
Tar	0.10	None	0.78
Phenol	0.05	None	0.04
H ₂ O	41.07	11.78	21.05
Temperature (°F)	370	2730	1000
Pressure (psia)	450	15.3	14.3
CO ₂ /H ₂ S	79.6	21.5	2.6

¹ All values in volume-percent

² Sub-bituminous

³ Texas Lignite (1.5%S)

⁴ Bituminous (1%S)

Reference 27 (P5, Table 1-2)

Table 3.2 Composition of Quench Wastewater From
Gasification and Coking Processes

Parameter	Coke Plant mg/l	Synthane mg/l	Lurgi mg/l	K-T mg/l
pH	8.4	8.6	8.9	8.9
Suspended Solids	4000	600	5000	50
Phenol	1000	2600	3500	None
COD	10000	15000	12500	70
Thiocyanate	1000	152	None	None
Cyanide	50	NR	NR	0.7
Ammonia	5000	8100	11200	25
Chloride	6000	500	NR	600
Carbonate	NR	6000	10000	1200
Sulfide	1250	1400	NR	NR

NR = Not Reported

Reference 27 (P8, Table 1-3)

Other removal processes that can be used for ammonia and phenols are biological oxidation and carbon adsorption. Dilution of the incoming stream may be required to avoid feeding excessively high concentrations of ammonia and phenols to these removal processes.

Biological treatment is often found to be the most cost-effective method to treat wastewaters containing organic pollutants. This type of treatment has been used for coking wastewaters pumped to municipal sewage treatment plants after dilution of the phenol concentration to 30-40 mg/l.

Extensive testing was done to optimize the biological treatment of these wastewaters in the 1960's. In 1969, pilot plant work by Kostenbader and Flecksteiner²⁸ at the Bethlehem Steel Corporation found that phenol could be oxidized at loadings of 0.86 mg phenol/mg sludge-day with detention times as short as 1.6 hours. This necessitated mixed liquor suspended solids (MLSS) concentrations of 5600 mg/l, which resulted in operational problems. The high loading, equivalent to 2 mg BOD/mg sludge-day, resulted in excessive foaming and sludge bulking. After much experimentation, it was found that at loadings of 0.7 mg phenol/mg sludge-day, phenol could be successfully removed. Recommendations from this study were:

- 1) Tar should be removed before biological treatment;
- 2) Ammonia concentrations in the aeration tank should be limited to 2000 mg/l;
- 3) The aeration tank temperature should be maintained between 80 and 95°F;
- 4) Phosphorus should be added as a nutrient in a ratio of 1 part phosphorus to 70 parts phenol; and
- 5) The pH in the biological reactor should be maintained between 6 and 8.

A summary of operating data from this study is shown in Table 3.3. It can be seen that influent phenol concentrations of about 3700 mg/l were reduced to less than 1.0 mg/l, a removal rate of 99.99%. There was no removal of ammonia by nitrification. Thiocyanate removal was very erratic, ranging from 10% to 99%. No evidence was found in Kostenbader's work that could explain this behavior. Cyanide removal paralleled thiocyanate removal.

Activated carbon has been used at the Cleveland District Coke plant²⁷, a facility of Republic Steel Corporation. Ammonia liquor blowdown, containing 1600 mg/l of phenol, is first pretreated with a solvent extracting process reduce the phenol content to about 30 mg/l. Other low-strength wastewaters containing less than 40 mg/l of phenol are also treated with activated carbon after oil and suspended solids removal. Minimal removals for ammonia and cyanide were obtained from activated carbon. Contact times over 60 minutes were required for optimum removals.

The application of activated carbon to treatment of coke plant wastewaters has also been reported by H. Juntgen²⁹. A sidestream was treated in an upflow pilot plant adsorption column. Average removals are shown in Table 3.4. During the pilot plant operation, the carbon loss in the regeneration cycle was only 3%. The wastewater was pretreated by filtering and oil and tar removal. Pilot plant data were used to design a 100 gpm demonstration plant built near a medium-size coking plant in Germany.

Activated sludge has been used²⁷ at the Lone Star Steel Company to treat ammonia still waste liquor. The plant was designed to reduce influent phenol concentrations of 100 to 800 mg/l to less than 1 mg/l at flow volumes of 500,000 gpd. The optimum operating conditions were a detention time of 24 hours and a phenol loading of 0.2 to 0.25 lb/day/lb MLSS at a MLSS concentration of 2500-3500 mg/l. During full-scale operation, phenol concentrations were reduced from 250-475 mg/l to 0.1 to 0.3 mg/l, with partial removal of cyanides.

Barker and Thomson³⁰ investigated the efficiency of using a carbonaceous removal unit, a nitrification unit, and a denitrification unit in series to remove both organic and ammonia compounds. In the carbon removal unit, COD is reduced from 3000 mg/l to 900 mg/l and phenols are reduced from 600 mg/l to below 1 mg/l. The detention time was 24 hours and the temperature was maintained between 75 to 90°F. Treatment efficiency was found to increase at higher temperatures. Thiocyanate was partially removed and 60% of the cyanide was removed in the carbon unit. The nitrification unit, operating with the influent diluted to 12% of its original concentration, oxidized the ammonia. The denitrification unit removed over 95% of the oxidized nitrogen.

Table 3.3 Operating Data From Pilot Plant Activated Sludge Units Processing
Raw Coke Plant Weak Ammonia Liquor (WAL)

Parameter	Operating Periods						
	1	2	3	4	5	6	7
WAL Flow (GPM)	0.74	0.85	1.21	0.95	0.82	0.40	0.44
Dilution Flow (GPM)	2.9	3.9	5.5	4.5	3.5	2.0	2.0
Dilution Ratio	1:3.9	1:4.6	1:4.5	1:4.7	1:4.3	1:5	1:4.5
Hydraulic Residence Time (Hours)	1.6	2.2	1.6	1.9	1.9	3.0	4.4
Temperature (°F)	90	92	92	90	87	80	80
pH	7.5-7.6	7.4-7.7	7.3-7.5	7.3-7.4	7.3-7.4	7.1-7-3	6.9-7.3
Influent Phenol (mg/l)	3700	3900	3500	3700	3400	3450	3350
Phenol Loading	0.68-	0.76-	0.85-	0.80-	0.66-	0.43-	0.51-
mg Phenol/Day/mg Sludge	0.75	0.80	0.90	0.83	0.89	0.48	0.63
Effluent Phenol (mg/l)	0.3-0.5	0.4-0.5	0.4-0.7	0.5-0.8	0.2-0.4	0.2	0.2-0.3

Reference 28 (P 202, Table 1)

Table 3.4 Coke Plant Wastewater Influent Concentrations and
Activated Carbon Removal Efficiencies

<u>Impurities</u>	<u>Influent Concentration (mg/l)</u>	<u>Removal Efficiencies</u>
Phenol	650-1400	99%
Cyanide	5-35	45-70%
Thiocyanate	120-450	30-80%
Iron	40-150	30%
Solids	300-3000	99%
TOC	800-2000	85-95%
COD	2000-4000	80-99%

The Alon Wood Steel plant²⁷ treats coking wastewaters by ammonia stripping, biological treatment, evaporation, and incineration. The raw wastewater contains 300-4000 mg/l of phenols, 3900-6000 mg/l of NH_3 , 10-100 mg/l of cyanide, 50-500 mg/l of thiocyanate, 20-40 mg/l of tars and oils, 30-120 mg/l suspended solids, and 4000-13000 mg/l of dissolved solids. The wastewater is pretreated in a downflow pressure filter to remove suspended solids, oil, and tar. The filtered effluent is stripped of ammonia and processed through an evaporator. The condensed vapors from evaporation are treated for phenol reduction by biological oxidation followed by ozonation or carbon adsorption polishing. The treated distillate is recycled back to the process. The evaporator bottoms are incinerated. It is not known what removal efficiencies are obtained at this plant.

Work performed by Adams³¹ on coking wastewaters showed that phenol concentrations in treated wastewaters can be expected to be less than 0.1 mg/l only 40% of the time at loadings of 0.2-0.3 lb BOD per lb of mixed liquor volatile suspended solids (MLVSS) per day. Nitrification was observed, but was not significant at BOD loadings above 0.3. A two-stage activated sludge process was recommended to reduce ammonia-nitrogen levels to less than 10-15 mg/l.

Pretreatment of wastewaters for phenol and ammonia removal is widespread in the coking industry. Further reduction in contaminants can be accomplished by biological oxidation if the ammonia concentration is below 1800 mg/l and the treatment system is well insulated from influent volume and composition variations. Activated carbon adsorption is also used, but extensive pretreatment is required. Carbon adsorption will remove only low concentrations of phenols and color. Another disadvantage of activated carbon treatment, besides the high cost, is its inability to remove ammonia.

3.2.2 Petroleum Refinery Institute

Petroleum refineries and coal gasifiers generate wastewaters that are similar in composition; these wastewaters require sour water stripping and oil/water separation. Refinery sour gas has higher H_2S concentrations and very low CO_2 concentrations compared to gasification raw gases. Refinery wastewaters contain

high levels of sulfides and little or moderate quantities of ammonia, whereas gasification wastewaters have low levels of sulfides and moderate levels of ammonia. The processes used to treat these wastewaters are sufficiently similar for qualitative comparison.

Stripping is commonly used in refineries to remove H_2S and NH_3 from sour waters. Conventional steam stripping can achieve greater than 99% removal of H_2S and up to 95% removal of NH_3 . Patented processes are used to simultaneously strip and recover sulfur and ammonia from wastewaters. These processes can reduce H_2S concentrations to 5 mg/l and ammonia concentrations to 50 mg/l. Phenols are also removed from wastewaters in steam stripping operations.

The first treatment step for the removal of oil and suspended solids from oily wastewaters is gravity separation. The API-type separator is the most widely used for this purpose. Chemicals may be added to assist in the removal of solids in gravity separators.

Oil and solids concentrations are reduced further by treatment in dissolved air flotation (DAF) units. DAF units may reduce oil by up to 80% and COD by 70%. Addition of phosphate before treatment has been found to increase the COD removal to 90% and the oil removal to 98%. These higher removal levels are very beneficial because of the decrease in downstream contaminant loadings. The added phosphorus is also needed as a nutrient in downstream biological processes. DAF units can reduce oils to 10 mg/l if gravity separators are used upstream.

Many refineries reduce organics concentrations in wastewater still further by using biological oxidation. Refineries use either activated sludge units or aerated ponds and lagoons to achieve biological oxidation of the wastewaters. Ponds and lagoons are used when wastewaters have relatively low organics concentrations and when land is available near the refinery. If the organics levels are higher, or land is not available, the activated sludge process is used.

Some refineries have installed activated carbon adsorption systems for reducing organics levels without bio-oxidation or for polishing wastewaters after biological oxidation. Operating parameters are lacking in the literature.

Ozone has also been used as a polishing step after bio-oxidation, primarily for reducing phenol concentrations. It is not clear if ozonation has advantages over other tertiary processes, but its high cost limits its use.

3.2.3 Coal Gasification Industry

Treatability studies have been performed on wastewaters from most coal gasification pilot plants under development in the U.S. These studies have focused on the reduction of organic contaminants in the raw gas quench condensates. The treatment process most often investigated has been activated sludge. Wastewaters have been obtained from pilot plants or made up synthetically from characterization data obtained from pilot plants. Single pollutants, such as phenol, have also been studied. Some process parameters for the biological treatment of coal gasification raw gas quench condensate have been obtained from these treatability studies.

It must be pointed out that these studies are at the bench scale, and much more information is required for the design of a wastewater treatment system suitable for demonstration or commercial coal gasification facilities. Coal gasification pilot plants have not generated wastewater streams under ideal testing conditions. Most pilot plants generate small amounts of process wastewaters during a relatively short run. This limits the scale of a continuous treated-as-produced experiment. This problem has been circumvented by accumulating larger amounts of wastewater in containers and treating the accumulated wastewater offsite. However, this procedure introduces significant errors into the treatability study results. The effects of process variations on the wastewater treatment process are eliminated. Even though some flow equalization will take place prior to biological treatment in larger-scale plants, the effects of variations in volume flow and composition of influent wastewaters on the wastewater treatment system should be determined.

The validity of pilot plant test results is also compromised by the lack of steady state operation. Pilot plant gasification runs are on the order of days, or even hours. Wastewater data from these short steady-state runs, or from non-steady-state runs, may not be applicable to full-scale plants.

Most coal gasification processes are in the development stage. The composition of quench condensates and other wastewaters depends on the coal being gasified and the conditions under which gasification takes place. At this time, dependable wastewater treatability data are not available because the composition of wastewaters to be tested is uncertain. Nevertheless, data obtained in the previous limited tests, combined with experience in treating similar wastewaters, allow treatability predictions to be made with some degree of assurance.

Oil and Suspended Solids Removal

Johnson, et al.¹⁵ investigated the removal and recovery of tars, oils, and greases from Synthane wastewaters. These contaminants must be removed before other downstream wastewater treatment because they will coat and foul equipment surfaces and will inhibit biological treatment. Tars and oils appear both as insoluble and soluble fractions in Synthane wastewaters.

Soluble tar-like materials were precipitated from Synthane wastewater by depressing the pH to 2.0. The precipitate was sequentially extracted with freon and acetone. Tar removal from wastewaters by sedimentation was also investigated using pH depression, alum addition, and organic polyelectrolyte addition at various pH levels. The results are described below.

Synthane raw gas condensate typically contained about 22,000 mg/l of tar, oils, and greases. Settling for 3-6 hours reduced this concentration by 95% to 1100 mg/l. The supernatant was treated by addition of alum after depressing the pH to about 2.0. Alum dosages in the range of 100-150 mg/l achieved the best and most consistent removal rates. Up to about 47% of the tar/oil remaining in the supernatant could be removed with alum. The remaining 3% of the original tar/oil can be removed by biological and/or adsorption methods.

The use of alum to remove only 2% of the original tar/oil is questionable from an economic standpoint. Even if alum addition is used to also reduce settling time, its use is debatable. This highly alkaline and well-buffered Synthane wastewater requires large quantities of acid to lower the pH for alum treatment. There are also various operational problems associated with pH depression, such as equipment failure caused by corrosion, foaming, and liberation of gases during acid addition. Studies with polyelectrolytes on similar wastewaters showed a lack of consistent removal rates.

P.C. Singer and others at the University of North Carolina-Chapel Hill³² have investigated tar and oil removal from a synthetic wastewater. No additional solids were precipitated by depressing the pH below 5.3. TOC and COD removals were optimal between pH's of 6.5 and 4.8. These reductions in TOC and COD are due to the removal of settleable solids and tars. Tars could be effectively precipitated by acidification to pH levels between 4.5 and 5.0, where 94% of acetone-soluble tar, 16% of COD, and 22% of TOC were removed. Alum was found to be an ineffective coagulant. Organic cationic polyelectrolytes were found to be effective coagulants, but at uneconomical doses.

Dissolved Gas Removal

Slack³³ found that the use of NaOH as a pH conditioner for ammonia stripping resulted in high levels of dissolved solids (TDS) (10,000-20,000 mg/l), which appeared to impair the settling of biomass in the downstream biological oxidation processes. Raising the pH with lime resulted in lower TDS levels and better settling in the biological reactor. It was concluded that lime would be the preferred method for raising the pH of wastewaters for ammonia stripping.

Pretreatment of Hygas wastewater to remove alkalinity and ammonia is necessary before biological oxidation.³⁴ A residual alkalinity of 1000 mg/l is needed to buffer pH fluctuations during bio-oxidation. Higher alkalinity resulted in a pH rise as CO₂ was stripped by the bio-reactor aeration. Alkalinity was reduced to the necessary residual value by adding 18 to 20 milligrams of lime per liter of wastewater.

Ammonia was removed by air stripping the wastewater at a pH of 10. The wastewater effluent from the stripping unit contained between 100 and 150 mg/l of ammonia. Use of this method of pre-treatment removed about 92% of the alkalinity and 95% of the ammonia in the raw wastewater. At the commercial or demonstration plant scale, ammonia can be removed by steam stripping at high temperatures. This would eliminate the need for lime sludge disposal and remove more ammonia than would be removed by low temperature air stripping.

Further results³⁵ indicate that 95 to 99% of the ammonia in certain wastewaters can be removed by steam stripping without pH adjustment.

Organics Removal

Most of the research in coal gasification wastewater treatment is focused on organics removal. Organics can be effectively removed from coal gasification wastewaters using biological or chemical oxidation, carbon adsorption, or solvent extraction processes. Upstream pretreatment units are needed to remove contaminants that inhibit or that are not removed by oxidation, adsorption, or extraction processes. Pretreatment also modifies and buffers the wastewater entering bio-oxidation processes, thus preventing system upsets.

A large portion of the Total Organic Carbon (TOC) content of coal gasification wastewaters has been found to be phenolic in nature. Most subsequent research has concentrated on the oxidation of phenolic compounds and on the identification of inhibitory effects from wastewater contaminants. Wastewater samples from pilot plant and bench scale gasification processes have undergone treatability studies to determine the optimum design parameters for wastewater treatment processes.

Treatability studies for organics removal from Synthane wastewaters were done by Johnson, et al.¹⁵. At the time of these studies, wastewater from the Synthane pilot plant was not available. Wastewater samples were obtained from the Synthane Process Development Unit (PDU), which produced 120 pounds of wastewater during a normal 5-hour run time using Montana Rosebud subbituminous coal. The

wastewater was air stripped at a pH of 11 for ammonia removal and treated for oil, tar, and grease removal before biological oxidation treatment for organics removal.

The microorganisms for biological oxidation were obtained from a nearby coke plant wastewater treatment facility and acclimated to the Synthane wastewater before treatability testing. Experimental constraints necessitated fixing the detention time at 24 hours. The food-to-microorganism (F/M) ratio was varied to maximize oxidation rates. Nutrients were added in the form of mono- and di-basic phosphates. The ammonia level was maintained below 500 mg/l.

Steady state oxidation was achieved after four hydraulic retention times. Table 3.5 shows operating conditions during steady-state conditions. Of interest is the relative insensitivity of oxidation rates when the F/M ratio was increased to 0.71. Slight decreases in organic removals took place while the sludge volume index (SVI) fell, indicating a more settleable sludge. The SVI is a measure of sludge settleability. It is defined as the volume, in milliliters, occupied by one gram of sludge that has settled for 30 minutes. In general, values under 100 are considered acceptable, while values below 30 are excellent.

Phenol removal was relatively constant at 99% up to an F/M ratio of about 0.8, but began to fall off at greater F/M ratios. COD removals remained rather steady at about 60% up to an F/M ratio of 1.0. TOC removals remained fairly constant at about 70% up to an F/M ratio of 0.6. At F/M ratios above 0.6, TOC removals fell rapidly, reaching 40% at an F/M ratio of 1.0. The sludge volume index (SVI) steadily decreased with increasing F/M ratios to a minimum of 30 at an F/M ratio of 0.8.

Extensive treatability testing of Hygas wastewaters for organic removal by biological oxidation has also been reported.^{34,36} The wastewater was pretreated by blending the cyclone and quench condensates, removing excess alkalinity by lime treatment, and air stripping ammonia to residual levels of 100 to 150 mg/l. It was found that phosphorus was required for biological growth.

Table 3.5 Average Operating Conditions During Steady State
Oxidation of Synthane Wastewaters*

Applied F/M Ratio (LB TOC/LB MLVSS/DAY)	TOC (mg/l)		TOC % Removal	COD (mg/l)		COD % Removal	Phenol (mg/l)		Phenol % Removal	MLVSS (mg/l)	Sludge Volume Index
	Infl.	Eff.		Infl.	Eff.		Infl.	Eff.			
0.71	1960	850	57	5690	2030	64	1205	25	98	2750	30
0.20	500	150	70	1250	390	69	175	<1	99	2520	47

* Reference 15 (P 17, Table 4)

The stripped wastewater was treated at mean cell residence times of 10 to 40 days and hydraulic retention times of two to three days. Influent phenols were reduced from 1600 mg/l to below 0.5 mg/l, while COD was reduced 80% to 800 mg/l. Cyanide levels were not reduced. Thiocyanate removals were 80 to 90%. Sludge produced by the process had acceptable SVI's in the 50 to 75 range.

Experiments run with unstripped Hygas wastewaters showed that maintaining high concentrations of ammonia (3200 mg/l) for three weeks caused biological system failure. A 1:1 dilution of the wastewater with uncontaminated water produced stable reactions.

The wastewater was found to inhibit nitrification. It was unlikely that excessive loading was the cause, because nitrification was not observed even in reactors with relatively low loadings. High concentrations of boron were suggested as the cause.

Recommended design parameters from this study are a mean cell residence times of 15-40 days, a hydraulic retention time of 3 days, alkalinity of 1000 mg/l, and a pH between 7.0 and 7.5. Unstripped wastewater can be successfully treated only after a 1:1 dilution.

Stable biological reactions were also established in subsequent treatability studies³⁴ using wastewater from a later Hygas run. The biological reactor was operated at a hydraulic retention time of 5.4 days, a mean cell residence time of 20 days, and a MLSS of 1500 mg/l. COD removal was 78%, BOD was 80%, and phenol effluent levels averaged 0.35 mg/l at an influent level of 650 mg/l. It was discovered that boron levels up to 160 mg/l did not inhibit oxidation as was previously thought. Again, cyanide was not removed, but thiocyanate was reduced from 37 mg/l to 1 mg/l during biological oxidation. Nitrification, evidenced by both reduced ammonia levels (from 135 down to 30 mg/l) and increased nitrate levels, was also observed in these subsequent treatability studies.

Wastewater from another later Hygas run was used to evaluate wastewater reuse treatment technology³⁷. The wastewater was steam stripped to remove approximately 97% of the ammonia. Biological oxidation achieved a COD reduction of

16% and a thiocyanate reduction of 96%. The effluent contained 1200 mg/l of hardness as CaCO_3 . This effluent cannot be directly used as cooling tower makeup because the remaining COD would promote significant biological activity and the hardness would cause scaling problems.

Most of the hardness present in the effluent is non-carbonate because alkalinity is consumed during biological oxidation. Softening required a larger portion of soda than lime, which resulted in the replacement of equivalents of hardness by sodium. Flocculation and/or filtration was necessary to clarify the sludge formed by softening. Further dissolved solids and organics removal was attempted by reverse osmosis, carbon adsorption and resin adsorption. Only reverse osmosis showed promise.

A biological treatment study of GFETC slagging fixed-bed gasifier wastewaters³⁸ found that ammonia-stripped wastewaters could be treated after dilution to 33% of the initial concentrations. At 50% dilution, extreme operational difficulties were experienced. Treatment of the 33% feed (influent diluted to 3840 mg/l phenol) achieved BOD removals of 95% and COD removals of 81%. Phenols were reduced by greater than 99.8%, thiocyanate was reduced by 89%, and organic nitrogen by 55% (influent at 160 mg/l). Reactor operating conditions were 10 to 40-day mean cell residence time and 1550 mg/l MLSS. The resulting sludge had a SVI index of 35. This study used mean cell residence time as the controlling factor rather than the hydraulic detention time.

During the runs, a significant amount of nitrification took place (50 to 90% removal). It was found that nitrification was favored at COD removal rates below 0.4/day.

Concern was raised over the possibility of an undetected cyanide interference with the biological reactions. Cyanide in wastewaters degrades rapidly. The cyanide levels in the wastewaters being treated in this study may have degraded to levels much lower than what would be expected during normal operations because of the storage times involved. Cyanide levels in GFETC wastewaters have been observed to drop from 200 mg/l to 25 mg/l in three days. Wastewaters were

spiked with potassium cyanide to a concentration of 100 mg/l in separate tests to resolve this concern. Cyanide at this concentration did not affect biological oxidation or nitrification.

Subsequent tests showed that raw GFETC wastewater could be processed at a 40% dilution. Nitrification reactions were effective with this wastewater in reducing the ammonia concentration from 2700 mg/l to 1000 mg/l. It was concluded that the inhibition of nitrification reactions is dependent upon ammonia loadings. Nitrification was not inhibited by influent ammonia concentrations as high as 3000 mg/l.

Isolation of bacteria capable of oxidizing wastewaters from the SASOL Lurgi plant was done by M. Bromell¹⁶. *Pseudomas*, *Arthrobacter*, and *Microoccus* bacteria were isolated from North Dakota soils and used to treat various wastewaters from the SASOL plant. The highest COD removals obtained were 70%.

A combination biological and physical wastewater treatment process was investigated by M. Suidan, et al.³⁹ at the Georgia Institute of Technology. Wastewaters containing phenol and/or glucose bearing substrates were treated in an anaerobic filter. In these filters, anaerobic bacteria grow on the filter medium and remove biologically degradable organics. In this study, activated carbon was used as the filter medium to also remove refractory organics. The advantages of using an anaerobic process rather than an aerobic process are that the anaerobic process forms methane gas as a byproduct and that higher loading rates, lower sludge production. Hydraulic residence times of almost 12 hours reduced the 2000 mg/l of glucose substrate 92% with respect to TOC and 95% with respect to COD. The 200 mg/l phenol feed first produced gas 135 days into the experiment and reached steady state conditions after 240 days. Removals at the second stage of the filter were 86% for TOC, 87% for COD, and 99.9% for TOC, COD, and phenol respectively. A final test was performed in which the readily biodegradable and poorly adsorbable glucose was added to the strongly adsorbable phenol. There were no antagonistic effects found.

This type of treatment has also been investigated by E. Witt and W. Humphrey of the Celanese Polymer Specialties Company⁴⁰. The process of the anaerobic filter is modified slightly to buffer the system with respect to toxic surges and modify the pH to acceptable levels. This is accomplished by diluting the feed with effluent from the filter. This recycle flow was found to improve the performance and reliability of the system. Feed concentrations of 11,500 mg/l of COD have been reduced by 60%. In this configuration, the effluent from the anaerobic filter is then processed aerobically.

Treatability studies performed by W. Slack at West Virginia University³³ analyzed biological treatment of wastewaters from the METC gasifier. Tests were done to investigate the effects of dilution and detention on performance, to determine the desirability of adding powdered activated carbon, and to establish kinetic data on biological reactors.

In the first set of experiments, four samples of wastewaters were obtained from different runs to simulate different gasifier conditions. The oils and tars were allowed to separate, and sample withdrawal took place at mid-depth. This procedure simulated expected pretreatment of the wastewaters. Wastewater samples were air stripped at a pH of 11.5 for 24 hours. The ammonia concentrations dropped from 2200-3000 mg/l to 450-550 mg/l. Cultures obtained from a coking plant wastewater treatment facility were used for inoculation. It was found that during bio-oxidation, the pH rose to 8.5 or higher and had to be controlled by addition of phosphoric acid because the high alkalinity of the wastewater caused the pH to rise as CO₂ was stripped off. Adding lime instead of NaOH during ammonia stripping operations should reduce the alkalinity of the wastewater. It was found that a feed of 75% wastewater could be treated biologically. Further experiments revealed that a detention time of 4-6 days resulted in stable performance. Reduction of phenols and BOD was over 90%, while TOC removals were above 60%. Organic loadings were 0.13 to 0.47 gm BOD/day/gm MLSS. MLSS concentrations were around 4000 mg/l and the SRTs were 18 days for the 4 day reactor and 15 for the 6 day reactor.

To evaluate the effects of powdered activated carbon (PAC) during stressed operation of the biological oxidation unit, two reactors were set up to process the same wastewater. The water was stripped of ammonia to a level below the inhibitory level (600-1000 mg/l). Full strength wastewater was processed at a 4 day detention time. At the 8-day mark, when both reactors were showing signs of biological system failure, 3000 mg/l of PAC were added to one reactor. The PAC reactor recovered after day 11 and eventually, at day 24, had TOC removals of 70% and phenol removals of 87%. The non-PAC reactor failed on day 13, as noted by zero oxygen consumption. Use of PAC appeared to control process fluctuations caused by influent variations.

In unstressed conditions, a wastewater with 500-600 mg/l of ammonia was processed by a biological reactor with 6000 mg/l of PAC. Without PAC, the reactor functioned, but TOC and phenol removals were 55% and 64% respectively. The removals, upon addition of PAC, rose to 75% and 90% respectively. The PAC also seemed to control foaming problems with the reactor at higher loading rates.

Biological oxidation with PAC addition was also tested with GFETC wastewaters, processed at a 33% dilution under conditions previously determined to be optimum.³⁵ Without PAC, the biological reactor reduced an influent BOD from 3700 mg/l to 30 mg/l. The addition of PAC reduced the COD, BOD, and color of the effluent relative to the run without PAC. However, based on more detailed analysis, it was found that little reduction in soluble organics was achieved by adding PAC.

An important constituent of gasification wastewaters, besides ammonia and phenol, is thiocyanate. These compounds are present in coke plant wastewaters, and it has been found that biological removal is unpredictable. The traditional method of removing thiocyanate by chlorination is not possible in this case, because the phenol also present would react with chlorine to form chloro-phenols. Results obtained through experimentation are that mixed cultures from coke plants can degrade thiocyanate from 2000 mg/l to 1 mg/l at 9 hours of detention time, and substrate inhibition takes place at thiocyanate concentrations in excess of 500 mg/l.

Biological oxidation of synthetic gasifier wastewater has been done by Singer, et al.³² at the University of North Carolina - Chapel Hill. The wastewater components were established by reviewing gasifier wastewater characteristics. The wastewater originally contained 2000 mg/l of phenol, and 3820 mg/l of NH_3CL , had a TOC of 4636 mg/l, and contained inorganic buffers and nutrients. It was then diluted to 25% of its original concentration to reduce its toxicity to micro-organisms. The synthetic waste was treated in a continuous flow activated sludge system with no recycle of biosludge. Hydraulic retention times varied from 5 to 10 to 20 days.

With retention time and sludge age at 20 days, 85-97% of TOC, 86-96% of COD, and 99.8% of BOD were removed. Phenol was removed at a sludge age as low as 5 days. MLSS concentrations ranged about 900 mg/l for all reactors.

Fluidized bed treatment of phenolic wastes was investigated by Lee, Scott, and Hancher at the Oak Ridge National Laboratory⁴¹. In this type of treatment, the biological growth adheres to inert particles in a fluidized bed. Phenol concentrations of 260 mg/l were degraded to less than 1 mg/l in 15 minutes of detention time. The maximum feed concentration of phenol that can be degraded on a continual basis by this method appears to be about 200-300 mg/l. Degradation of other organics in the feed began about 14 hours after they were added. It was also found that the bioreactor was easy to operate and could be left for long periods of time unattended. At the scale tested, this process looks very promising.

Chemical oxidation of phenolic wastewaters was reviewed by Suidan, et al.³⁹. Treatment processes included hydrogen peroxide, ozone, and chlorination. Hydrogen peroxide in the presence of ferrous salts has been shown to reduce phenol concentrations of 50 mg/l to less than 1 mg/l in thirty minutes. The inability of this process to efficiently remove high concentrations of phenols relegates it to effluent polishing status.

Ozonation has been shown to be an effective oxidizing agent for phenols. A survey of 10 coking plant wastewaters shows that influent phenol concentrations

were reduced from an average of 1500 mg/l to 0.60 mg/l. To achieve this removal, an ozone/phenol weight ratio of 1:41 was used. As in the case of hydrogen peroxide, the economics of this process will probably limit its use to effluent polishing.

Klein⁴ in his review of treatment processes concludes that the use of ozone can only be economical when a low waste concentration is to be reduced or when a small change in the waste composition is desired. A prime example of the latter is ozonation preceding biological treatment to reduce toxic and refractory materials to biodegradable forms.

Chlorination was found not to be an acceptable oxidation process because of its tendency to form hazardous chloro-phenols.

The Synthane process produces a char as a by-product that is planned to be incinerated to generate steam. Because the char has a surface area of over 300 M²/gram, its use in adsorption processes was investigated by Johnson, et al.¹⁵. The char after adsorption could then be fired to produce heat. Isotherm tests were run using Montana coal chars and biologically treated Synthane process wastewaters.

Adsorption tests were run and an isotherm was established for the char. Column tests were then performed to evaluate removal efficiencies. The phenol concentration into the char column was generally less than one mg/l, and the effluent from the char column contained no phenols to the detection limits of GC-Mass Spectrometry methods. Color in the wastewater was also eliminated with char adsorption. Non-biodegradable TOC was reduced by about 90% by use of char adsorption.

Experiments were performed³⁷ in which stripped, biologically treated, and softened Hygas wastewater was treated in an activated carbon adsorption column. The influent was maintained at a pH of 7.0, and the carbon column provided a contact time of 17 minutes at a loading of 1.2 gpm/sq. ft. The results indicated that 80% of the COD and 95% of the color could be removed by carbon adsorption.

Hygas wastewater treated as above was considered to be of sufficient quality for use as cooling tower makeup. Without data on TDS for the effluent, it seems premature to reach such a conclusion. It was assumed that the biological growth resulting from the residual COD of about 100 mg/l could be effectively controlled by a biocidal program.

Further analysis by Vajda⁴² of these data resulted in the conclusion that carbon adsorption in this case is economically impractical without regeneration because of the large quantity of carbon usage. It was estimated that, at present prices for activated carbon, the cost for treatment without regeneration would be approximately \$52 per thousand gallons. If the carbon is thermally regenerated, the carbon loss will drop to approximately 5% of the usage, which would make the process cost effective.

Phenol removal was investigated⁴³ using toluene, isopropyl ether, and n-butyl acetate. Because most solvent extraction processes are proprietary, obtaining their solvents to test removal efficiencies is not feasible. It was found that Hygas quench condensate phenol removals, using a five-step extraction process, paralleled removals found in the proprietary processes. The wastewaters pretreated by solvent extraction removed 99% of the phenolic compounds, or about 75% of the COD. Subsequent biological oxidation removed 78% of the remaining COD. The pretreated effluent contained more refractory materials because the easily oxidizable phenols were removed by solvent extraction. Wastewaters pretreated by solvent extraction also had a decreased tendency to foam during aeration.

Phenol removal from Hygas quench wastewaters was tested, using amberlite resins in a resin adsorption column. The process was ineffective, due to the large quantity of regeneration wastewater evolved.

Ozone treatment of Synthane wastewaters in a bench scale unit was performed by R. Neufield and A. Spinola at the University of Pittsburgh⁴⁴. Wastewater obtained from the bench scale Synthane plant was contacted countercurrently with the ozone in a packed adsorption tower. The results of the tests run were

that marginal removals were obtained at rates as low as 25 ml/min of wastewater at a dosage of 74 mg/l of ozone.

Dissolved Inorganics Removal

Klemetson and Scharbow⁴⁵ have experimented with reverse osmosis (RO) and ultrafiltration to reduce pollutants in a synthetic representation of Lurgi wastewaters. The zirconium oxide-polyacrylic acid RO membrane had a maximum phenol rejection rate of 80% at a pH of 10. The feed was 100 mg/l each of phenol, catechol, resorcinol, and o-cresol. The salt rejection rate was greatest (92%) near a neutral pH. This characteristic is beneficial if phenol concentrations are required to be reduced without removing all the salts from the wastewaters. Long-term effects of the wastewater on the membrane were investigated for runs of 60 hours. During this period, the flux rate stabilized at 150 gal/day/sq ft with no further deterioration.

Ultrafiltration runs showed rejection rates similar to RO membranes. Temperature caused significant variations in the flux but little change in rejection rates for some ultrafiltration membranes. For the zirconium oxide membrane, the flux increased by over 2-1/2 times to 160 gal/day/sq ft as the temperature increased from 75°F to 130°F. The flux rate also increased with increasing pressure. No observable long-term deterioration of either type of membranes was caused by the feed water.

Experimentation by Vajda⁴² using RO to treat biologically processed Hygas wastewaters found that significant deterioration of a polyamide membrane had occurred in two weeks. The efficiency of preventing the passage of dissolved solids was reduced by a factor of seven for one and ten for another membrane. In addition, it was found that the feed became saturated by calcium sulfate at 50% water recovery. Attempting to recover more water would precipitate out the calcium sulfate, fouling the membrane. The high turbidity of the wastewater also caused membrane fouling.

Lime/soda softening was investigated as a means of removing calcium sulfate in a pretreatment step prior to RO. Although more lime and soda than expected were required, this step did remove calcium sulfate to acceptable levels. Tests also showed that phenols were reduced by 40% and total COD by 15% by lime/soda softening.

Work done by Chu, et al.⁴⁶ provides information on the use of lime/soda softening to remove dissolved metals from powerplant bottom-ash effluent. The purpose of this treatment was to investigate the reusability of the wastewater. Results indicate that lime/soda softening effectively removes turbidity, calcium, magnesium, and silica. The addition of soda ash was required because of non-carbonate hardness. If the system was operated in a water reuse mode, sulfate buildup could be controlled by the addition of excess lime. Raising the pH to 10 with lime addition removed over 90% of the cadmium, copper, iron, lead, and zinc in the power plant effluent.

Preliminary results reported have indicated that a hollow fiber polyamide membrane operated at 400 psi and 25% recovery produced a high quality permeate, with about 20 mg/l COD passing through the membrane.³⁵

The addition of a polyphosphate inhibitor was thought to have prevented observable fouling. A decline in membrane flux did occur, but it was attributable to membrane compaction. The polyamide resin was compared to the cellulose triacetate hollow fiber membrane; the polyamide membrane produced a higher quality effluent, but higher flux rates were provided by the cellulose membrane.

Further work on long term membrane effects caused by fouling and on membrane cleaning techniques is being done at the present time.

3.3 DATA GAPS

A review of the data base showed gaps that require investigation. The information gaps are as follows:

- 1) Little work has been done synthesizing a complete treatment train. Rather, the same wastewater is being used to investigate different processes that would normally be connected in series. This does not allow potential problems in interfacing these processes to surface.
- 2) Advanced treatment processes have not been shown to eliminate refractory organics. With a recycled wastewater, a consistent method of removing these organics must be found. A possible choice for processes would be some form of pretreatment prior to biological oxidation to reduce refractory organics to biodegradable form. Ozonation has been shown to be effective for this pretreatment. Reverse osmosis is another potential treatment process that could be perfected. Other tertiary processes should be investigated to remove these refractories.
- 3) Operational problems encountered in 100% recycle systems should be explored. The buildup of various substances with time must be prevented to eliminate possible upsets to a biological or other process.
- 4) The form and severity of the effluent regulations for these plants is a data gap because there is no indication of what they will be. A 100% recycle design is obviously the most stringent design requirement.
- 5) The largest data gap is the absence of studies performed on a steady state gasifier producing enough wastewater to be treated on an as-produced basis. This gap will not be filled until the demonstration plants come on line.

3.4 DESIGN CONSIDERATIONS

General recommendations for design considerations of a coal gasification wastewater treatment system are summarized in the following paragraphs. These recommendations are proposed to aid engineers in selecting a suitable technology to design and in reviewing and evaluating the adequacy of a treatment scheme once it is designed. They are grouped in six categories of wastewater sources: coal pile storage and runoff, domestic sanitary wastes, solid waste leachate, ash quench, raw water treatment discharges, and process/gasifier quench condensates.

3.4.1 Coal Pile Storage and Runoff

- A. All coal storage piles should be made impervious to infiltration and all pile runoff should be collected and treated.
- B. The decision to recycle or discharge treated runoff should depend on the climatic conditions, net plant water availability, the accessibility of water reuse facilities, and areas of potential discharge.
- C. Simple containment, lime addition, and possibly aeration should be the only processes needed prior to discharge.
- D. Containment and treatment for several days should be provided in the design.
- E. NPDES permits should be obtained regardless of plant design and reuse.
- F. Oil removal should not be necessary for this wastewater source.
- G. Depending on the total dissolved solids (TDS) content of the runoff, consideration should be given to blending with cooling tower blowdown for further treatment.

3.4.2 Domestic Sanitary Wastes

- A. Domestic sanitary systems should be completely segregated, if possible, from the process wastewater treatment system.
- B. The domestic wastewater system should be plumbed and sized for the construction workforce.
- C. The plant should be sized for construction of the commercial facility.
- D. The discharge or reuse of treated domestic wastes should be evaluated as 3.4.1B.
- E. Chlorination should be avoided, if possible, for final bacteriological control. Ozonation, UV, or other should be used.
- F. NPDES and state permits should be obtained regardless of plant design.
- G. Laboratory facilities solely for the domestic wastewater system should be supplied.

3.4.3 Leachate Water Quality Control from the non-RCRA Solid Wastes Disposal Area

- A. Surface and groundwater quality monitoring should be conducted for the duration of the demonstration operations.
- B. The disposal area should be designed as a small area that can be expanded as operational data indicate the need. The incremental size should be for 6-month periods. Containment, control, and changes in water quality should be monitored for the individual disposal units.
- C. Onsite surface and leachate wastewater treatment should consist of, as a minimum, collection, detention, quality analysis, and bleeding to other

treatment facilities if the quality is insufficient for direct surface water disposal.

- D. NPDES permits should be secured for direct surface water disposal following treatment, if necessary.
- E. The reuse of leachates would be analyzed as per 3.4.1B.
- F. The concept of zero discharge from this wastewater source is not valid, since this is a perpetual source of wastewater even if the plant is shut down, mothballed, or decommissioned. NPDES permits should be secured.
- G. Unless otherwise noted, oil removal treatment would not be a part of this wastewater stream treatment.

3.4.4 Ash Quench Wastewater

- A. Ordinarily this wastewater will be completely recycled in the slag quench process area.
- B. If small blowdown streams are required, the streams would be carefully bled from this area and discharged into the product gas quench wastewater stream.
- C. Slag quench wastewater makeup should be the first area within the plant where water recycling is used. It is, therefore, desirable to recycle the cooling tower blowdown to the gasifier slag quench area.

3.4.5 Raw Water Treatment Aqueous Discharges

- A. The sludge treatment dewatering waste streams from the potable and process water supply plants should be considered as a wastewater source in all plant designs.
- B. The demineralizer wastewater stream should be considered in all wastewater treatment plant designs.

- C. Treatment and direct disposal of these non-process contaminated waste streams would be preferable to possibly contaminating them by treatment in the main process wastewater treatment system.

3.4.6 Process/Quench Condensates

- A. Enough equalization capacity (e.g. 2 days) should be provided to damp out potential toxics loading fluctuation caused by process upsets.
- B. Prior to ammonia/phenol removal and further waste treatment steps, consideration should be given including some kind of emulsion breaking steps, e.g., pH adjustment.
- C. Using two different treatments in sequence rather than relying on one treatment only to treat high organically contaminated wastewater can be most cost effective.
- D. Lime-soda can be effective in inorganics removal; countercurrent regenerated ion exchange should be considered when a concentrated waste stream is preferred to a higher volume dilute waste; reverse osmosis should be considered when a dilute waste stream with a minimum salt content is preferred.
- E. Forced evaporation of wastewater should be considered as the last resort in-organics removal step.
- F. Treated water should be reused to its maximum extent rather than discharged; decision of reuse or discharge should be evaluated per 3.4.1.B.
- G. NPDES permits should be obtained in all cases.

SECTION 4 - INDUSTRIAL WASTEWATER TREATMENT PROCESSES

4.1 INTRODUCTION

Most coal gasification technologies are still in the pilot plant or bench scale stage. Operating times are on the order of hours or weeks. Steady-state operation is too short for adequate characterization of wastewaters or wastewater treatment system operation. Pilot plant and bench scale operation is used more for trouble-shooting processes than for characterizing wastewaters and other environmental factors.

This section describes the function, applicability, efficiency, and reliability of various wastewater treatment unit processes operating at commercial site and at steady state. Both conventional and unconventional technologies are analyzed. The analyses of conventional wastewater treatment technologies rely on the operating experience of a variety of industrial applications. The impact of current and evolving effluent standards on the design of gasification facilities and approved instrumental methods for wastewater characterization are also presented in this section.

Wastewater treatment processes for industrial wastewaters are evaluated in terms of removal efficiencies, reliability, and resistance to upsets. Alternative processes within each unit operation must be analyzed to determine the most efficient method to remove the projected pollutants. The critical impact of upstream processes and the critical requirements of downstream processes in a complete wastewater treatment system require a system analysis that is considerably more complex than analyses of the performance of the individual processes in the system. At the demonstration scale, the primary design criteria must include reliability and resistance to overall system upsets and failures. It should be the purpose of the demonstration plant to prove the reliability and effectiveness of the wastewater treatment system design.

No single process can remove all the pollutants to environmentally acceptable limits or process reuse requirements. Therefore, it is necessary to combine

various processes to effect the desired treatment. The required treatment will be dictated by reuse water specifications and discharge requirements. The selection of the processes should be based upon meeting those effluent constraints in the most cost effective manner. The wastewater may contain impurities in sufficient quantities to make recovery and resale economical, which could influence the treatment selections.

4.2 TREATMENT PROCESS DESCRIPTIONS

Contaminants in wastewater can be removed to meet discharge or reuse requirements by converting them to other forms or by separating them for recovery or disposal. Many organics in wastewaters can be converted by chemical or biological treatment processes to produce biosludge and/or carbon dioxide or methane, depending upon the wastewater composition and the treatment process. Phenols, ammonia, and other dissolved weak electrolytes can be stripped from wastewaters and recovered. Tars and oils can also be separated and recovered. Dissolved strong electrolytes can be separated from wastewaters by such processes as reverse osmosis, electrodialysis, ion exchange, and evaporation and disposed in a concentrated aqueous solution, a slurry, or a solid waste.

Treatment of gasification wastewaters can be broken into several discrete operations. These operations are oil and suspended solids removal, dissolved gas removal, dissolved and suspended organics removal, and dissolved inorganics removal. The treatment processes available within each section are varied, and the choice of which process to use will be dependent upon many factors. Factors to be considered are process efficiency, effluent targets, cost effectiveness, reliability, and resistance to process upsets. The following is a description of available treatment processes that are available for treating gasification wastewaters.

4.2.1 Oil and Suspended Solids Removal

One of the first steps in treating wastewaters from gasification plants is oil and suspended solids removal. Gas quench water (which at this stage has usually been treated for the recovery of tars/oil, ammonia, and phenols) will undergo

coarse removal of settleable solids and floating oils because these materials will clog and coat downstream process mechanisms.

Oil and suspended solids removal, in some cases, allows the wastewater to be re-used directly after treatment or decreases the load on a downstream unit. The major processes used are gravity separation, flocculation-flotation and floc-sedimentation. Another process, filtration, is normally used as an effluent polishing step.

Gravity Type Separators

The most well known gravity separator is the API unit, which is designed in accordance with standards adopted by the American Petroleum Institute (API). The separator is essentially a basin in which solids heavier than water settle to the bottom and oil globules lighter than water float to the top. A collector skims the oil off the water surface and scrapes the sludge off the bottom. The collected oil is sent to a recovery unit and the solids or sludge is dewatered and disposed of.

These units will, in general, remove 60-99% of the separable incoming oil, 50-80% of the suspended solids, 5-35% of the BOD, and 5-30% of the COD, depending upon the wastewater. This process provides coarse treatment and is usually followed by other processes that remove solids and oils to acceptable levels. The treatment efficiencies are affected by the temperature of the wastewater (the temperature determines the viscosity, the density, and the size of oil droplets, all of which affect rise velocity) and the types of solids in the wastewater. The process advantages are high reliability (derived from extensive use in the petroleum industry), low energy consumption, and that it is a simple and effective process to remove grit, heavy suspended solids and non-emulsified or separable oils from wastewaters. Disadvantages of the process are the large amount of space the units require, the fact that it is only a coarse treatment process requiring further treatment, and that it is only effective on high concentrations of non-emulsified oils.

Flocculation-Flotation

This process is generally used in conjunction with, or in lieu of, gravity separators for the removal of dilute quantities of oils and suspended solids. To overcome electrostatic repulsion of suspended solid and oil particles so that they may agglomerate and be removed more rapidly, coagulants are added to the wastewater. These chemicals allow the charged colloidal particles to come close enough to contact each other through a reduction in surface charge on the particles. After chemicals are added to the wastewater, it is gently stirred (flocculated) to bring the particles close enough to contact each other and form groups or flocs.

Flocculated wastewater is then sent to the flotation unit, where gas injected at the bottom of the unit rises, intercepting solids and oils, and carries them to the surface, where they are removed by a skimmer. Flocs of solids and oils will intercept more rising gas bubbles in the flotation unit and rise faster than non-flocced solids and oils. Flotation can be accomplished by injecting air through diffusers in the bottom of the tank. Another type of flotation is dissolved air flotation (DAF) in which a sidestream, or the entire wastewater flow, is pressurized, injected with a gas (usually air) that is allowed to dissolve in the pressurized water, and then introduced into the bottom of the tank. The pressurized water, on exposure to atmospheric pressure, evolves the dissolved gas in the form of small bubbles, which rise to the surface. The rising bubbles entrap particles as they rise and carry them to the surface.

Flocculation-flotation systems can achieve the following removal efficiencies: 10-60% for BOD, 10-50% for COD, 50-70% for suspended solids, up to 75-95% for separable oils, and 50-70% for emulsified oils. These removal efficiencies may not be as high as stated for some wastewaters because different components may contribute to COD and BOD.

Because of the ionic nature of the process, the main disadvantage of the system is its high sensitivity to temperature, pH, and hydraulic loading variations in the incoming wastewater. This can be solved by the use of an equalization

basin to dampen any fluctuations in influent characteristics, but it is still an operating problem that must be considered. The advantage of the process is the high removals of BOD, COD, and oils. This unit plus an API separator can reduce highly polluted wastewaters to water suitable for biological oxidation.

Flocculation-Sedimentation

Flocculation-Sedimentation is similar to the flotation process just described except in the way solids are removed from the wastewater. In flotation, dissolved gases lift the floc to the surface. In this process, the floc formed is allowed to settle in a clarifier. The removal efficiencies of the sedimentation and flotation processes after flocculation are similar.

The advantage of flocculation-sedimentation is that it is a very simple process with few moving parts. Its disadvantages are that the process requires more space than a dissolved air flotation (DAF) unit and the solids withdrawn from the bottom of the clarifier are more dilute than the solids from a DAF unit.

Filtration

When very high removal efficiencies are required for suspended solids or oil, conventional treatment can be followed by filtration through a bed of granulated inert material, usually anthracite, sand, or diatomaceous earth. Suspended solids and oils are retained within the filter bed and gradually fill up all interstitial spaces in the bed. When the head loss across the bed is large enough, it is backwashed to remove retained particles. During backwash, the trapped particles separate and flow out with the backwash water as the bed is fluidized through agitation. The cleaned filter bed is then drained and is ready to be returned to service.

There are two main types of filtration, gravity and pressure. The deciding factor on which type of filter to use is the solids concentrations in the wastewater. The length of time a filter is in service is a function of the wastewater flow, solids concentrations, and filter bed volume. A pressure filter

is normally used to treat a waste stream low in solids. Pressure filters have a much higher flow capacity than gravity filters because of the higher differential across the bed. However, a solids concentration in excess of 50 ppm will blind a pressure filter's bed so rapidly that the filter may be frequently out of service. If a high solids concentration is to be treated, a gravity filter, having a large bed volume to absorb the solids, should be used.

As a polishing step for an API separator, the following removal efficiencies can be obtained by a sand filter: 80-99% suspended solids, 50-80% free oil, 25-40% COD, and 35% BOD. Filtration is relatively insensitive to temperature, easily maintained, relatively inexpensive, and has been successfully used to treat gasification wastewaters at the SASOL Gasification complex in South Africa. The process limitations are that the process functions best as a polishing step, the filter bed must be periodically regenerated by backwashing, and the backwash water must be treated prior to disposal.

4.2.2 Dissolved Gas Removal

Gasification wastewaters typically contain high concentrations of dissolved gases such as ammonia, carbon dioxide, and hydrogen sulfide. Many of these gases require removal to prevent lethal concentrations from reaching downstream biological treatment processes. In some cases, the concentrations of gases are sufficiently high to make recovery processes economical.

Stripping

Stripping of gases from wastewaters takes place when a stripping medium, such as steam or air, is forced countercurrently through the wastewater, commonly in a packed tower or a tray tower. The gases are transferred from the wastewater into the stripping medium. Steam is the most common stripping medium and is widely used in the petroleum industry for the treatment of sour waters containing ammonia and/or hydrogen sulfide.

Hydrogen sulfide (H_2S) can be removed from gasification wastewaters by stripping with a small quantity of steam. Wastewater to be treated is preheated to almost stripper temperatures and then poured down a coarse packed column. Steam flows upward, removing H_2S from the wastewater. Steam rates necessary to achieve H_2S removal with minimal ammonia stripping is about 0.5 pounds of steam per gallon of waste. The H_2S laden steam is then conveyed to sulfur recovery.

Ammonia present in gasification wastewaters exists in two forms, free and fixed. In the free form, ammonia molecules are weakly bonded to other molecules such as carbon dioxide and phenol. The fixed form consists of ionic ammonium ions. In the stripping process, weakly bonded free ammonia is removed first from the wastewater. The fixed form can be removed by the addition of NaOH or lime to a pH of about 11. The high pH shifts the equilibrium constant so that the ammonium ions are converted to molecular ammonia. Ammonia reductions from 4000 ppm to about 50 ppm of NH_3 have been obtained using about 1 pound of steam per gallon of waste with appropriate pH control.

Stripping of dissolved gases can achieve the following removal efficiencies: H_2S 99%, NH_3 99%, phenol 20-40%, and hydrogen cyanide up to 90%. The disadvantages of steam stripping are that the efficiency is dependent upon steam rates, NH_3 and cyanide removal is sensitive to pH, and hydrogen sulfide in stripper water is corrosive.

Chevron WWT Process

This patented process strips and recovers hydrogen sulfide and ammonia from wastewaters. In this process, the differences in solubilities of H_2S and NH_3 at different pressures are used to remove the impurities for recovery. The gas evolved can be processed to convert the ammonia to anhydrous or aqueous solutions and to convert the H_2S to sulfur. Sales of sulfur and ammonia byproducts are expected to offset the higher cost of this process over conventional steam stripping. This process can achieve better than a 99.9% removal of H_2S and a 99.99% removal of NH_3 . The flexibility of the process allows for lower removal efficiencies, if required, with lower steam usage and correspondingly

lower cost. The main disadvantages of this process are that it has not been used on coal gasification wastewaters, phenol recovery is low, and, because it is a proprietary process, royalties must be paid for its use.

USS Phosam W Process

This proprietary process removes contaminants present in sour wastewaters and recovers NH_3 for resale. The process uses phosphoric acid phosphate salts to recover ammonia from wastewaters. Sour gases, mainly H_2S and CO_2 , are also removed. Ammonia removal and recovery efficiencies will normally range between 98 and 99.5%. These efficiencies can, depending on desired outputs, be decreased or increased. H_2S removal is expected to be in the same range as NH_3 . The process has been commercially operating in coke ovens for over 10 years with a service factor of 95%.

4.2.3 Dissolved and Particulate Organics Removal

Coal gasification wastewaters contain high levels of organic contaminants. The major component of the Total Organic Carbon (TOC) in gasification wastewaters is phenols. A wide variation in concentrations of many other organic compounds can be expected.

The treatment processes discussed below will most likely form the core of any system to treat coal gasification wastewaters. At this step, most of the organic pollutants are removed. The processes to accomplish this include biological oxidation for removal of biodegradable organics, chemical oxidation for removal of biodegradable organics, chemical oxidation for the destruction of refractory or non-biodegradable organics, carbon adsorption for the removal of refractory organics, and solvent extraction for phenol removal.

Biological Oxidation

Biological oxidation is the process in which living microorganisms consume dissolved and colloidal organic molecules. In aerobic processes, the bacteria

use oxygen to convert the organic material to more cellular material, carbon dioxide, and heat. These reactions are usually carried out by a heterogeneous mixture of organisms. In anaerobic processes, the conversion of organics to cell matter and other constituents takes place without the presence of oxygen. This process is dependent upon a few specific types of bacteria. The byproducts of this type of conversion are cell matter and methane. Aerobic treatment is preferred because of higher efficiencies and lower costs. With either type of process, the wastewater pollutants are converted into gases and a settleable mass of dead and living organisms.

Some organic materials, termed refractory, are not amenable to biological degradation. These compounds will have to be oxidized chemically or removed from the wastewater by other processes. Most of the data available for gasification wastewaters indicate that a large portion is biodegradable, however.

To maintain aerobic oxidation, oxygen and oxidizable substrates must exceed certain values. Conversely, there are maximum concentrations of some substrates - for example, phenol and ammonia - above which biological oxidation is not possible. Phenol, although readily biodegradable, begins to limit oxidation at concentrations above 1000 mg/l. Ammonia becomes toxic to bacteria above 600 mg/l. To treat wastewaters exceeding these concentrations, either the wastewater must be pretreated before biological treatment or the incoming wastewater must be diluted to achieve acceptable influent concentrations.

The two types of aerobic treatment processes utilized are fixed film and suspended growth. Both types have advantages and disadvantages. Fixed film processes are used for roughing operations and first stage biological treatment. The fixed film is more resistant to physical and chemical shock than are suspended growth systems. Fixed film systems also produce less biomass per unit of BOD removed, and the sludges produced are more compact. Examples of this type are trickling filters and rotating biological contactors.

Suspended growth systems are generally capable of higher removal efficiencies for BOD, COD, nutrients, metals, and dissolved organics than fixed film systems.

In this process, the bacteria are suspended in the wastewater. Oxygen is continually dissolved into the water by using diffusers or mixers. Since the bacteria are in suspension, their entire surface area can contact and degrade organics. In the most common example, activated sludge, the aeration tank effluent is sent to a clarifier, where the bacteria settle to the bottom. From the bottom, most are recycled back to the aeration reactor, with a small portion being disposed of. Recycling of solids is necessary, in this case, to keep the bacteria at the average age where maximum growth occurs, even though the hydraulic residence is much less. This ensures that substrate consumption is maximized. Other examples of suspended growth include aerated lagoons and oxidation ponds.

The process is sensitive to temperature, pH, oxygen content, organic and hydraulic loadings, toxic material content, and nutrient concentrations. Optimum temperature for biological growth ranges from 60-100°F. Activity increases as temperature increases but, above 100°F, the organisms are adversely affected and the process is upset. The pH level of waste stream is the most important factor influencing the efficiency of biological oxidation. These organisms cannot exist at pH levels below 5.5 or above 9.5, with 7.0 being optimum for growth.

The presence of oxygen is required for aerobic biological growth, and the more oxygen available, the better the process is able to withstand shock organic loadings. Biological oxidation is highly dependent upon both organic and hydraulic loadings. As the organic loading increases, the percent of organics oxidized decreases but the total amount oxidized increases. The optimum feed to micro-organism ratio is 0.2-0.5:1.0. Excessive hydraulic loading results in a decrease in the efficiency of biological oxidation. The presence of heavy metals can have adverse effects on the efficiency of oxidation, particularly if a rapid change in concentration occurs. Nitrogen and phosphorus must be present for biological oxidation to occur. In gasification wastewaters, phosphorus is sometimes required as a nutrient.

Process advantages of biological treatment are that effective reductions in BOD and phenol concentration can be obtained. In addition, wide applicability and

reliability have been proven in numerous industrial applications. It is comparatively inexpensive, will remove some amounts of heavy metals, and can be designed to remove significant amounts of ammonia and cyanides from influent streams.

The disadvantages of the process are its sensitivity to pH, temperature, shock hydraulic and solid loadings, toxics, nutrients, and oxygen. This process must be monitored carefully to prevent upsetting the reactor, causing process shut-down.

Chemical Oxidation

Chemical oxidation processes use oxidants such as chlorine compounds and ozone for the treatment of cyanide, sulfide, and thiocyanate wastes.

Ozone is a very strong oxidizing agent that is used to oxidize hydrocarbons and other organics to less complex compounds. Ozonation can proceed to complete oxidation, resulting in inert compounds such as water and carbon dioxide. Thiocyanate oxidizes to sulfate and cyanide, with the cyanide oxidizing slowly to cyanate. The destruction of phenols requires about 2 pounds of ozone per pound of phenol.

Theoretical energy consumption to produce ozone is about 34 kcal per gram-mole produced. However, actual operating experience has found that the value is 20 times that figure. The low efficiency and high cost is a major drawback to the use of ozonation for the destruction of large amounts of organics.

Chlorine compounds have historically been used for disinfection of wastewater and drinking water. In these applications, low concentrations of bacteria are removed because of the toxic effects of chlorine on the bacteria. The ability of an installation to treat large concentrations of organics, principally phenols, is highly questionable. Chlorine reacting with phenol will produce chlorophenols, which have been determined by the EPA to be hazardous chemicals, as are phenols.

The potential application of chemical oxidation of gasifier wastewaters will probably be limited to effluent polishing. Even with polishing applications, the required ozone dosage can be high, and ozonation may not be cost competitive with more conventional treatment processes.

Carbon Adsorption

The adsorption of dissolved organics on activated carbon is a well developed process. This type of treatment has been used for treating industrial wastewaters and as a final effluent polishing step for municipal wastewaters. Adsorption by activated carbon involves the accumulation of substances on the surface of the carbon.

To form activated carbon, organic material such as coal or wood is pyrolyzed to a carbonaceous residue. During the activation step, the carbon particles are treated so that pores are formed throughout the particle. The pore sizes generally range from 10-1000 angstroms. Estimates of the amount of surface area that activated carbon has are that one cubic foot of activated carbon has a surface area of about 10 square miles. The large surface area coupled with pores throughout the particles make activated carbon well suited for dissolved organic removal. The production of char by some gasification processes may be an advantage in that the char could be substituted for activated carbon.

Adsorption from wastewaters onto activated carbon requires that the dissolved organics being removed from the wastewater have two properties. One is a low solubility of the solute being removed in the wastewater. The solute must also have a high affinity for activated carbon. If a solute has these two properties, it will be adsorbed by activated carbon in three steps. First, the solute must come in contact with the surface film of the carbon particles. The solute must then diffuse through the film to the surface of the carbon. In this step, the solute enters the pore matrix within the particle. The final step is the adsorption of the solute on the carbon surface. The adsorption is thought to be by chemical bonding, or electrical attraction of the solute to the carbon, or because of Van der Waals attractive forces.

Carbon adsorption normally takes place in a packed bed of granular carbon, with either upward or downward flow. To expose all surfaces to the solute, upward flow can be increased to the point where the bed becomes fluidized. Under these conditions, each carbon particle is suspended in the wastewater with minimal contact with other carbon particles. Activated carbon can also be used in powdered form where granular carbon will not work. An example is the addition of powdered activated carbon (PAC) to the activated sludge process. Here PAC is suspended in the wastewater to remove non-biodegradable organics. PAC could also improve the efficiency of an activated sludge system by enhancing the bio-activity and improving the settleability of biomass.

As adsorption takes place, the pores on the surface fill up, and eventually the carbon particle is in equilibrium with the wastewater. In a packed column, this saturation line moves through the bed co-currently with the wastewater flow. When the bed is completely consumed, breakthrough occurs, and the carbon must be regenerated. Regeneration is the heating of the carbon to temperatures sufficient to volatilize the adsorbed organics from the carbon. For heavier organics, temperatures up to 2000°F are necessary to remove them from the carbon.

The advantages of activated carbon are its ability to purify wastewaters of refractory materials and its insensitivity to organic, toxic, or hydraulic loadings.

Because of the high cost of activated carbon, its use is restricted to the removal of high levels of toxic or refractory materials, removal of residual organics from biologically treated effluents, or for recovery of byproducts such as phenols. In some cases, activated carbon can be used in combination with other chemical-physical processes as a treatment system.

The main disadvantage of this process is the high cost of the activated carbon. This makes it necessary to thermally regenerate it for re-use, and this process is also an expensive proposition. The regeneration will also produce liquid and gaseous streams that must be treated to environmentally acceptable levels.

Solvent Extraction

The use of solvent extraction for coal gasification wastewaters is used primarily to recover phenols for resale. Some gasification processes may produce phenols in concentrations high enough to make recovery economical. When used, solvent extraction processes precede wastewater treatment and ammonia recovery. Solvent extraction is based on the principle that phenol is more soluble in some liquids than in others. The ability of this process to function correctly requires the selection of a solvent in which the phenol is much more soluble than in the wastewater. In addition, the wastewater must not be soluble in the solvent.

Most solvent extraction processes for phenol recovery are proprietary. They include Phenosolvan, Chem-Pro, and Benzene-caustic. The use of the word phenol implies monohydric phenols, such as phenol, cresol, and xlenol, and polyhydric phenols, such as catechol and resorcinol. The distribution of these compounds depends upon the coal being gasified and the type of gasification process used. In general, monohydric compounds constitute as much as 85% of the organics present in gasification wastewaters, polyhydric compounds account for up to 34%. Phenols recovered for resale must be further refined to separate the different components.

The Phenosolvan, Chem-Pro, and Benzene-caustic processes are basically similar, with the major difference being the type of solvent used. The phenol-bearing wastewater is usually pumped to a solvent contact reactor. Here the wastewater is completely mixed with the solvent, which extracts the phenol from the wastewater. The phenol-rich solvent is separated from the wastewater by difference in densities. The wastewater is stripped in a packed column to remove any solvent carryover and then pumped to further treatment.

The phenol-rich solvent is distilled to separate the components. The solvent is recovered overhead, condensed, and recycled back to the process. The phenols are recovered from the bottom of the column. This stream can either be directly taken as a byproduct or be distilled further into separate components for resale.

The Phenosolvan and Chem-Pro processes remove about 99.5% of the monohydric, and 60% of the polyhydric phenols. They also remove 15% of other organic compounds. Both processes are reliable, having been in operation for over 20 years. The advantages of these processes are that the removal of phenol, which in most cases is necessary, can be accomplished so that the phenol can be recovered and sold. The disadvantage of the process is that the initial cost is substantial. This disadvantage can be offset by the sale of the phenol compounds.

4.2.4 Dissolved Inorganics Removal

A desired end use of treated gasification wastewater would be as a recycle flow back to the process. This reuse may be dictated by effluent restrictions that force a zero-discharge constraint on the plant or by economics of the plant's water consumption. The continued recycle of water within the plant will cause a buildup of dissolved inorganic compounds that must be removed.

Concentrations of these materials are reduced only slightly by the previously mentioned treatment processes. This, together with additional waste streams high in dissolved solids, such as boiler blowdown, will raise concentrations of these solids beyond acceptable limits.

To reduce this buildup of dissolved solids, either the entire recycle flow or selected streams high in dissolved solids must be treated. Treatment processes available include ion exchange, reverse osmosis, distillation, evaporation, and ultrafiltration.

Ion Exchange

Ion exchange is the process of exchanging objectionable ions (Ca^{++} , Mg^{++} , Fe^{++}) for non-objectionable ions (H^+ , OH^-). The reaction is reversible and can take place in a batch reactor or as a continuous process in a packed column. Ion exchange resins must contain ions in their structure, be insoluble in water, and have space in their porous structure for ions to pass freely in and out of

the solid. Synthetic resins, as well as some naturally occurring clays, can be used as the ion-exchange medium. Ion-exchange materials can be either anionic or cationic, depending upon the composition of the particular resin. The classification of resin indicates the the type of ion removed. Ion-exchange materials or resins contain mobile active sites on their surfaces that are replaced by ions of the same charge from solution. Equal charge quantities are exchanged to ensure charge neutrality. The exchange process continues until the chemical driving forces are the same in the solution and in the pores of the solid. When this occurs, the resin must be regenerated with a highly concentrated solution of the ions that were originally on the exchange material.

The quantity of ions that can be removed by an exchange resin from solution is an important factor. This capacity is a function of a specific material and is expressed in equivalents per gram dry weight. Another property of an ion-exchange material is the selectivity or relative preference for adsorbing different types of ions. Since electrostatic forces between ions and resins increase with increasing charges, ions with higher valences are preferentially adsorbed. Relative size of ions in solution also affects the selectivity of ion exchange. For a series of ions with equivalent charge, the resin prefers the ion with the smallest diameter.

Ion exchange usually takes place in a packed bed in which the wastewater is fed continuously from the top or bottom. Ions are exchanged in a zone within the bed that moves slowly in the same direction as the wastewater. Behind the zone is spent resin and ahead of the zone is fresh resin. When all the resin in the bed is spent, breakthrough occurs, and the bed must be regenerated.

This process is used for water softening, demineralization of boiler feedwater, purification of chemicals, and material recovery. It is an efficient and cost effective process, it can be automated, and it has a relatively low operating cost, not including the treatment of regeneration wastewater.

Use of ion exchange resins has several limitations. Cationic exchange resins cannot withstand temperatures greater than 250-300°F. Anionic resins break

down at temperatures exceeding 140°F. Strong oxidizing agents, as well as iron, manganese, and copper, will degrade the resins in the presence of oxygen. Resins become fouled by precipitation or irreversible adsorption of suspended solids, oils, and other dissolved materials. Rapid exposure to alternating high and low electrolyte concentrations induces osmotic shock, resulting in resin fracture. For dissolved solids in concentrations in excess of 500-1000 mg/l, pretreatment to reduce dissolved solids to below 500 mg/l may be required to prevent clogging of beds.

Reverse Osmosis

Reverse osmosis (RO) is the process of reversing the normal flow of dissolved material in solution across a membrane separating a dilute from a concentrated mixture. When separated by a semi-permeable membrane, water molecules in the dilute solution will migrate through the membrane to the concentrated side because water in pure form is at a higher energy state than in a solution and tends to move to the lower energy state. In reverse osmosis, the pressure on the concentrated side of the membrane is raised above the pressure forcing the water to move from the dilute side, called osmotic pressure. Once the concentrated solution has a pressure exceeding the osmotic pressure applied to it, the water molecules in the concentrated solution will be at higher energy and will flow across the semi-permeable membrane to the dilute side, reversing the normal osmotic flow.

RO membranes can operate only within certain ranges of pH and temperature and will be destroyed by high concentrations of oxidizing agents. As an example, cellulose acetate membranes are limited to a pH range of 5 to 8 and cannot withstand a chlorine concentration of 5 mg/l for more than 15 minutes. A polyamide membrane is limited to a pH range of 4 to 11 and chlorine concentrations of 0.1 to 0.25 mg/l. Both membranes will fail at operating temperatures in excess of 95°F. Newer membranes have been developed that greatly extend the range of applicability of RO. Membranes are also limited in that solutions can be concentrated only to the solubility of the least soluble salt in solution. Further attempted concentration will result in membrane fouling and plugging because of salt precipitation.

RO is presently used to produce fresh water from salt or brackish water on a large commercial scale, to purify industrial chemicals and pharmaceuticals, and for material recovery. The advantage of the process is that most wastewater components can be removed in a single operation. The disadvantages of the process include maintenance problems, such as membrane fouling and degradation, a relatively high energy requirement, and a high initial cost.

Evaporation

Evaporation is the process of liberating pure water in the form of water vapor from a solution. Examples include evaporation ponds, multiple effect evaporators, multistage flash evaporators, and vapor compression evaporators.

In evaporation ponds, wastewater is discharged to the ponds and the water is evaporated by solar heating. After the water has evaporated, the remaining salt cake is disposed of. Ponds can be covered by glass or plastic covers to recover the vaporized water. The vapor condenses on the underside of the cover and is then collected for reuse.

Multiple effect evaporation is a system that incorporates a number of evaporation chambers in series. Each uses steam from the preceding stage to evaporate water at a lower pressure than that of the preceding stage. The recovery of heat from each stage of the evaporation process reduces the operating costs of this system.

In multistage flash evaporation, the incoming water is pressurized and heated to just below the boiling point. The water is then depressurized in stages, evaporating the water. Water vapor is then condensed by exchanging heat with the incoming feedwater.

Vapor compression evaporates and recovers water through the use of mechanical energy. In this system, the incoming water is heated to 212°F at atmospheric pressure. The steam formed is collected and then compressed. The superheated steam then is allowed to release its energy to the water in the evaporator,

heating the contents. The condensate is then used to heat the incoming water to the process.

In general, evaporation systems are extremely energy intensive because of the high heat of vaporization of water. Solar processes are relatively cheap in operating costs, but the extensive land requirements of 10 to 12 square feet per gallon and the variability of solar heating limit its use. The most efficient evaporation process is vapor compression, but it requires a high capital investment. A drawback of evaporation systems is the fouling of heat exchanger surfaces by solids. The multistage flash process avoids this problem by not using an exchanger surface to evaporate water. Common methods used for the control of solids deposition are use of antiprecipitant chemicals or operation at levels not exceeding the solubility limit. Equipment has also been developed which resists fouling. The temperature difference driving force is often limited by the solubility limit of the dissolved solids.

The largest disadvantages of evaporation processes are the high energy requirements, high maintenance, and high capital costs. The advantage of this process is that dissolved solids can be effectively removed from wastewaters, and the resulting product water is exceptionally pure.

Ultrafiltration

Ultrafiltration is the use of a membrane to separate a moderately high molecular weight solute from an aqueous solution. Ultrafiltration requires solute molecules about ten times larger than solvent molecules and a negligible pressure across the membrane. Ultrafiltration membranes retain relatively large solute molecules by a sieving process in which the solvent appears to move through the membrane in viscous flow while the larger solute particles cannot pass through.

Ultrafiltration has disadvantages in that the membrane is subject to fouling and degradation. The process has been used to concentrate solids in a sludge reactor and to recover protein and sugar products from waste streams in cheese

and candy factories. It is still very much in the experimental stage with coal gasification wastewaters. Its primary usefulness will be in the removal of relatively large organic molecules, such as oil.

Electrodialysis

The electrodialysis process removes ions from water by using a direct current electric field to force their migration through a semipermeable membrane. The solute ions and other charged materials are the mobile molecules and cross through the membrane in contrast to reverse osmosis, where the solvent (water) is forced through the membrane. A series of parallel membranes is used to separate the charged ions. The induced electric field causes the ions to migrate towards oppositely charged membrane. The ions pass through the membrane into a concentrated solution of ionic impurities. Purified water is produced between every other set of membranes. This arrangement of membranes may be repeated as many as 700 times to produce ion-free water.

Electrodialysis is capable only of removing charged ionic particles from solutions. Unlike reverse osmosis, electrodialysis has little effect on uncharged dissolved particles and suspended solids. The process is somewhat energy efficient, with the energy costs directly proportional to the impurity of the feed. Membrane fouling, particularly of the anionic type, is a problem. The membranes are ion exchange resins manufactured in sheet form and therefore, like exchange resins, require pretreatment.

The concentration of the brine solution is limited by the precipitation of solids out of solution onto the membrane. Chemical compounds can be added to the solution to prevent the precipitation.

Electrodialysis is presently used for demineralization of brackish water, and there are pilot plants for testing wastewater treatment. The advantage of this process is that 40-50% of the dissolved salts can be removed in a single pass. A disadvantage of the process is membrane fouling. There is limited experience in using this process for wastewater treatment.

4.3 EFFLUENT STANDARDS AND APPROVED INSTRUMENTAL METHODS

Water quality is protected through the enforcement of both ambient water quality standards and effluent discharge standards. Ambient standards vary from state to state and vary for different receiving waters within states. These ambient standards depend upon current water quality and the environmental and recreational values that are designated for protection in each receiving stream, river, or lake. Effluent discharge standards, on the other hand, depend upon the type of industry and the type of process. They are formalized as New Source Performance Standards (NSPS).

4.3.1 Effluent Standards

The Federal Water Pollution Control Act of 1972 (Public Law 92-500) required the EPA to establish standards for effluent discharges from point sources into the navigable waters of the United States. Point sources are usually considered to be effluents from pipes or sewers rather than runoff during rainfall.

Stormwater discharges are included if the water is contaminated in a particular area (i.e., coal storage). Presently, Federal regulations for the control of water pollution are issued on an industry-wide basis. Since the coal gasification industry is just emerging, Federal regulations for that industry have not been developed. Examination of effluent standards for similar industries will assist in estimating the forecoming regulations.

Public Law 92-500 makes it illegal to discharge certain wastewaters without a National Pollutant Discharge Elimination System (NPDES) Permit. The permit must stipulate that a certain minimum technology is to be used in treating the effluent. The minimum standard to be achieved by July 1, 1977 is that of Best Practicable Technology (BPT) currently available. This technology is based upon the average of the best performances of existing treatment technology in the industry category. By July 1, 1983 the treatment of point sources will be based on the Best Available Technology (BAT). BAT will not be based upon the average

of the best performance but will be determined by the very best treatment technology to treat a specific point source. The final goal is the elimination of all discharges by July 1, 1985, commonly referred to as zero-discharge.

In the case of coal gasification, the New Source Performance Standard (NSPS) have not been established. These standards will, for the most part, use BPT guidelines. As BAT standards become enforceable, they will replace NSPS and BPT regulations. Furthermore, when zero-discharge regulations become enforceable in 1985, the treatment plants must be upgraded to achieve this new performance. All of these regulation changes, coupled with the absence of any new source performance standards, have placed the effluent standards for the coal gasification industry in a state of confusion. One solution would be to bypass all interim regulations and base design upon zero-discharge constraints. This would eliminate the successive updating of designs and construction as the regulations become stricter. The other solution is to estimate effluent standards from NSPS from related industries by identifying processes similar to gasification processes and using standards applied to those processes.

Industries that are under NSPS regulations and also in some way related to coal gasification are iron and steel, petroleum refining, coal mining, and steam electric power generation. Regulations for these industries are shown in Table 4.1. Comparison of standards among industries is difficult because the standards vary widely. This is due to a trend in Federal regulations that permits an industry that emits a large amount of a certain pollutant to have a more liberal standard than is applied to an industry that discharges a small amount of the same pollutant. Also industry reports effluents on a pound per pound of product or feedstock, making comparison with ppm concentrations very difficult.

Iron and steel industry processes applicable to gasification are ammonia stripping, ammonia recovery, and acid-gas removal. Regulations applied to these processes are concerned with the pH, phenol, total suspended solids (TSS), cyanide, oil and grease, and ammonia discharges in the wastewater. The regulations were normalized by assuming that 0.69 pounds of coke represented 1.0

Table 4.1 Wastewater Effluent Regulations

Pollutant Parameter	Petroleum Refining		Elec. Generating		Steel/Coke		Coal Mining	
	(1b/10 ³ bbl)	(1b/10 ⁶ lb) ^a	(ppm)	(1b/10 ¹ lb) ^b	(1b/10 ³ lb)	(1b/10 ⁶ lb) ^c	(ppm)	(1b/10 ⁶ lb) ^d
TSS	1.20-15.4	1.80 -23.1	30	15	0.0104	7.18	35	0.24
Phenols	0.01- 0.125	0.015- 0.188	-	-	0.0002	0.138	-	-
Oil and Grease	0.44- 5.8	0.66 - 8.72	15	7.5	0.0042	2.90	-	-
CN	-	-	-	-	0.0001	0.069	-	-
NH ₃	0.28-11.0	0.42 -16.5	-	-	0.0042	2.9	-	-
S	0.008-0.10	0.012- 0.15	-	-	0.0001	0.069	-	-
<u>Trace Elements</u>								
Al	-	-	-	-	-	-	2.0	0.138
Mn	-	-	-	-	-	-	2.0	0.138
Ni	-	-	-	-	-	-	2.0	0.0014
Cl	-	-	0.2	0.1	-	-	2.0	0.0014
Pb	-	-	-	-	-	-	-	-
F	-	-	-	-	-	-	-	-
Ba	-	-	-	-	-	-	-	-
Ag	-	-	-	-	-	-	-	-
Cd	-	-	-	-	-	-	-	-
Cu	-	-	1	0.5	-	-	0.5	0.024
Total Fe	-	-	1	0.5	-	-	0.3	0.0021
Dissolved Fe	-	-	-	-	-	-	-	-
Hg	-	-	-	-	-	-	-	-
As	-	-	-	-	-	-	-	-
Total Cr	0.037	0.055	-	-	-	-	-	-
Cr ⁶⁺	0.0025	0.0038	-	-	-	-	-	-
Zn	-	-	-	-	-	-	0.2	0.0014
Se	-	-	-	-	-	-	-	-
BOD	1.4 -18.9	2.1 -28.3	-	-	-	-	-	-
COD	7.1-131	10.6-196	-	-	-	-	-	-
pH	6-9		6-9		6-9		6.9	

^a Based on 3 bbl of oil per ton of coal^b Based on 0.5 lb of water-to-river per lb of coal^c Based on 0.69 lb of coke per pound of coal^d Based on 37x10⁶ gal of runoff/5.50x10⁶ tons of coal = 6.71 gal per ton of coal

pound of coal feed. This is reflected in the second column of numbers in Table 4.1 under Steel/Coke.

The petroleum refining industry is similar to coal gasification in such processes as methanation, acid-gas removal, sulfur recovery, and ammonia stripping and recovery. Wastewaters from this industry have limits for pH, BOD, COD, TSS, oil and grease, chromium, ammonia, phenols, and sulfide content. These standards have been normalized to a per pound of coal basis by assuming that one ton of coal is equivalent to three barrels of oil. Storage of coal is similar for gasification plants and coal mining and steam power generation. The standards are shown in Table 4.1.

The other treatment alternative is to design for the most stringent requirement, zero-discharge. Under zero-discharge constraints, no aqueous wastewater streams can leave the plant boundaries. Water will be evaporated to the atmosphere, or reused, and most pollutants will leave in solid form. It is interesting to note that potential air pollution, as a result of zero discharge constraints, may be sufficient reason to eliminate solar evaporation as a viable treatment option.

Gasification facilities must use tertiary treatment processes to clean up effluent water for reuse. This high degree of treatment is necessary for reducing alkalinity, dissolved solids, suspended solids, and hardness. These tertiary processes, unfortunately, have not demonstrated technical feasibility at commercial scale recycle conditions. In addition, their cost effectiveness is questionable at commercial scales. Certain sidestreams may be identified for specific tertiary treatment rather than treating the entire plant flow. Zero-discharge treatment facilities must be investigated thoroughly for reliability and cost effectiveness prior to incorporating them into a design.

The individual states are being given the primary responsibility for attaining and maintaining water quality standards established by the Federal government. The state programs are required to be at least as strict as the Federal regulations. States may consent to NPDES permits granted by the EPA, or they may qualify for and administer the program themselves.

States have been required to classify their waters according to their potential quality. These classifications depend upon the use of which the state intends for the water (e.g., drinking, recreation). No discharges can be allowed that will degrade the receiving body of water below its classification. Local water quality programs can affect coal gasification plants by imposing pre-treatment standards on the discharging of waste. Pre-treatment standards become part of the NPDES permit and are imposed on a case-by-case basis.

The states have other standards for establishing water quality standards. The EPA listing of toxic water pollutants names compounds that have been identified as toxic and must not be discharged into bodies of water. The National Interim Primary Drinking Water Standards state maximum allowable concentrations of chemicals for drinking water.

The three gasification plants specifically discussed in this report are sited in the states of Illinois, Ohio, and Tennessee. The effluent standards for each state are summarized in Table 4.2. The standards show allowable concentrations of various elements and other pollutants. For these three proposed gasification plants, these standards will be the basis for estimating the effluent requirements.

At the present time, regulations for liquid discharges from coal gasification facilities are in the developmental stage. The best available information on what the regulations could be can be obtained from regulations for similar industries. Until an official NSPS is promulgated by the EPA, regulation of wastewaters from gasification plants will be done through normal permitting procedures.

4.3.2 Approved Instrumental Methods

The U.S. EPA has published guidelines for approved instrumental methods for wastewater analyses⁴⁷. Public Law 92-500 and the subsequent development of the National Pollution Discharge Elimination System (NPDES) allow or require instrumental methods for enforcement of the Permits Program. These approved instrumental methods are listed in Table 4.3. Table 4.4 identifies those metals that

Table 4.2 State Wastewater Effluent Standards
Daily Maximum Concentrations [mg/l]

<u>Parameter</u>	<u>Illinois</u>	<u>Ohio</u>	<u>Tennessee</u>
Aluminum	-	-	250
Ammonia	3.0	-	-
Antimony	-	-	1.0
Arsenic	0.25	0.05	1.0
Barium	2.0	1.0	5.0
Boron	-	-	50.0
Cadmium	0.15	0.005	0.01
Chlorine (total)	-	-	2.0
Chromium (total)	-	-	3.0
Chromium (Hexavalent)	3.0	0.05	-
Cobalt	-	-	10
Copper	1.0	-	1.0
Cyanide	0.025	0.025	0.05
Dissolved Solids	-	500	-
Fluoride	15.0	1.0	20.0
Iron	2.0	-	10.0
Lead	0.1	0.05	0.1
Manganese	1.0	-	10.0
Mercury	0.0005	0.005	0.05
Nickel	1.0	-	3.0
Oil and Grease	15.0	-	30.0
Phenols	0.3	-	1.0
Phosphorus	1.0	-	-
Selenium	1.0	0.005	0.01
Silver	0.1	0.05	0.05
Suspended Solids	15	-	40
Zinc	1.0	-	2.0

Table 4.3 Approved Instrumental Methods*

<u>FR No.</u>	<u>Parameter</u>	<u>Instrument</u>
1	Acidity	pH meter
2	Alkalinity	pH meter
3	Ammonia	Automated Colorimetric Analyses Ion Selective Electrode Meter
10	Biochemical Oxygen Demand	Automated Colorimetric Analyses
13	Chloride	Ion Selective Electrode Meter
14	Chlorinated Organic Compounds (except pesticides)	Automated Colorimetric Analyses Gas chromatography
16	Color	Spectrophotometer
17	Cyanide	Spectrophotometer
18	Cyanide Amenable to Chlorination	Spectrophotometer
19	Dissolved Oxygen	Ion Selective Electrode Meter
20	Fluoride	Ion Selective Electrode Meter Spectrophotometer
21	Hardness	Automated Colorimetric Analyses
22	Hydrogen Ion (pH)	Automated Colorimetric Analyses
23	Kjeldahl Nitrogen	pH Meter
24-87	Metals	Automated Colorimetric Analyses
88	Nitrate	Atomic Absorption Spectrophotometer
89	Nitrate	Automated Colorimetric Analyses
90	Oil and Grease	Automated Colorimetric Analyses
91	Organic Carbon	Balance
93	Orthophosphate	TOC Analyzer
94	Pentachlorophenol	Automated Colorimetric Analyses
95	Pesticides	Gas Chromatography
96	Phenols	Gas Chromatography
97	Phosphorus (elemental)	Spectrophotometer
98	Phosphorus (total)	Gas Chromatography
99-103	Radiological	Spectrophotometer Automated Colorimetric Analyses Proportional or Scintillation Counter
104-108	Residue	Balance
109	Specific Conductance	Conductivity Meter
110	Sulfate	Automated Colorimetric Analyses
111	Sulfide	Photometer
113	Surfactants	Spectrophotometer
115	Turbidity	Nephelometer

* Reference 47

Table 4.4 Metal Analyses by Atomic Absorption

Aluminum	Molybdenum
Antimony	Nickel
Arsenic	Osmium
Barium	Palladium
Beryllium	Platinum
Cadmium	Potassium
Calcium	Rhodium
Chromium	Ruthenium
Cobalt	Selenium
Copper	Silver
Gold	Sodium
Iridium	Thallium
Iron	Tin
Lead	Titanium
Magnesium	Vanadium
Manganese	Zinc
Mercury (flameless AA)	

can be measured by atomic absorption. Methods that are also appropriate for measurements in the field are separately listed in Table 4.5.

The approved instrumental methods are appropriate for measuring the lower contaminant concentration associated with wastewaters treated for discharge. They are also applicable for measurements of the raw or intermediate wastewater undergoing processing in a wastewater treatment system.

Table 4.5 Approved Field Instrumental Methods

<u>FR No.</u>	<u>Parameter</u>	<u>Instrument</u>
1	Acidity	pH Meter
2	Alkalinity	pH Meter
3	Ammonia	Ion Selective Electrode Meter
19	Dissolved oxygen	Ion Selective Electrode Meter
20	Fluoride	Ion Selective Electrode Meter
22	Hydrogen ion (pH)	pH Meter
109	Specific conductance	Conductivity Meter
115	Turbidity	Nephelometer

SECTION 5 - GASIFICATION DEMONSTRATION PLANT WASTEWATER TREATMENT SYSTEM ANALYSES

5.1 INTRODUCTION

This section analyses the wastewater treatment systems that have been designed, for an industrial low Btu fuel gas demonstration plant and two high Btu pipeline gas demonstration plants, which were proposed by the U.S. DOE. The fuel gas plant of the Memphis Light, Gas, and Water Division (MLGWD), located in Shelby County, Tennessee, uses the U-Gas process. The CONOCO pipeline gas demonstration plant, located in Noble County, Ohio, uses the Slagging Lurgi (BG) process. The Illinois Coal Gasification Group (ICGG) is designing a high Btu gasification facility for a site in Perry County, Illinois, using the COGAS process.

This section identifies and characterizes the internal plant wastewater streams from all individual sources for each plant and discusses the wastewater treatment systems designed for each plant. Treatment system designs are analyzed; any information gaps that hinder these analyses are identified. Particular attention is given to individual wastewater treatment unit reliability. Unit reliability is critical to total treatment system reliability.

5.2 ICGG PIPELINE GAS DEMONSTRATION PLANT

The ICGG demonstration plant is designed for a site in Perry County, Illinois, to convert approximately 2220 tons of coal per day into high Btu, pipeline quality gas and liquid products. Gasification uses the COGAS process. The design has incorporated the use of Illinois #5 or #6 Bituminous, Pittsburgh #8 Bituminous, or Western Sub-bituminous coal.

The wastewater treatment system is designed for zero discharge because the plant site is too far from a suitable receiving body of water. The wastewater treatment system must be capable of treating wastewaters to a quality suitable for plant reuse.

In the plant, oil-contaminated runoff, process wastewaters and sanitary wastewaters are processed by a pure oxygen-activated sludge plant and recycled as makeup to the cooling tower and boiler feedwater systems. Flows identified as being high in TDS are treated in multi-effect evaporators and recycled as boiler feedwater makeup. The treatment of quench condensates includes stripping for ammonia removal. The ammonia stripper bottoms has high phenolic concentrations. The proposed wastewater treatment system is shown in Figure 5.1.

5.2.1 Wastewater Sources and Characteristics

The wastewaters generated by the plant can be divided into the following sections: contaminated stormwater runoff, clean stormwater runoff, high dissolved solids wastewaters, sanitary sewage, process sewer, and ammonia stripper bottoms.

Contaminated Stormwater Runoff

The contaminated stormwater flow consists of runoff from the dead coal pile, the oil storage area, and the contaminated storm sewer. Data from the design engineer on the characteristics of this flow are not available. In the absence of such information, assumptions have been made to approximate the wastewater characteristics. Typically, a dead coal pile is treated with some type of agent to seal the pile from rainfall leaching. If no such treatment is performed on the dead pile, then a stormwater runoff similar to that from live coal storage can be expected. Runoff from a treated pile will be near neutral pH and contain few dissolved solids if the rain has been prevented from contacting the coal. Some suspended solids and some of the crusting agents can be expected to contaminate this runoff, however.

Stormwater runoff from the oil storage area and the process area is expected to be contaminated by oils and suspended solids. There are no data on the composition of this flow. It is estimated that oils will have concentrations in the 1000-5000 mg/l range, suspended solids in the 400-800 mg/l range, and dissolved solids less than 500 mg/l. The dilution and temporary storage of this

intermittent flow in the stormwater holding basin will minimize surge loading of the wastewater treatment system.

Clean Stormwater Runoff

Collected stormwater from uncontaminated areas is impounded prior to being pumped to the raw water reservoir. If the stormwater is contaminated or not suitable for raw water feed, it is diverted to the process wastewater treatment plant. Live coal pile runoff is collected separately and pumped to the high TDS wastewater evaporators for treatment.

High Dissolved Solids Wastewaters

Waters that contain high levels of dissolved solids and low levels of organic impurities are processed by evaporators prior to treatment for use as boiler makeup. These wastewaters include cooling tower blowdown, lime reactor regenerant, deionizer backwash water, live coal pile runoff, and cation exchanger regenerant. The flow to the evaporators is maintained steady using an inorganic waste hold tank to avoid fluctuations during backwash cycles and rainfall events. Dissolved solids concentration in this combined wastewater is estimated to be 12,000 mg/l. This value is reasonable for this type of wastewater.

Sanitary Sewage

Sewage collected within the plant is sent to a septic tank for primary treatment. The effluent from the septic tank contains fairly high concentrations of BOD (300 mg/l) and suspended solids (500 mg/l). It is assumed that the 100 mg/l of oils and grease reported by the designer originate from a kitchen facility. This wastewater will also be expected to have 500-900 mg/l of TDS and 40-90 mg/l of nitrogen. These two constituents are not included in the mass balance. Because of the small flow, this omission will not have a major impact on wastewater treatability.

Process Sewer

The process sewer collects wastewaters from plant areas and conveys it to the wastewater treatment area. Contaminated stormwater is also conveyed to the main wastewater treatment area. Wastewaters high in dissolved solids are collected and treated separately in an evaporation system. The process sewer has been estimated to contain about 13 mg/l of phenols, 30 mg/l of BOD, 200 mg/l TSS, 160 mg/l oil and grease, and 53 mg/l of NH_4Cl . These concentrations appear reasonable at this time but may change as the plant becomes operational.

Ammonia Stripper Bottoms

A major process wastewater is the ammonia stripper bottoms from the ammonia recovery area. This wastewater has a high phenol and suspended solids concentrations and is high in BOD.

5.2.2 Wastewater Treatment System Analysis

The following sections investigate the treatment systems for the wastewaters described above.

Contaminated Stormwater Runoff

Contaminated runoff is collected and pumped to an oil/water separator for treatment. If the assumed influent concentrations are correct, this type of treatment is sufficient to reduce oils and suspended solids to levels that will not impede further treatment. The separator removes about 75% of the oil, 25% of suspended solids, and 20% of BOD and COD, resulting in an effluent with 250-1250 mg/l oil and 300-600 mg/l of suspended solids. Flow is then stored for a period of time in the contaminated stormwater basin before being pumped to the front of the process wastewater treatment plant. Provisions are included for pH adjustment of the water before storage in the basin, if necessary. Further treatment of the wastewater by the process wastewater plant should remove all remaining contaminants to levels sufficient for reuse of the water.

It is not clear at this time what parameters would be used to determine the suitability of the runoff as raw water feed. Presumably, critical factors are TDS, suspended solids, and organic pollutants. The selection criteria should be identified.

Process Sewer

The process sewer wastewater, which is weak, is mixed with the ammonia stripper wastewater before treatment to dilute the stronger wastewater.

Sanitary Sewage

Sanitary sewage is treated in a septic tank to remove suspended solids and BOD and reduce the volume of solids through digestion. The supernatant from the septic tank is pumped to the aeration basin of the process wastewater treatment plant. Because this flow is only 3% of the plant flow, the septic tank effluent is not expected to influence the plant operation significantly.

Process Wastewaters

Process wastewaters are treated by using various physical-chemical processes and by biological oxidation, as shown in Figure 5.1.

Process wastewaters are first treated in a crossflow corrugated plate oil separator for coarse removal of floating oils and settleable solids. The process sewer flow is added to the stripped bottom flows from the ammonia stripper unit prior to the separator. Free floating oil is collected and recovered in the separator. Settleable solids are pumped to a filter press and then sent to a landfill.

The oil separator is designed to remove 60% of the oil and grease, 97% of the suspended solids, and 52% of the Ca^{++} . Removal of calcium is most likely due to the excess lime added to the ammonia stripper water. This lime forms insoluble hydroxides with calcium and is then precipitated out of solution in the

separator. The above explanation for calcium removal is an assumption because pH information is lacking. The estimated removal of solids at this stage of treatment seems high. Typical values should be in the 80% range. Zero removal of BOD in this unit does not seem consistent with solids removal. Some BOD should be removed unless solids are totally inert. The area cannot be examined further without test results on the solids at this stage of treatment. Oil and grease removals appear consistent with the literature.

Separator effluent is pumped to an equalization tank to dampen hydraulic and pollutant surges to the treatment system. The tank is sized for a 2-day detention time and provides mixing of wastewater and suspension of solids by bubbling air through the contents. If the hydraulic or contaminant shock is too great, the wastewater can be diverted to an emergency storage basin until treatment can be performed. The methods used to determine that a contaminant shock is too great before operational damage is done to the system (i.e. biological failure) are unknown.

The wastewater from the equalization tank is then mixed with a polymer and treated in a flocculation/flotation system for removal of solids and both separable and emulsified oils. Mixing in the flocculation tank and gas for flotation is provided by electrolytically hydrolyzing the water at the bottom of both tanks. Removals for this process are 70% for suspended solids and 73% for oil and grease. These removals are consistent with the literature for conventional air flotation processes. It is not known what removals can be expected from an electrolysis process.

Effluent from the flotation unit is joined by a recycle flow from the aeration clarifier. The purpose of the recycle stream is to dilute the phenols in the aeration tank feed to 500 mg/l. The combined stream is then cooled, if necessary, to 90°F. This temperature has been determined to be the optimum oxidation temperature. The cooled, diluted wastewater is then pH adjusted to 7.0 with phosphoric acid, which also serves as a nutrient for biological oxidation. Added nitrogen may also be needed as a nutrient.

The stream is then treated by a pure oxygen activated sludge system. The oxygen plant provides a concentrated oxygen source to the biomass and allows the process to withstand higher organic shock loadings than a conventional air system does. The expected 100% removal of ammonia during the pure oxygen activated sludge process is unreasonably high. Actual removals will be less (even if nitrification takes place). The biomass is settled from the wastewater in a clarifier. A portion of the sludge produced in the clarifier is recycled to the aeration tanks to maintain the desired mixed liquor concentration of organisms in the aeration tank. The remainder of the sludge is thickened by a flotation unit and is then processed in an aerobic digester. The aerobic digester can supply biomass to start the process again in the event of an aeration tank failure.

From the biotreatment clarifier, the wastewater is pumped to the lime/soda softening system at a controlled rate. This system reduces calcium ion and magnesium ion concentrations to those found in the raw water. Lime/soda softening processes also remove some organics from the wastewater. If there is not sufficient alkalinity in the wastewater to remove the non-carbonate hardness, soda ash (Na_2CO_3) will be added to precipitate the remaining calcium. Excess lime ($\text{Ca}(\text{OH})_2$) may be necessary to remove magnesium. If this is the case, Ca^{++} ions from the excess lime will be removed by bubbling CO_2 into the water. The CaCO_3 precipitate formed will be flocculated and clarified. Within the recarbonation system, it is noted that there is no control over the pH of the wastewater during recarbonation. It is strongly suggested that the pH be maintained above 9.5 if excess Ca^{++} ions are to be removed using recarbonation, or the insoluble CaCO_3 precipitate will begin to go back into solution, making recovery impossible. A modification to the recarbonation system that would reduce the capital cost is the use of CO_2 in the flocculation tank as a mixing medium. Elimination of a separate recarbonation drum and bubbling CO_2 into the flocculation tank would keep the wastewater mixed as the CO_2 adds carbonate to the wastewater. The combination of these two processes could result in a more efficient process.

The effluent from the recarbonation facility is then filtered by a gravity sand filter to further remove solids generated in the biological treatment plant. The filtered water is then treated in an ozonation tank, where refractory organics are reduced to simpler compounds and further degraded. The ozone contact tank effluent is then used as make-up to the cooling tower and the boiler water treatment system.

Data Gaps

ICCG's proposed treatment process has been analyzed against the gasification data base generated for this report and general knowledge of industrial treatment systems. From that analysis, the following data gaps and comments have been identified.

- 1) The composition of the stripper wastewater is a data gap because liquid effluent characteristics from the unified COGAS process are not available.
- 2) Data on the alkalinity, pH, TDS, and TOC of the wastewater should be added to the process flow diagrams to give a better indication of unit treatment efficiencies.
- 3) Adequate data do not exist on the process of producing bubbles for flocculation and flotation by electrolysis of water. The process seems to be very energy intensive, and the advantages of this system over other more conventional flotation systems is not clear.
- 4) The need for dilution of the flow into the aeration tanks to maintain phenol concentrations below 500 mg/l does not seem to be substantiated in the data base. Phenols in excess of 1500 mg/l have been successfully treated using biological oxidation. Unless some other factor is influencing the requirement for dilution, its need is questionable.

- 5) The selection of oxygen instead of air for the biological oxidation system is a data gap. Current literature provides no data on its use with gasification wastewaters. It is recognized, however, that oxygen processes should be successful wherever air processes are successful.
- 6) The ozonation system used to degrade refractory organics does not prevent the release to the atmosphere of simpler organics during cooling tower operation. In addition, the effectiveness of ozonation in degrading the coal-origin refractory organics is not fully proven. On the other hand, the cost of the designed ozonation system could be very high comparing with alternatives such as carbon adsorption.

5.2.3 Wastewater Treatment System Risk Analysis

Overall, the wastewater treatment system has been rated as a medium risk because treatment of wastewaters from an integrated COGAS facility has not been accomplished. Some treatment units used have not even been used in treatability studies for coal gasification wastewaters, and their performances are questionable. Other processes are completely novel in their design, and in a facility where reliability is most important, these unproven processes may create more problems than they propose to solve.

Contaminated Stormwater Runoff

The risk assigned this treatment system is low. Considerable experience from related facilities is available to evaluate this area. The composition of the runoff could be derived from data for runoff from other industrial facilities that use coal. The treatment processes are conventional and have been proven.

Wastewaters High in Dissolved Solids

Treatment of these waste streams by evaporation is considered to be a low risk. Evaporation is a commercially proven process; however, no commercial experience exists with wastewater from a gasification facility, and there may be problems

with scaling and foaming. The effluent from an evaporator is expected to be suitable for reuse in the boiler or cooling tower systems. The brine generated by evaporation may contain materials at hazardous concentrations. The disposal of the brine, if this is the case, will be under very strict Resource Conservation Recovery Act regulations.

Clean Area Stormwater Runoff

Although data from this area are lacking, clean area stormwater treatment shall be considered to be a low risk. Only minimal treatment of this flow stream should be required to bring it up to the quality of the raw water being brought into the plant.

Process Sewer

This area is assigned a low risk. The characteristics of this flow stream are unknown; however, it is expected that the treatment system used will be able to reduce the pollutants to acceptable levels. The only question in this area is that various materials in toxic concentrations must be prevented from entering the sewer. Any of these substances might upset the biological reactor.

Sanitary Sewage

This area is a negligible risk. The treatment of sewage via sequential septic tank and aerobic biological processes should pose no operational problems.

Process Wastewater (Condensate and Quench Wastewaters)

The degree of risk in this area is considered to be medium. Composition of the flows into the treatment system have not been substantiated in the data base.

The pure oxygen system has seldom been used to treat gasification wastewaters. This treatment train has serious data gaps, both on the unit operation level and the entire system level.

To fill these data gaps, tests must be run to obtain information on the liquid effluents from the COGAS process. The degree of risk can be reduced even further by conducting treatability tests at the same location. To reduce the risk of the electrolytic generation of fine bubbles for flotation and flocculation, a side-by-side comparison should be run between this type and conventional dissolved air flotation units. The comparison should include removal efficiencies, power consumption, operability, maintainability, and reliability. If electrolytic flotation units are more advantageous, then the risk of this unit will be reduced to low. Treatability studies are required to determine the operational constraints on the use of pure oxygen biological treatment of COGAS wastewaters.

The final test to reduce the risk of this system is to connect all these treatment processes together and perform treatability tests. Until some of the interactions between the processes proposed in the treatment system are known, the risk cannot be reduced.

5.3 CONOCO PIPELINE GAS DEMONSTRATION PLANT

The CONOCO plant is designed to produce 19 million scf/day of 960 Btu/scf pipeline quality gas using the Slagging Lurgi Process at a site in Noble County, Ohio. The facility is designed to consume 1,396 tons per day of Ohio #9 coal. The plant recycles all wastewaters back to the process, releasing no liquid effluents from the plant boundaries.

The wastewaters sources, characteristics, and treatment from the plant are described below.

5.3.1 Wastewater Sources and Characteristics

The major wastewater sources requiring treatment are clean area storm sewers, oily water sewers, sanitary sewers, coal preparation area runoff, slag quench water, and process wastewater.

Clean Area Storm Sewers

Clean area storm sewers collect storm water runoff from process areas that do not have significant quantities of oils and other contaminants in their runoff. This water is low in BOD (20 mg/l) and TSS (50 mg/l) but can be high in TDS (e.g., 500 mg/l), particularly during initial rainfall periods.

Oily Water Sewer

The oily water sewer collects vessel drains, seal-water drainage, laboratory drains, and equipment drains from areas about the plant. The wastewater in the sewer is very high in oil content (2000 mg/l). For this report, these estimated quantities can be assumed to be reasonable, as no background data are currently available on characteristics for these types of wastewaters.

Sanitary Sewer

Sewage generated by personnel at the plant site is collected and treated by a separate unit.

Coal Preparation Area Runoff

The coal used to produce synthetic natural gas at this plant will be held in silos. Consequently, there will be no runoff from coal storage. Coal preparation area runoff will have contaminants similar to normal coal storage runoff, but at significantly reduced amounts.

Slag Quench Water

Molten slag drops from the gasifier into a quench vessel and then into the slag lock hopper. From the slag hopper, the slag slurry is sent to a slag receiving tank before being pumped to hydrobins. Here the slag settles out prior to disposal. Effluent from the hydrobins is sent to a clarifier for further removal of solids. Clarifier overflow is pumped to the ammonia removal area.

Process Wastewater

The major portion of the process wastewater is gasifier quench water that has undergone pretreatment for removal of tars, oils, phenol, and ammonia. Other flows are added to the process flow stream, such as oily water sewer discharges and some stormwater flows. The combined process flow stream is characterized by high levels of dissolved solids, COD and BOD. Other characteristics of the equalization basin influent are shown in Table 5.1.

Table 5.1 Estimated Influent Concentrations to Equalization Tank

<u>Parameter</u>	<u>mg/l</u>
COD	1023
BOD	625
TOC	521
TSS	153
TDS	1964
NH ₃	15
Phenol	392
Oil	350
Thiocyanate	55
Cyanide	29

These wastewater characteristics are typical for a Lurgi gasifier wastewater stream that has undergone phenol and ammonia recovery processes. Available data for activated sludge treatment of gasification wastewaters show that most impurities are below the biological inhibitory level. Ammonia may have to be added to supply the required nitrogen for the activated sludge process; it would be more cost-effective to decrease the efficiency of the upstream ammonia stripper.

The blowdowns from the cooling tower and the slag quench are used as makeup for the slag quench and handling area. To prevent an unacceptable buildup of dissolved solids, a blowdown stream is sent to ammonia recovery for treatment.

Data on wastewater characteristics from this area are a data gap. Depending upon the composition of the flow from the gasifier, treatment of the blowdown may be necessary. If there are few organics present, treatment with carbon adsorption and evaporation or reverse osmosis may be satisfactory if a suitable disposal facility is available for the reject.

5.3.2 Wastewater Treatment System Analysis

The following sections investigate the proposed treatment systems. Special attention is given to the reliability of the system and the treatment efficiencies for the various wastewaters generated by the plant.

Clean Area Storm Sewer

The storm sewer serving the clean areas discharges into a holding basin. In the basin, a floating skimmer collects any oils that float to the surface and pumps them to the slop oil storage tanks for recovery. Stormwater is pumped to the treated wastewater holding tank for reuse. Stormwater can be pumped through the process water treatment plant if it is unsuitable for reuse. This condition could occur at the beginning of a rainfall when the first flush of the sewer system produces a large amount of grit and suspended solids. These initial contaminants should be removed by recycling the flow to the process water treatment plant. An inlet diverter should be considered to divert the clean stormwater runoff that is collected after initial washdown.

The treatment system involves oil removal and possible grit and solids removal only. If the system cannot handle the stormwater, it is pumped to the emergency holding basin and treated when the treatment plant can handle it. This stormwater is projected to contain as high as 500 mg/l of TDS. The blending of this flow with the effluent from the evaporator will raise the TDS level in the recycle flow from 10 mg/l to 80 mg/l. It is assumed that the conditions under which the cooling tower is operated make the return of 80 mg/l TDS water as makeup more cost effective than increasing the evaporator capacity by 20%, which would be necessary to treat the stormwater flow.

Oily Water Sewer

Waters discharged into the oily water sewer are treated in an API separator for removal of oil and suspended solids. Oil that is removed is sent to the slop oil tank for separation and recovery. Solids removed by the separator are dewatered by a belt press and disposed off-site. The effluent flows to the equalization basin and then to the wastewater treatment plant.

At the estimated influent concentrations, the separator should remove the oil by about 75% (to 50 mg/l), the total suspended solids by 80% (to 375 mg/l), BOD by 10% (to 50 mg/l), and COD by 20% (to 230 mg/l). These estimated effluent concentrations should be typical for this unit and will be suitable for feed into the wastewater treatment plant. Data have not been provided by the design engineer on the effluent conditions from the separator, so these estimates are only assumed to be representative.

Because the API Separator is typically very reliable, it is not expected to cause any major problems. The system may experience decreased removal efficiencies during periods of surges in the sewer that raise the overflow rate. If these surges result in undesirable operating conditions, it will be necessary to add an equalization basin ahead of the unit to dampen surges and provide a constant flow into the separator.

Sanitary Sewer

Sanitary sewage will be collected and treated in an extended aeration package plant. This type of treatment is suitable for this wastewater; the process has been proven to be reliable.

Coal Preparation Area Runoff

Because sized feedstocks will be stored in silos, the runoff from this area should not be as contaminated as runoff from a facility that uses open coal storage and handling.

Slag Disposal Area

Leaching tests performed by CONOCO on slag from the Westfield Development Center showed the leachate to be high in ammonia and dissolved solids. The metals and compounds found in the leachate were in concentrations treatable by evaporation, reverse osmosis, or lime/soda softening. The presence of ammonia at a concentration of 1100 mg/l, however, necessitates removal prior to reuse. The blow-down from this area is sent to the ammonia recovery area and given subsequent treatment along with the process wastewater. This treatment reduces contaminants to acceptable levels.

Process Wastewaters

A flow diagram of the treatment process is shown in Figure 5.2. The removal of the various contaminants is estimated for each unit process.

The gasifier quench condensate is first subjected to tar/oil separation. Here, coarse removal of tars and oils takes place. This wastewater is then sent to the phenol recovery area. Use of a solvent extraction process reduces mono-phenols by 99.6% to 33 mg/l and multi-phenols by 60% to 1000 mg/l. These removals are typical of these processes. The effluent is then treated in the ammonia recovery section, where free ammonia is completely removed and 97% of the fixed ammonia is removed. These removals are also consistent with the literature.

All miscellaneous drains from the plant are conveyed to treatment via the oily water sewer. The sewer discharges into an API separator for removal of separable oil and solids. The effluent from the separator empties into an equalization basin that also receives all other plant flows, such as ammonia recovery effluent, landfill leachate, and clean area storm runoff (if contaminated). The equalization basin has sufficient volume for 3-day detention and will dampen hydraulic and contaminant surges. Air is bubbled into the wastewater to keep solids in suspension and to keep the contents well mixed. Provisions for pH control using sulfuric acid and caustic are provided.

PARAMETER \ STREAM	STREAM							
	①	②	③	④	⑤	⑥	⑦	⑧
PHENOLICS	610	—	391	391	4.0	4.0	0.04	0.0
BOD ₅	950	40	624	437	66	66	13	0.0
TSS	105	205	115	35	25	5	3	0.0
TDS	2820	245	2820	2920	2820	3115	4390	10
COD	1520	165	1029	720	220	220	44	0.0
NH ₃	23	—	15	15	4	4	3	0.0
OIL	60	80	132	26	8	2	0.0	0.0
TOC	775	80	521	417	100	100	20	0.0

*ALL VALUES ARE IN PPM

Figure 5.2 CONOCO Wastewater Treatment System Flow Diagram

This equalization basin is needed to prevent wide variations in contaminant concentrations from upsetting the biological unit. The equalization tank effluent is pumped to a dissolved air flotation (DAF) unit for removal of oils and suspended solids. Removal efficiencies are estimated to be 30% for BOD and COD, 70% for suspended solids, and 80% for oil. The effluent should not contain any oil droplets greater than 60 microns. With the equalization basin upstream of the DAF, process upsets caused by concentration fluctuations should be minimized. It is expected, therefore, that the DAF unit will have stable operation.

The DAF effluent is pumped to the activated sludge basin for removal of biodegradable organics. The process uses air as the oxygen source and operates in the extended aeration mode. With extended aeration, the plant will decrease its sludge production and increase the overall efficiency of the process relative to conventional activated sludge operation. Powdered activated carbon (PAC) can be added to the aeration tank, thereby increasing the process tolerance to toxic substances and to wide variations in concentrations.

Nutrient in the form of phosphoric acid is also added to the aeration basin. The biological solids and the PAC, if any, are settled from the wastewater in a clarifier. From the clarifier, the settled sludge and PAC are recycled to the aeration tank to maintain optimum conditions for biological growth. A portion of the recycle flow is wasted and sent to aerobic digesters for volume reduction. The waste flow is necessary to prevent a buildup in solids within the process. The digester also provides a storage of biomass active in case of an upset to the biological reactor.

Removal efficiencies were not supplied by the design engineer. They are estimated, without PAC addition, to be 99% for phenol, 85% for BOD, 75% for ammonia and TOC, 70% for COD and oil, and 55% for suspended solids.

Polymer is added to the clarifier overflow to reduce suspended solids leaving the gravity filters to low levels. Estimated removal efficiencies are 75% for suspended solids and oil. The filtrate is treated in a two-stage activated carbon unit. The 40-minute residence time of each reactor ensures removal of most non-biodegradable organics.

Dissolved solids are removed by the use of a vapor recompression evaporator. The condensate obtained from this unit is free of all impurities, except for small concentrations of dissolved solids. This water is recycled back to the cooling tower as makeup water. Since this plant is designed to produce high quality effluent, it would seem more cost effective to use the evaporator condensate for the most stringent requirements, e.g. boiler feedwater. Its use as cooling tower makeup does not justify the use of evaporation. The concentrated brine is sent to the sulfur recovery area, where it is spray dried, and then landfilled.

Data Gaps

CONOCO's proposed treatment processes have been compared to the gasification data base generated for this report and general knowledge of industrial treatment processes. The resulting data deficiencies in the CONOCO design that prevent the complete assessment of these treatment systems are given below.

- 1) The composition of the landfill leachate is a data gap. If the leachate is principally inorganics, direct treatment by evaporation will be applicable. The presence of organics will require treatment in a carbon adsorption unit before evaporation. It is not known why the leachate must be treated by the entire treatment train.
- 2) The use of carbon adsorption units to treat refractory organics from gasification has not been extensively investigated. Further testing should be done to determine the exact nature of the organics requiring removal and the efficiency of their removal.
- 3) Necessary loading rates and other operational parameters are not furnished for the activated sludge plant. To properly evaluate this treatment unit, these operational conditions must be known. A study done on the treatment and reuse of coal conversion wastewaters indicates that PAC-activated sludge treatment does not necessarily provide better effluent quality, especially with respect to trace organics removals.

- 4) The basis for selection of the evaporation process over other removal processes, such as reverse osmosis, is not available. Reverse osmosis appears to be an attractive technique to remove dissolved solids from coal conversion wastewaters. The effluent from a reverse osmosis unit will be of sufficient quality to be used as a boiler feedwater source. However, further study is needed to determine the extent of membrane fouling under long-term, steady-state operations.

5.3.3 Wastewater Treatment System Risk Analysis

The risk assigned to the CONOCO wastewater treatment system is low. However, vital operating conditions for the aeration basin are not furnished and the need for certain individual processes is questionable. Overall, the plant should function if proper operating parameters are selected and should achieve proper removal efficiencies.

Clean Area Storm Sewer

This system has a low risk. A potential problem associated with this area is the determination of when flow is to be pumped to the cooling tower or when treatment must be performed on the runoff before use as makeup. Selection of proper parameters to make the switch in flow direction will depend on runoff characteristics and the operating conditions of the cooling tower.

Oily Water Sewer

Treatment of this stream has a low risk if the flow is treated by the complete process wastewater treatment system. The only addition to this system should be a bypass to emergency storage for use when a large chemical spill enters the sewer. In spite of the equalization capacity of the treatment system, a spill of biologically toxic chemicals could inactivate the biological reactor.

Sanitary Sewer

The treatment of sanitary sewage is of negligible risk. The characteristics of sewage are well documented and the treatment process used has been proven effective. The quality effluent from the package plant after chlorination is usable as cooling tower makeup water. However, the potential air emissions of chlorinated hydrocarbons from the cooling tower should be examined.

Coal Preparation Area Runoff

Treatment of this runoff is of low risk. The only potential problem area is that discharges from this area cannot be diverted for treatment if the flow is not acceptable as makeup water. A diversion provision should be added.

Slag Quench Water

This area is assigned a low risk. Treatment through the wastewater treatment system should eliminate all impurities in the wastewater.

Process Wastewater

The treatment system used to purify this wastewater and other wastewaters entering the treatment system is assigned a medium risk. This evaluation is primarily based upon the lack of data on operating conditions for biological treatment.

5.4 MLGWD INDUSTRIAL FUEL GAS DEMONSTRATION PLANT

The gasification plant, using the U-Gas Process, is designed to produce approximately 50 billion Btu/day of product gas having a heating value of 300 Btu/scf at a site in Shelby County, Tennessee. Ninety-percent of the gas is for industrial fuel. The remaining 10% is enriched to pipeline quality of 900 Btu/scf.

5.4.1 Wastewater Sources and Characteristics

The wastewater treatment system for this plant can be segregated into five distinct sections. These sections are sanitary wastewater, normal stormwater flow, coal pile runoff, ash quench water, and the gasifier process effluent waters.

Sanitary Sewage

All sanitary sewage generated on the site is sent to a municipal sewage treatment plant. If there are no cross connections between this sewer and other process effluents, this is a satisfactory disposal method.

Stormwater Drainage

All stormwater that falls within the plant limits, except coal storage areas, and all spent service water are treated by a dissolved air flotation unit. Stormwater runoff is expected to be high in suspended solids and to include some oils and BOD. The concentrations indicated by the design engineer for stormwater runoff are within acceptable ranges. The wastewater from this area has BOD from 10 to 50 mg/l, TDS from 150 to 350 mg/l, suspended solids from 50 to 800 mg/l, and oil and grease from 10 to 200 mg/l.

The spent service water is obtained from various sources about the plant. Its pollutant content can only be estimated at this time. Data elsewhere prepared by the design engineer indicate the same stream has as much as 1.5 times the concentrations of pollutants indicated in the mass balance.

Coal Pile Runoff

The plant is presently designed to gasify washed Kentucky #9 bituminous coal, which has a sulfur content of 3.5% (moisture and ash free basis). This sulfur content will cause the formation of sulfuric acid when the coal is wet by rain, resulting in an effluent low in pH and high in suspended solids. The mass

balance indicates dissolved solids and suspended solids levels of 3,000 and 400 mg/l, respectively, with the pH of the water at 2.5-3.0. These concentrations are within expected limits for typical coal pile runoff wastewaters.

Ash Quench Water

Extensive testing by the design engineer of the leachate from the ash quench water effluent of the gasifier has indicated that this water is suitable for direct discharge. Dissolved and suspended solids are estimated to be under 200 mg/l for the ash quench water, with the pH at about 10 and COD under 30 mg/l. Since this water is constantly recycled, there will be no liquid discharge from this area other than the entrained water in the solids that are removed.

Gasifier Effluent Streams

The major process effluent streams requiring treatment are the stripped water effluent from sour water stripping, clarifier overflow from gas cooler/scrubber, char-fines filtrate from the utility area, and process condensate from the methane enrichment section. All these processes have been grouped together as combined process influent having the concentrations shown in Figure 5.3.

Sufficient background information to evaluate the composition of this flow stream is not available. Wastewater samples have been collected from the raw-gas quench scrubber at IGT's U-Gas pilot plant and analyzed by Energy Impact Associates. The results at steady-state conditions indicate that the U-Gas pilot plant produces a fairly clean scrubber effluent stream.

Wastewater Treatment System Analysis

The systems used to treat the various wastewater streams generated by the plant are analyzed in the following sections. The focus of attention is on the adequacy of treatment, based upon expected or possible influents.

PARAMETER \ STREAM	STREAM	
	①	②
TDS	2000-3000	1200-2400
TSS	200-300	20-30
COD	200-300	25-65
O&G	10-20	5-15
PHENOLS	<0.26	<0.1
NH ₃	25	0.5-3
H ₂ S	10	<0.1
CN ⁻	<0.1	<0.05
BOD ₅	—	10-30
TOC	—	5-20
SCN ⁻	—	<0.3
pH	6-9	6-9

* ALL VALUES ARE IN mg/l EXCEPT pH

Figure 5.3 MLGWD Wastewater Treatment Plant Flow Diagram

Stormwater Drainage

Stormwater, except from coal piles, and spent service water are normally pumped to a dissolved air flotation (DAF) unit for treatment. However, during a storm, excess stormwater is pumped to a holding basin, where it is stored until it can be treated by the DAF unit. This holding basin must be designed to contain the design storm runoff and operated so that this available capacity is maintained during normal operation. In the DAF, suspended solids are reduced by about 70%, from 140 mg/l to 40 mg/l and hydrocarbons are reduced by about 90%, to 9 mg/l, with no droplet size exceeding 60 microns.

Treated water from the DAF unit flows into a holding basin, from which it is withdrawn for cooling tower makeup. Stormwater and spent service water are not expected to be high in dissolved solids (200 mg/l) and should be suitable for makeup water. Excess makeup water will be discharged to the Mississippi River.

This type of treatment system has proven to be very reliable in extensive use in treating industrial wastewaters. Because a DAF unit is sensitive to hydraulic loading variations, some method of dampening flow variations is required. This is accomplished in this plant by having a storm water basin to hold flows in excess of the flotation unit's capacity. Over a period of years, the stormwater basin may require cleaning to remove accumulated grit and settled solids.

Polymer can also be added to the influent to this treatment system to promote removal of suspended solids and oil. Sludges from the DAF unit are sent to sludge pits, and froth skimmed off the top is sent to a separation tank for oil removal.

It is not anticipated that any normal variations in the influent to the unit will result in process upsets. It must be pointed out that the flows and concentrations are estimates. If other concentrated flows are combined when the plant becomes operational, the effluent from the flotation unit may not be suitable for the uses selected.

Coal Pile Runoff

All rain falling on the plant's coal piles is collected and conveyed to a holding basin. From the holding basin, it is pumped to a neutralization tank, where lime is added to raise the pH to about 8.5. The neutralized wastewater then flows to an aeration basin, where the air causes mixing to occur and oxidizes inorganic materials, causing them to form insoluble precipitates. The wastewater then flows to a clarifier, where under quiescent conditions the precipitate settles to the bottom of the tank and is collected and pumped to the sludge pits. Clarifier effluent flows to the effluent holding basin for storage before reuse in the cooling tower. It is also planned to discharge clarifier effluent to the river as an alternative.

A properly operating flocculation system will remove up to 75% of the suspended solids (SS) from the wastewaters. With a maximum estimated SS concentration of 800 mg/l, this removal efficiency would result in an effluent of 200 mg/l SS. A 94% removal efficiency was estimated; this is high for a flocculation operation. Estimated total dissolved solids (TDS) removal efficiencies are in the 90% range, which is much higher than should be expected. Dissolved solids in the form of Fe^{+++} could account for this high removal rate. However, a more reasonable TDS distribution would include Cl^- , $\text{SO}_4^{=}$, Fe^{+++} , Al^{+++} , and smaller concentrations of other ions. With the pH elevated to only 8.5, it seems doubtful that a 90% removal of dissolved solids from a coal pile runoff can be obtained. If 90% removals are required, the pH will probably have to be raised to 10. However, because this flow stream is intermittent in nature and relatively small, deterioration of the overall plant effluent as a result of the increased quantities of suspended and dissolved solids from coal pile runoff treatment should be minimal.

Ash Quench Water

The ash quench water system is self-contained and reuses the water after agglomerated ash particles are settled out. Settled ash is removed to a solid waste storage site. The storage site will have provisions for collecting leachate

from the pile and for pumping leachate to a treatment unit. Makeup water for the quench water system is treated effluent from the process water treatment plant.

The slurry is sent to a dewatering bin, where most of the slag is removed. Overflow from the dewatering bin is sent to a clarifier, where additional slag is settled out. Clarifier overflow is cooled and then sent to the gasifier ash quench lock.

Gasifier Effluent Streams

The treatment of process wastewaters is accomplished by various processes, as shown in Figure 5.3. All major wastewaters are collected and pretreated by lime addition. The lime reacts with dissolved metals and alkalis to form insoluble precipitates. As these precipitates settle, they also remove suspended solids and oils from the wastewater. Oxygen is also bubbled through the water for oxidation and mixing purposes. The solids are precipitated in a clarifier.

The clarifier effluent is pumped through a recarbonation drum. Here, vent gas rich in carbon dioxide is bubbled through the wastewater. The purpose of this step is to lower the pH to neutral and to restore the alkalinity of the wastewater to a minimum of 1000 mg/l. These values are necessary for proper operation of the downstream biological processes.

The wastewater is then treated with a pressure filter for the removal of solids and oils to prevent plugging of the downstream pressure biological filter. Filtered effluent is pretreated in an ozone contact chamber before being biologically treated in a second pressure filter. The use of a pressure filter, such as the preozonation filter, to remove solids as high as 100 mg/l to less than 30 mg/l is not recommended. The filter will clog rapidly and require frequent backwashing. The use of pressure filtration with oily waters is also not recommended for the same reason. Because of the uncertain wastewater composition, this factor could be critical. The usefulness of dual filters in series is also not clear. The purpose of ozonating is to render the organics more susceptible

to biological degradation. Refractory organics may be reduced at this stage to biodegradable forms.

The ozonated wastewater is pumped through pressure filters for biological removal of organic impurities. The wastewater is then treated in an activated carbon unit and discharged to the effluent holding basin. The expected composition of this effluent is given in Table 5.2. The design of the treatment plant should include a provision for 100% recycle (zero discharge) retrofit because that regulation may be enforced in the future.

Data Gaps

A review of this treatment plant and the data base indicates the following data deficiencies.

- 1) The purpose of the lime treatment step is to reduce the 200-300 mg/l of suspended solids to 50 mg/l. More data are needed on the effects of this step on other pollutants, such as oils, and dissolved solids, specifically Ca^{++} , Mg^{++} , Fe^{++} , etc., and alkalis.
- 2) The estimates generated in the design report are based upon wastewaters from other similar processes and pilot plant data. The wastewater concentrations assumed for this gasification process are not consistent. Phenol exerts a theoretical COD of 2.4 times its concentration. With a phenol concentration of 200 mg/l, the minimum COD would be 480 mg/l. This is assuming that all the organics are phenolic in nature, which is a minimum condition. The COD assumed by the design engineer is 300 mg/l, which does not account for all the phenols. Since other soluble organics are present, the COD should be in excess of 500 mg/l. These wastewaters should be characterized before the treatment system is designed.
- 3) The ozonation system is designed to break organics into a more biodegradable form. It is not fully understood from experimentation what effect ozone has upon gasification wastewaters and what dosages are

Table 5.2 Expected Effluent Quality of MLGW Wastewater Treatment System

<u>Component</u>	<u>Concentration (mg/liter)</u>
Total dissolved solids (TDS)	1200 to 2400
Total suspended solids (TSS)	20 to 30
Chemical oxygen demand (COD)	25 to 65
Five-day biological oxygen demand (BOD ₅)	10 to 30
Oil and grease	5 to 15
Priority organics	<0.5
NH ₃ -N	0.5 to 3
Thiocyanate (SCN ⁻)	<0.3
Hydrogen sulfide (H ₂ S)	<0.1
Phenols	<0.1
Cyanide (CN ⁻)	<0.05
Silver	0.005
Arsenic	0.3
Beryllium	0.005
Cadmium	0.05
Chromium	0.06
Magnesium	0.03
Mercury	0.002
Nickel	0.03
Lead	0.5
Antimony	0.03
Selenium	0.1
Thallium	0.03
Zinc	0.3
pH	6-9

Source: Ref. 48, P 2-7

required. There is also no information supplied by the design engineer on expected results from the ozonation system.

- 4) The purpose of the post-ozonation filter is unclear. In one part of the design report, stated function of the filter is to remove suspended solids to less than 10 mg/l. In another, its function is substantial removal of organic pollutants, which it cannot do. If biological growth on the filter is intended to remove organics, operational problems can be expected. To remove the organics from the wastewater as intended would require an amount of organisms that would cause rapid blinding of the filter. This would result in short filtration times and excessive backwashing. It is also unknown where the accumulated biomass originates, as during backwash cycles all solids would be removed from the filter bed. To maintain biological activity, the backwashed bed would have to be inoculated with organisms before coming on line. This is obviously impractical.
- 5) It is not stated in the design report where removals of major pollutants, such as ammonia, phenol, TOC, COD, and BOD, are to occur. Some assignment must be made of where these pollutants are being removed so that a proper evaluation of the treatment system can be made.
- 6) The use of this entire process wastewater treatment system is questionable. The technology behind these treatment units has not been proven to be effective with gasification, or any other, wastewaters. Although this treatment train has been used in a pilot plant for an industrial wastewater, there are no data available on removal efficiencies.

The unit processes included in this treatment train have numerous operational problems that should be investigated before inclusion in a demonstration plant design. The design engineer even states that the technology for this plant will be proven in three to four years. It is recommended that, as a minimum, the two pressure filters and the ozonation unit be replaced by an activated sludge unit and a filter. Provisions

could be added to the plant to connect the filters and ozone unit in parallel operation, if desired. There is no provision for the equalization of flow into the treatment plant as designed. Because variations in process wastewaters are detrimental to biological processes, some form of equalization should be included.

- 7) The use of activated carbon to treat refractory organics formed during gasification processes has not been shown to be entirely successful. More experimentation should be done to eliminate questions concerning its use.
- 8) The effluent of treated coal pile runoff and cooling tower blowdown would not be suitable for either discharge or reuse after simple lime treatment. Dissolved solids may be lowered to acceptable levels through dilution with other flow streams. Lime treatment will remove metals and alkalis, but not all dissolved solids. A question is raised as to the accuracy of the estimated low dissolved solids (600-1000 mg/l) concentrations and the high oil and grease levels in the cooling tower blowdown.

5.4.3 Wastewater Treatment System Risk Analysis

Overall, the wastewater treatment system is assigned a high risk because of the processes selected to treat the process wastewater. Wastewater compositions are unknown and the assumed characteristics are not internally consistent.

The treatment system employs untried technology and is therefore considered of high risk.

Sanitary Sewage

This area is assigned a negligible risk. The sewage will be treated in a conventional manner and no problems are expected from this area.

Stormwater Drainage

This treatment is assigned a low risk because the treatment of stormwater by DAF units should render an effluent suitable for reuse or discharge.

Coal Pile Runoff

Treatment of this wastewater is considered to be of low risk. Although the dissolved solids will not be removed to levels suitable for discharge or reuse by themselves, expected dilution should make it usable.

Ash Quench Water

This treatment is assigned a low risk. The slag has been shown to be relatively inert to leaching.

Gasifier Effluent Stream

The treatment of this wastewater is considered a high risk. The wastewater composition is unknown and the values assumed for wastewater composition are internally inconsistent.

The basis for the treatment plant relies upon data from a pilot plant treating an unrelated wastewater. Reducing this risk can be accomplished by obtaining wastewater characterizations from the U-Gas process, performing treatability studies on the wastewater, and using gasification treatability studies as a basis for a treatment plant design.

Since the effluent from the MLGWD wastewater treatment system will be discharged to the Mississippi River, a buoyant plume model was applied to assess the impacts from normal plant operation. The results are given in Table 5.3. The behaviors of ammonia nitrogen, cadmium, cyanide, hydrogen sulfide, lead, mercury, phenol, and selenium are of particular interest because their proposed maximum concentrations in the MLGWD demonstration plant effluent exceed water quality criteria

Table 5.3
Comparison of MLGW Demonstration Plant Effluent with Water Quality Criteria^a

Chemical Constituent	Water Quality Criterion Concentration C_r	Effluent Limitations from Industrial Wastewater Treatment ^b	Maximum Concentration in IFGDP effluent C_e	Maximum Ambient Concentration C_a	Maximum Dilution Required to Meet Criterion ^c	Distance Downstream from Outfall Criterion Net (m)
Ammonia nitrogen	0.02 as unionized ammonia (assumed) to be approximately equal to 1 mg/liter of total ammonia nitrogen)	Not listed	0.5 to 3.0	0.84	10	<23
Cadmium	0.0012	0.01	0.05	<0.01	C_a may exceed criteria; chemical detection limits too insensitive	Criterion may not be met because of high C_a
Chromium	0.05	3.0	0.06	0.016	1.3	Immediately at outfall
Cyanide	0.005	0.05	<0.05	0.009	C_a exceeds criteria frequently	Criterion may not be met because of high C_a ; reduced to 0.0061
Hydrogen Sulfide	0.002 as undissociated hydrogen sulfide	Not listed	<0.1	No data Assume 0	50	<65
Lead	0.05	0.01	0.5	0.022	17	<23
Mercury	0.05 ug/liter	50 ug/liter	2 ug/liter	1 ug liter	C_a exceeds criteria; chemical detection limits too insensitive to calculate how frequently	Criterion may not be met because of high C_a
Phenol	0.001	1.0	<0.01	0.025	C_a exceeds criteria consistently	Criterion may not be met because of high C_a
Selenium	0.01	0.01	0.1	0.01	C_a exceeds criteria occasionally	Criterion may not be met because of high C_a
Physical Property: Temperature, °C	Summer: 30.5	Not Listed	26.7	28.9	Criterion met without dilution	Criterion met prior to discharge
	Winter: 3 = 3.3		18.3	0.3	6	5

^a Data taken from ER, Sect. 3A and 4A; chemical constituents as mg/liter unless otherwise specified.

^b Data from Bureau of National Affairs; "Tennessee Effluent Limitations and Standards," Environ. Reporter 916: 1001-1002 (1978).

^c Calculated by the following equation: $(C_e - C_a) / (C_r - C_a)$

Source: Ref. 48, P 4-13

(Table 5.3). In addition, effluent concentrations of cadmium, lead, and selenium exceed recommended effluent limitations for treated industrial wastewaters. However, further modeling results indicate that, even under the most conservative conditions, chemical constituents in the plant effluent are rapidly diluted by the Mississippi River. However, more stringent future regulations (e.g., zero discharge) may require redesign, or retrofit, of the wastewater treatment system.

SECTION 6 - CONCLUSIONS

From this investigation of state-of-art coal gasification wastewater treatment, the following conclusions have been drawn.

- 1) It has been reported in the literature that gasification process wastewaters could be treated to levels sufficient for discharge under current regulations.
- 2) Although commercial scale systems to achieve 100% recycle of process wastewaters are in use, 100% recycle operation with gasification wastewaters is unproven. The reliability of the advanced treatment processes has not been substantiated and knowledge of the characteristics of wastewaters is not complete enough to predict the possible buildup of contaminants, or the effects of buildup, during extended recycle operation. The absence of information in this area is a substantial data gap.
- 3) The inability of many pilot plants to achieve long-term, steady-state operation has made characterization of wastewaters difficult. The low wastewater productions of many pilot plants has also limited treatability studies. Accordingly, a question arises concerning the applicability of current characterization and treatability data to larger scale demonstration plants. It is suggested that treatability data be continuously revised as gasification processes evolve.
- 4) It should be understood that the gasification industry in the U.S. is in its infancy. At the current stage of development answers to all design questions are not available. It is necessary to utilize the best available information in the design of wastewater treatment modules, while maintaining sufficient flexibility for future modifications as required.
- 5) Phenol and ammonia recovery/removal processes tend to normalize wastewaters from different gasifiers because of the 99.9% removals of phenolic compounds and ammonia. This allows the use of one treatment plant type for most

gasification wastewater treatment rather than a distinct plant for each gasification process. If the recovery of ammonia and phenols is not economical, the same removal processes may be used to remove these compounds to levels that do not inhibit downstream biological processes. This can also be accomplished by diluting the wastewater, but dilution will also increase the size and costs of the treatment plant. The choice between a removal system or dilution should be made on a plant-by-plant basis.

- 6) It has been determined that wastewater characteristics are sensitive to gasification process conditions. This makes it important to conduct treatability studies on wastewaters from a gasifier operating at the same condition as the the plant under design.
- 7) Further work will be required to optimize treatment processes already shown to be effective. The most significant step in this direction would be the completion and operation of demonstration-size and commercial-size plants. Studies of alternative treatment processes and system optimization should be done at full-scale conditions.
- 8) Gasification process wastewaters, in general, are highly buffered, making pH adjustment difficult until much of the carbon dioxide has been removed from solution.
- 9) A flow equalization basin is recommended prior to biological processing to dampen potentially toxic fluctuations in influent concentrations.
- 10) Biological processes have been shown to remove soluble organic pollutants to levels suitable for discharge under existing effluent regulations. Depending upon the influent Chemical Oxygen Demand (COD), some dilution may be required for stable operation. Satisfactory treatment can be obtained with COD concentrations up to 4000 mg/l and loadings in the range of 0.3 to 0.5 mg COD/mg MLSS/day. The influent phenols concentration should be limited to 1500 mg/l and ammonia to below 600 mg/l for stable operation. Nitrification has been observed in some cases but has been inconsistent.

- 11) The ability of advanced treatment processes to treat gasification wastewater to the extent necessary to achieve zero discharge has had little study. The absence of information in this area is a substantial data gap.
- 12) Much of the available data are for analysis of condensates from process development units (PDUs) or pilot plants. It should be expected that any changes anticipated between pilot plant and commercial scale gasifier operating conditions may have significant effects on gasifier effluent production, especially with respect to organic contamination. It should also be recognized that data available now are not of design quality for a larger scale commercial operation. Thus, scalability of the pilot plant data is still a major issue. Factors to consider may include coal type and pretreatment, gasifier geometry, configuration and operating parameters, and raw-gas quench system design and operation.
- 13) The technology for phenol and ammonia removal/recovery is proven and is commercially available.

SECTION 7 - RECOMMENDATIONS

The following program recommendations are designed to fill data gaps that presently exist in the treatment of coal gasification wastewaters. Further bench-scale studies, with the exception of those proposed below, will not yield significantly valuable data. The scale of study must be increased. This point is important because larger scale gasification plants are years into the future. However, the continued generation of useful data until larger plants come on stream is required. These recommendations are proposed to meet that requirement.

General recommendations

- 1) All design decisions for coal gasification wastewater facilities should be based upon the concept of 100% reuse of the wastewaters generated. This is the worst case condition and will eliminate future modifications to designs or retrofits to facilities when stricter effluent standards are implemented.
- 2) Bench-scale biological treatment should be applied only to wastewaters from gasification processes that are the closest to commercial development, and then only for significant process variations or system optimization.
- 3) The environment of the testing facilities should be shifted from the laboratory to the pilot plant site. With this shift, the wastewaters can be treated on an as-produced basis and will be subjected to the actual effects of ambient conditions rather than to the closely controlled conditions of the laboratory.

Program recommendations for further bench-scale experimentation

- 1) Studies of the use of advanced wastewater treatment processes for water recycle should be performed. Processes to be investigated should include reverse osmosis, evaporation, electrodialysis, ozonation, activated carbon, and ultrafiltration. The scale of the experiment should be as large as

the supply of available wastewater permits. The treatment processes should be arranged so that the effluent from one unit operation is the influent to the next. This will simulate the conditions at commercial scale. The overall purpose of these studies is to remove refractory organics and dissolved solids in a most cost-effective manner.

- 2) Experimentation should also be performed to determine if ozonation of wastewaters prior to biological treatment will convert refractory organics into a more biodegradable form. If this is the case, the treatment of organics can be greatly simplified. The scope of the work should be as large as possible within the limitations on wastewater availability and the size of the biological treatment units.

Program recommendations for pilot scale or larger experimentation

- 1) Present treatability studies have been limited in scope because of small wastewater production from the existing gasification pilot plants. It is recommended that wastewater from metallurgical coking plants be used to simulate gasification wastewaters. The wastewaters from gasification and metallurgical coking processes are similar and the coke plant will produce a wastewater flow large enough to be treated on a continuous basis. The latter point is especially important in assessing the stability of various unit processes because the wastewater composition varies with time. The treatment processes and the conditions under which they will be operated should be determined in bench scale studies. It should be pointed out, however, that optimization of process parameters will not be possible until demonstration-size or larger gasification facilities are in operation.
- 2) Another alternative would be to perform treatability studies on wastewaters from commercial coal gasification plants operating outside the U.S. In this case, gasification wastewaters can be treated in full-scale units. Treating actual gasification wastewaters would make it possible to optimize the operating conditions for the treatment units.

SECTION 8 - GLOSSARY

ACIDITY	The quantitative capacity of aqueous solutions to react with alkalinity. It is measured by titration with a standard solution of a base to a specified end point. Usually expressed as milligrams per liter of calcium carbonate.
ALKALINITY	The capacity of water to neutralize acids, a property imparted by the water's content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates, and phosphates. It is expressed in milligrams per liter of equivalent calcium carbonate.
ANAEROBIC WASTE TREATMENT	Waste stabilization brought about through the action of microorganisms in the absence of air or elemental oxygen. Usually refers to waste treatment by methane fermentation.
BIOCHEMICAL OXYGEN DEMAND (BOD)	The quantity of oxygen used in the biochemical oxidation of organic matter in a specified time, usually 5 days, at a specified temperature, and under specified conditions.
BIOLOGICAL WASTEWATER TREATMENT	Forms of wastewater treatment in which bacterial or biochemical action is intensified to stabilize, oxidize, and nitrify the unstable organic matter present. Intermittent sand filters, contact beds, trickling filters, and activated sludge processes are examples.
BUFFER	Any of certain combinations of chemicals used to stabilize the pH values or alkalinities of solutions.
CAUSTIC (Caustic Soda)	Sodium hydroxide.

CHEMICAL COAGULATION	The destabilization and initial aggregation of colloidal and finely divided suspended matter by the addition of a floc-forming chemical.
CHEMICAL OXYGEN DEMAND (COD)	A measure of the oxygen-consuming capacity of inorganic and organic matter present in water or wastewater. It is expressed as the amount of oxygen consumed from a chemical oxidant in a specific test. It does not differentiate between stable and unstable organic matter and thus does not necessarily correlate with biochemical oxygen demand.
CHEMICAL PRECIPITATION	(1) Precipitation induced by addition of chemicals. (2) The process of softening water by the addition of lime or lime and soda ash as the precipitants.
CHLORINATION	The application of chlorine to water or wastewater, generally for disinfection, but frequently for oxidation purposes.
CLARIFICATION	Any process or combination of processes, the primary purpose of which is to reduce the concentration of suspended matter in a liquid.
COAGULATION	In water and wastewater treatment, the destabilization and initial aggregation of colloidal and finely divided suspended matter by the addition of a floc-forming chemical or by biological processes.
DIALYSIS	The separation of a colloid from a substance in true solution by allowing the solution to diffuse through a semi-permeable membrane.

DISSOLVED SOLIDS	Theoretically, the anhydrous residues of the dissolved constituents in water. Actually, the term is defined by the method used in determination. In water and wastewater treatment, the Standard Methods tests are used.
FLOCCULATION	In water and wastewater treatment, the agglomeration of colloidal and finely divided suspended matter after coagulation by gentle stirring by either mechanical or hydraulic means. In biological wastewater treatment where coagulation is not used, agglomeration may be accomplished biologically.
FLOTATION	The rising of suspended matter to the surface of the liquid in a tank as scum by aeration, the evolution of gas, chemicals, electrolysis, heat, or bacterial decomposition, and the subsequent removal of the scum by skimming.
FOOD TO MICROORGANISM RATIO (F/M)	Measurement of a system's organics loading rate expressed as unit mass per unit reactor volume per unit time.
GREASE	In wastewater, a group of substances including fats, waxes, free fatty acids, calcium and magnesium soaps, mineral oils, and certain nonfatty materials. The type of solvent and method used for extraction should be stated for quantification.
HARDNESS	A characteristic of water, imparted by salts of calcium, magnesium, and iron, such as bicarbonates, carbonates, sulfates, chlorides, and nitrates, that cause curdling of soap, deposition of scale in boilers, damage in some industrial processes, and sometimes objectionable taste. It may be determined by a standard laboratory procedure or computed from the amounts of calcium, magnesium, iron, aluminum, manganese, barium, strontium, and zinc, and is expressed as equivalent calcium carbonate.

INDUSTRIAL WASTES	The liquid wastes from industrial processes, as distinct from domestic or sanitary wastes.
INORGANIC MATTER	Chemical substances of mineral origin, or more correctly, not of basically carbon structure.
LAGOON	(1) A shallow body of water, as a pond or lake, which usually has a shallow, restricted inlet from the sea. (2) A pond containing raw or partially treated wastewater in which aerobic or anaerobic stabilization occurs.
LIME	Any of a family of chemicals consisting essentially of calcium hydroxide made from limestone (calcite), which is composed almost wholly of calcium carbonate or of a mixture of calcium and magnesium carbonates.
MIXED-LIQUOR SUSPENDED SOLIDS (MLSS)	An engineering measurement of cell population on the basis of mass concentration expressed as milligrams per liter. Materials retained on a specified filter (normally glass fiber filter disks) dried at 105°C is reported as MLSS. This material may include organic constituents of waste, inorganic particles, and dead cells as well as viable cells.
MIXED-LIQUOR VOLATILE SUSPENDED SOLIDS (MLVSS)	An alternative engineering measurement of cell population. The solids that volatilize at 550°C expressed as milligrams per liter.
NEUTRALIZATION	Reaction of acid or alkali with the opposite reagent until the concentrations of hydrogen and hydroxyl ions in the solution are approximately equal.
NITRIFICATION	The conversion of nitrogenous matter into nitrates by bacteria.

ORGANIC MATTER	Chemical substances of animal or vegetable origin, or, more correctly, of basically carbon structure, comprising compounds consisting of hydrocarbons and their derivatives.
ORGANIC NITROGEN	Nitrogen combined in such organic molecules as protein, amines, and amino acids.
OXIDATION	The addition of oxygen to a compound. More generally, any reaction that involves the loss of electrons from an atom.
OXIDATION POND	A basin used for retention of wastewater before final disposal, in which biological oxidation of organic material is effected by naturally or artificially accelerated transfer of oxygen to the water from air.
pH	The reciprocal of the logarithm of the hydrogen ion concentration. The concentration is the weight of hydrogen ions in grams per liter of solution. Neutral water, for example, has a pH value of 7 and a hydrogen ion concentration of 10^{-7} .
PRIMARY TREATMENT	(1) The first major (sometimes the only) treatment in a wastewater treatment works, usually sedimentation. (2) The removal of a substantial amount of suspended matter but little or no colloidal and dissolved matter.
SANITARY SEWER	A sewer that carries liquid- and water-carried wastes from residences, commercial buildings, industrial plants, and institutions, together with minor quantities of ground-storm and surface waters that are not admitted intentionally.
SECONDARY WASTEWATER TREATMENT	The treatment of wastewater by biological methods after primary treatment by sedimentation.

SEDIMENTATION	The process of subsidence and deposition of suspended matter carried by water, wastewater, or other liquids, by gravity. It is usually accomplished by reducing the velocity of the liquid below the point at which it can transport the suspended material. Also called settling.
SLUDGE DIGESTION	The process by which organic or volatile matter in sludge is gasified, liquified, mineralized, or converted into more stable organic matter through the activities of either anaerobic or aerobic organisms.
SLUDGE THICKENING	The increase in solids concentration of sludge in a sedimentation or digestion tank.
SLUDGE VOLUME INDEX (SVI)	The volume in milliliters occupied by 1 g of activated sludge after settling the aerated liquor for 30 minutes.
SRT	Sludge retention time.
SUSPENDED SOLIDS	(1) Solids in suspension in water, wastewater, or effluent. (2) Solids in suspension that can be removed readily by standard filtering procedures in a laboratory.
TOTAL ORGANIC CARBON (TOC)	The total organic carbon concentration in a wastewater is a measure of pollution, and these values can often be correlated with COD and occasionally BOD values. The organic carbon is evaluated either by acidifying and purging the sample of all inorganic carbon before analysis or by providing a dual combustion tube for total carbon analysis, and a low temperature combustion tube for inorganic carbon analysis, the difference being taken as total organic carbon.

TOTAL OXYGEN
DEMAND. (TOD)

The total oxygen demand of a substance as measured includes organic and inorganic substances, but at varying reaction efficiencies. The chemical reactions involved include: (1) Carbon is converted to CO_2 ; (2) hydrogen is converted to water; (3) nitrogen in a 3-valence state is converted to nitric oxide; (4) the sulfite and sulfide ions are partially converted to sulfate.

TOTAL SOLIDS

The sum of dissolved and undissolved constituents in water or wastewater, usually stated in milligrams per liter.

TURBIDITY

(1) A condition in water or wastewater caused by the presence of suspended matter, resulting in the scattering and absorption of light rays. (2) A measure of fine suspended matter in liquids. (3) An analytical quantity usually reported in arbitrary turbidity units determined by measurements of light diffraction.

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