ENVIRONMENTAL CONTROL OPTIONS FOR SYNFUEL PROCESSES

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Ultimately, the large scale production of synfuels from U.S. coal and oil shale will become a reality. The U.S. Department of Energy (DOE) has a charge to foster the commercialization of energy conversion technology that is environmentally acceptable. "Environmental acceptability" is perceived to extend beyond meeting environmental compliance standards at a given plant and to include the "acceptability" of subtle, longterm health and ecological effects and the composite of low level environmental effects associated with an aggregate of synfuel installations. DOE has a hierarchy of site-specific environmental assessments integral to DOE development and demonstration activity. The objective of these assessments is to provide a data base for a determination of environmental readiness by the Assistant Secretary for Environment. An evaluation of the adequacy of the environmental control technology is a key component of these determinations.

In assessment of control adequacy, many alternative approaches present themselves. Some of these control options result from a natural synergism of combining process needs; for example, an auxiliary power plant that recovers flue gas SO_2 in a concentrated stream can be advantageously coupled to H_2S recovery from the conversion process to produce by-product sulfur via Claus, or an entrained type gasifier can be included with a series of Lurgi gasification units to handle rejected coal fines and oxidize highly contaminated condensate wastewaters. Other control options follow from making controls more cost-effective and/or environmentally superior. Wastewater reuse to extinction (zero discharge) and the catalytic incineration of process tail gases are examples of improvements over conventional technology. In the case of small, site oriented industrial gasifiers, process simplicity and reliability are a driving force for improved controls or the absence thereof; for example, in-gasifier sulfur scavenging to eliminate subsequent H_2S cleanup or "dry-quenching" of product gas to eliminate the difficulty of wastewater treatment.

This presentation will overview a number of select environmental control options whose technical and economic feasibility has been recently established. The direction that future resultant control technology is expected to take will be outlined.

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INTRODUCTION

There has been considerable activity within the Department of Energy recently with regard to synfuels related initiatives. Some of this proliferation results from synfuel process development activity, which has been a long time in being and is now reaching the critical pilot plant or demonstration phase (Figure 1). However, much of this activity stems from industrial response to DOE's alternative fuels initiative (Figure 2). Most of these synfuel projects are in various stages of engineering and design. The alternative fuels efforts include both feasibility studies (preliminary design efforts) and cooperative agreements to share preconstruction and construction costs.

To one who has been "exposed" to these designs, several premises become clear:

- the energy conversion process design is tailored to the feedstock, end-product mix, and specific site;
- the environmental control technology is integrated with the process (end-of-the-pipe philosphy does not generally prevail); and
- a large number of environmental control options exist.

The innovative integration of environmental controls with the conversion processes is a relatively new area of process design. This innovation has resulted in new and different controls required as a result of recent and evolving environmental standards (especially in the synfuels area). The evolution of controls with the technology facilitates a beneficial synergism that can be missed if considered mutually independent. The development of such control synergisms can involve different sections of the plant and be based on the integration of both multimedia and multipollutant interactions. It has long been the contention of the Assistant Secretary for Environment that environment control development should be handled integral to the technologies.

In this symposium Pollution Control Guidance Documents (PCGD) will be discussed. These documents attempt to develop an environmental data base for synfuels process configurations. A number of representative plant configurations have been selected and preferred control options concomitantly delineated. These generalized studies reinforce the fact that a large number of control options exist for a given synfuel process. Because of these many options and their different effect on overall process characteristics, it is indeed a challenging and difficult task to specify a "Best Available Control Technology" (BACT) for these emerging technologies. Perhaps it is best to return to the BACT concept after a brief discussion of control options.

In this presentation I would like to develop an appreciation for the complexity of the control systems and their high variability as reflected in recent designs, to stress the potential benefits resulting from integrating multimedia controls to the conversion process, and to outline some control options that possess an economic incentive for further development. The intent is to provide an overview of the numerous control options that are emerging and the direction future controls may take. The discussion will be confined to coal based synfuel processes and the conversion process per se, however, it may be considered representative of other areas such as oil shale and biomass conversion.

FIGURE 1. MAJOR DOE FOSSIL ENERGY DEMONSTRATION ACTIVITY — COAL SYNFUEL PROCESSES (SEPT 1980)

	PROJECT	LOCATION	COAL DEMAND Ton/Day	MAJOR PRODUCTS	STATUS
Gasification	Gasifiers-in-Industry	Duluth, Minn.	75	Heating Gas, Fuel Oil	Operative
	Memphis	Memphis, Tenn.	3200	Medium Btu Fuel Gas, SNG	In Detailed Design
	Grace	Baskett, Ky.	2300	Ammonia	In Preliminary Design (Reoriented toward Methanol and Mobil-M Gasoline)
	Conoco	Noble County, Ohio	1080	SNG	In Detailed Design
	ICGG	Willisville, Ill.	2300	SNG, Fuel Oil	In Detailed Design
Liquefaction	SRC I	Newman, Ky.	6000	Solid Boiler Fuel	In Detailed Design
	SRC II	Morgantown, W.Va.	6000	Fuel Oil	In Detailed Design
	H-Coal	Catlettsburg, Ky.	200-600	Fuel Oil, Syncrude	Pilot-Plant in Shakedown
	EDS	Baytown, Tex.	250	Fuel Oil, Syncrude	Pilot Plant in Shakedown

FIGURE 2. SELECT COAL SYNFUELS ALTERNATIVE FUELS SOLICITATION — FEASIBILITY STUDIES AND COOPERATIVE AGREEMENTS (JULY 1980)

	CONTRACTOR	POTENTIAL SITE	FUNDING REQUEST*	MAJOR PRODUCT
Feasibility Studies	W.R. Grace	Moffat Co., Colo.	$ 786,477	Methanol
	Clark Oil & Refining	S. Ill.	$4,000,000	Gasoline
	General Refractories	Florence, Ky.	$ 922,555	Low Btu Industrial Fuel Gas
	Houston Natural Gas	Covent, La.	$3,260,000	Fuel Grade Methanol
	Central Me. Power	Waldo Co., Me.	$3,624,658	Medium Btu Gas for Combined Cycle
	EG&G	Fall River, Mass.	$4,000,000	Combined Cycle Power and Methanol
	Crow Tribe	East Billing, Mont.	$2,729,393	SNG
	Nakota Co.	Dunn, N. Dak.	$4,000,000	Methanol
	Phil. Gas Works	Phil., Penn.	$1,168,108	Medium Btu Gas
	Celanese Corp.	Bishop, Tex.	No Cost	Syngas
	Transco Energy	Calvert, Tex.	$1,874,005	Medium Btu Gas
	Union Carbide	Houston, Tex.	$3,945,676	Low/Medium Btu Gas
	Hamphire Energy	Gillette, Wyo.	$4,000,000	Gasoline
Cooperative Agreements	Texas Eastern Synfuels	Henderson, Ky.	$24.3M	SNG—44%, Transportation Fuel—30%
	Great Plains Gasification	Beulah, N. Dak.	$22M	SNG
	Wycoal	Douglas, Wyo.	$13.1M	SNG

*To be Negotiated

CONTROL OPTIONS

In considering the environmental impact of coal conversion, the total process train should be taken into consideration (coal mining, beneficiation, transporation, preparation, synfuels production, and product upgrading, distribution and end-use). The conversion process is typically supported by an auxiliary boiler/power plant. At the synfuel plant site, the auxiliary boiler plant is normally the major source of emission of criteria pollutants.

The major synfuel conversion processes, gasification and liquefaction (direct and in-direct), are environmentally similar relative to inorganic pollutants, i.e., sulfur, NO_x precursors, particulates, solid wastes, trace elements, etc. With regard to the production of heavy organics, there is a wide variation between processes, not so much as to "type" of organics, but to degree, since a wide range of aromatic based tars and oils are typically produced. However, there can be a marked difference in the bioactivity of the liquid fractions; as a disproportionate portion of mutagenicity (which is indicative of carcinogenicity) has been found to reside in high boiling primary aromatic amines which can vary widely between processes. Entrained gasification, being a high temperature process, cracks most of the organics thereby producing a product gas and quench water which is nearly devoid of heavy organics. This is in contrast to the heavily organic laden condensate/quench waters associated with direct, low temperature gasification processes and/or liquefaction. For catalytic processes, the effect of spent catalyst on solid and aqueous wastes varies process to process.

Environmental control options are conventionally segregated into types which deal specifically with gaseous, liquid and solid pollutants. This follows in part from the environmental legislation which is primarily concerned with impact on the accpetor media, e.g., air, water, and land. However, in evaluating a control option, effects on other media must be taken into consideration. Ideally, the pollution control process is fully integrated with the conversion process to take advantage of economics of energy consumption, reduced pollutant production, water reuse potential and by-product production.

Complexity and Variability of Environmental Controls

Major potential pollutant sources which require the use of control processes are:

1. flue gas from auxiliary power plant/boilers
2. sulfur containing tail gases from acid gas separation
3. wastewater from multiple sources (product gas quench, coal pile runoff, sanitary sewer, etc.)
4. auxiliary power plant/boiler solids (bottom ash, fly ash, scrubber sludge)
5. conversion process solids (ash/slag, wastewater sludges, spent catalyst, etc.)

power plant/boiler flue gas -

EPA, DOE, and industry continue to develop a large inventory of control options to reduce the emissions of sulfur oxides, nitrogen oxides and particulates from the combustion of coal. For sulfur control, coal beneficiation and lime/limestone flue gas desulfurization (FGD) have received primary emphasis and are considered commercial processes. A number of other alternatives are at various stages of development and demonstration, e.g., double alkali, dry-FGD, fluidized bed combustion (FBC), and co-generation. In the area of NO_x control, combustion modification including low excess air, staged combustion, and burner modifications appears capable of meeting the emission requirements specified by current New Source Performance Standards (NSPS). NSPS particulate release standards (0.03 lb/MBtu) can be met by deploying enhanced electrostatic precipitators or fabric filters. It is emphasized that these NSPS apply to compliance criteria and are current. Future changes can be expected in the regulations concomitant with major synfuels activities over the next 10-20 years.

tail gases -

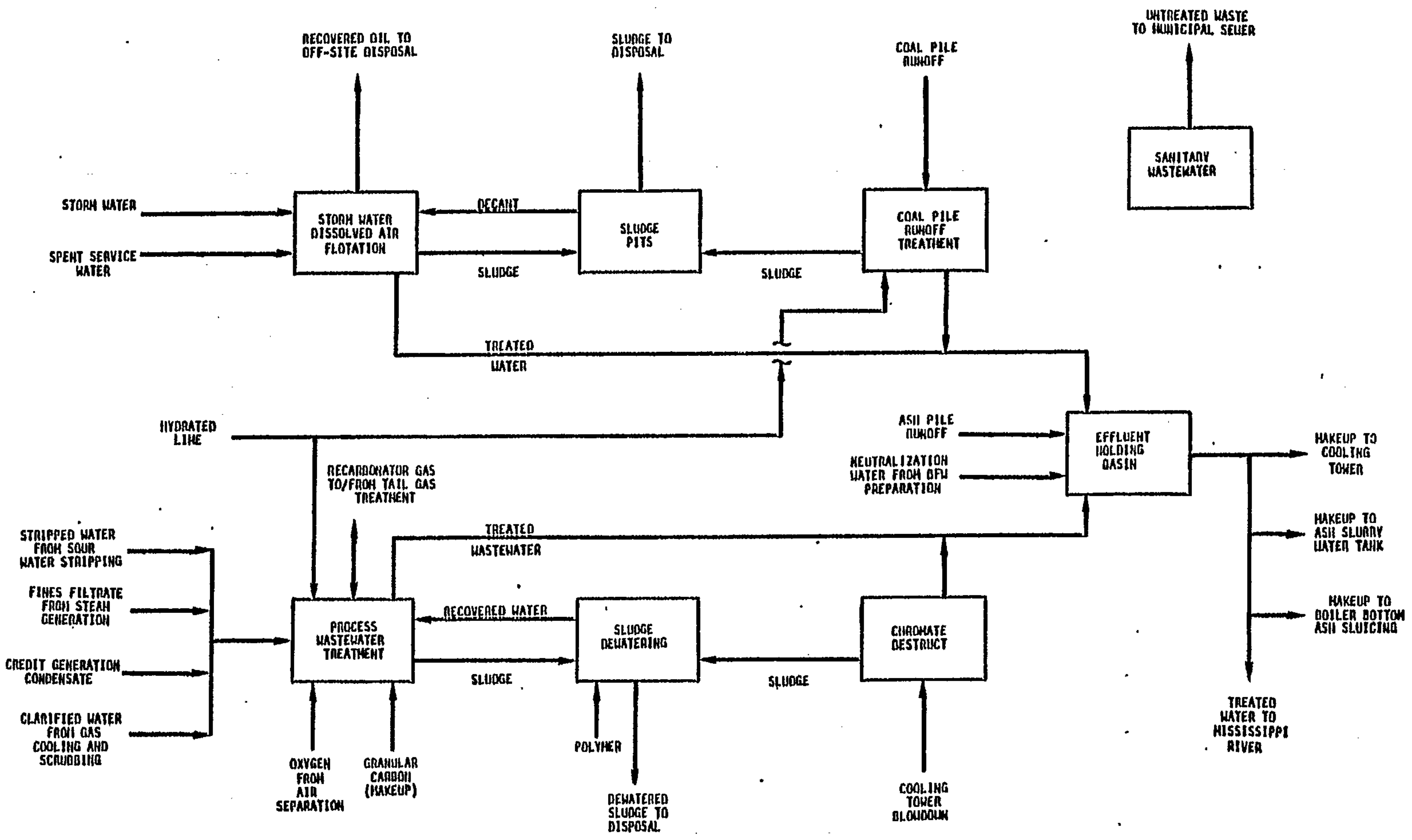
The gaseous sulfur compounds generated during the coal conversion process (primarily H_2S, some COS, CS_2, mercaptans, and thiophenes) are generally removed along with CO_2 by the acid gas treatment train. The acid gases may be non-selectively absorbed and partitioned into a H_2S enriched stream (40-60%) and a H_2S lean stream (2-10%); the enriched and lean streams are typically routed to a Claus unit and a selective absorption unit, respectively, for sulfur recovery (Figure 3). The nominal CO_2 tail gases from these systems generally contain trace residual sulfur--the Claus system removes all but a few percent of the H_2S, while the absorption system can produce a tail gas with about 100 ppm H_2S. Incineration represents the preferred treatment for the H_2S-depleted streams which also may contain some low level hydrocarbons. Stringent sulfur emission standards could necessitate additional H_2S absorption prior to incineration or scrubbing of the incineration flue gas with a conventional FGD system. In any event, it is apparent that high H_2S removal efficiency ($>$97%) can be confidently achieved with existing commercial equipment.

wastewater -

Coal gasification and liquefaction typically produce a highly contaminated "condensate" water which represents a by-product of the conversion reaction, extra steam for cooling, a quench for direct cooling and scrubbing product gases, etc. A wide range of organic loading is experienced; however, compositions tend to be similar with phenolic compounds usually predominating. Condensate waters originating from a high temperature process (non-tar producer) can be essentially devoid of organic material.[1] Most plants tend to design for "zero" discharge of condensate waters, that is, no condensate water is discharged to a surface acceptor; however, such water may be rejected to the atmosphere through evaporation and concentrated aqueous wastes, or may be disposed of via land-fill, ash surface wet-down, deepwell injection (in accordance with applicable underground injection control regulations), etc. Some process schemes consume the contaminated water as recycle to gasification. In addition to condensate waters, various blowdowns produced from feedwater treatment, boiler and cooling tower operation, coal pile runoff, and sanitary wastes are generally integrated into the overall wastewater treatment train. For example, if one examines the design of the wastewater treatment trains for the major gasification projects DOE is involved with, one finds a wide variation of process trains (Figures 4-8). The wastewater treatment options may involve the combination of streams to enhance treatability and evaporation of salt laden blow-downs. The variability between these wastewater treatment schemes is stressed.

FIGURE 3. COMMERCIAL ADSORPTION PROCESSES FOR CONTROL OF HYDROGEN SULFIDE

					Efficiency of S Removal		Absorbent Characteristics				
Process	Absorbent	Type of Absorbent	Temp. °F	Pressure	% H_2S Influent	Effluent H_2S ppm	Life	Regeneration	Selectivity Toward	Makeup Rate	Form of Sulfur Recovery
Chemical Solvent Type:											
1. MEA	Monoethanolamine	Aqueous Solution	80 to 120	Insensitive to Variation in Pressure	99	~100		Thermal	Forms nonregen. comp. with COS, CS_2	50 to 100%	As H_2S gas
2. DEA	Diethanolamine	Aqueous Solution	100 to 130	Insensitive to Variation in Pressure	99	~100		Thermal	Absorbs CO_2 does not absorb COS, CS_2	<5%	As H_2 gas
3. TEA	Triethanolamine	Aqueous Solution	100 to 150	Insensitive to Variation in Pressure	99	~100		Thermal	H_2S	<5%	As H_2S gas
4. Alkazid	Potassium Dimethylamino Acetate	Aqueous Solution	70 to 120	Insentive to Variation in Pressure 1-80 Atm	99	~100		With steam	H_2S		As H_2S gas
5. Benfield	Activated Potassium Carbonate Solution	Aqueous Solution	150 to 250		99	H_2S + COS ~100	Unlimited. No degradation	With steam	H_2S is high		As H_2S gas
6. Catacarb	Activated Potassium Carbonate Solution	Aqueous Solution	150 to 250	Insensitive to Variation in Pressure generally >300 psi	99	H_2S + COS		With steam	H_2S partial also absorbs COS, CS_2	<5%	As H_2S gas
Physical Solvent Type:											
7. Sulfinol	Sulfolane + Diisopropanamine	Organic Solvent	80 to 120	High Pressure Preferred	99	H_2S + COS ~100		Low pressure heating or with steam	H_2S and also absorbs COS, CS_2 and mercaptans		As H_2S gas
8. Saloxol	Polyethylene Glycol Ether	Organic Solvent	20 to 80		99	H_2S + COS ~100			H_2S, also absorbs COS		As H_2S gas
9. Rectisol	Methanol	Organic Solvent	<0		99	~100			H_2S		
Direct Conversion:											
10. Stretford	Na_2CO_3 + Anthraquinone Sulfonic Acid	Alkaline Solution			99.9	~10			H_2S	50 to 100%	Elemental sulfur
11. Townsend	Triethylene Glycol	Aqueous Solution	150 to 250		99.9	~10			H_2S		Elemental sulfur
Drybed Type:											
12. Iron Sponge	Hydrated Fe_2O_3	Fixed Bed	70 to 100		99	H_2S + COS ~100			H_2S and also towards COS, CS_2 and mercaptans		Elemental sulfur



(U-GAS FLUID BED GASIFIER)

FIGURE 4. WASTEWATER TREATMENT SYSTEM — MEMPHIS INDUSTRIAL FUEL GAS PLANT

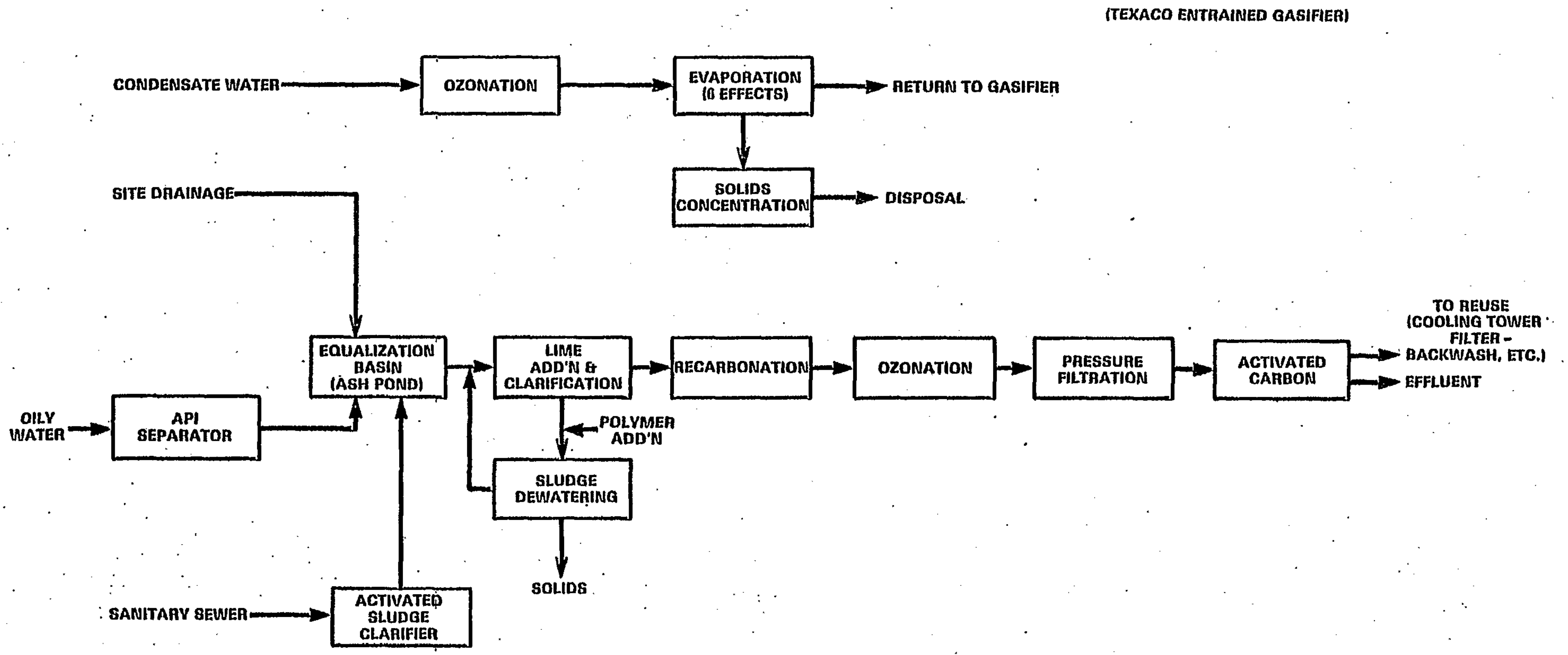


FIGURE 5. WASTEWATER TREATMENT SYSTEM — GRACE AMMONIA DEMO PLANT
(CURRENTLY IN REDESIGN TO PRODUCE METHANOL AND M-GASOLINE)

(BRITISH GAS/LURGI SLAGGING FIXED BED GASIFIER)

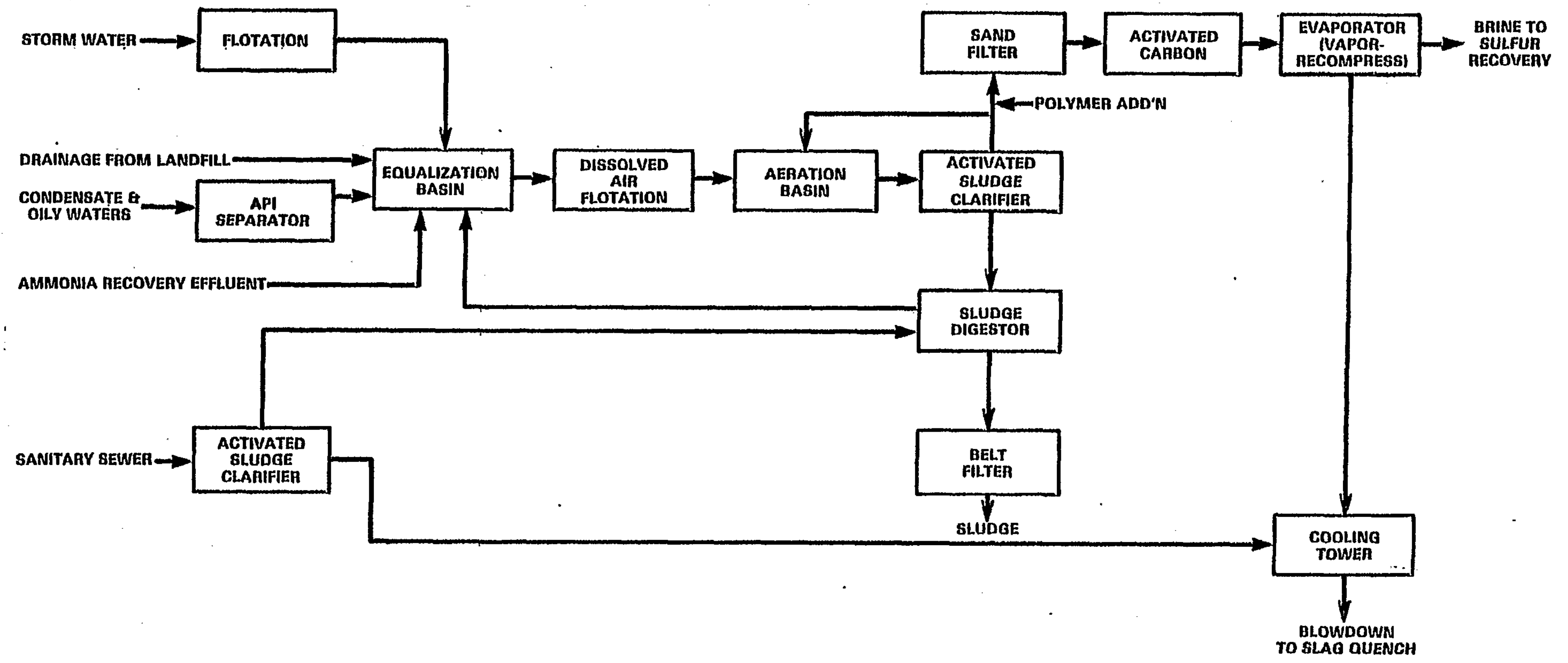


FIGURE 6. WASTEWATER TREATMENT SYSTEM — CONOCO SNG DEMO PLANT

(COGAS STAGED PYROLYSIS GASIFIER)

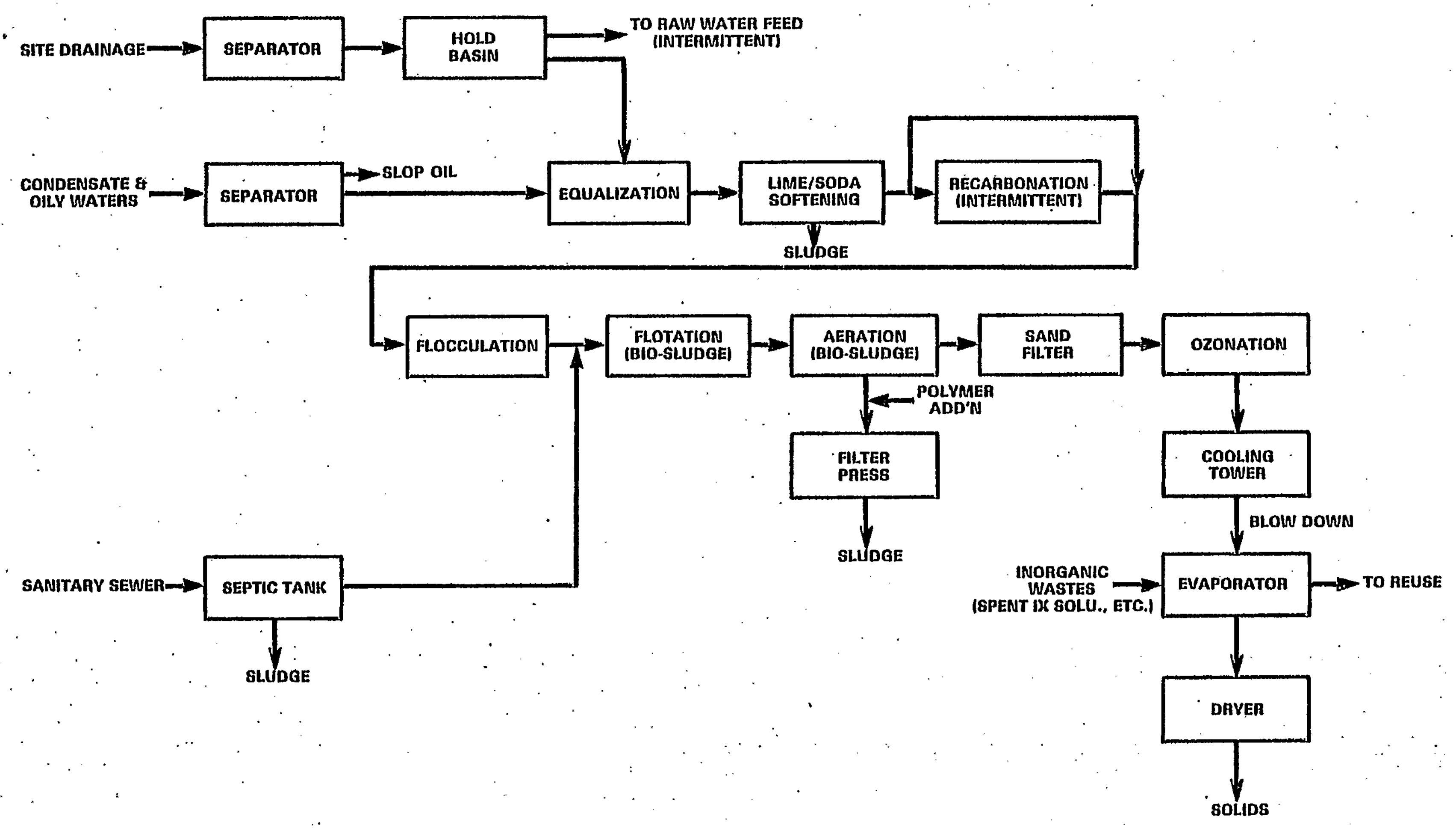
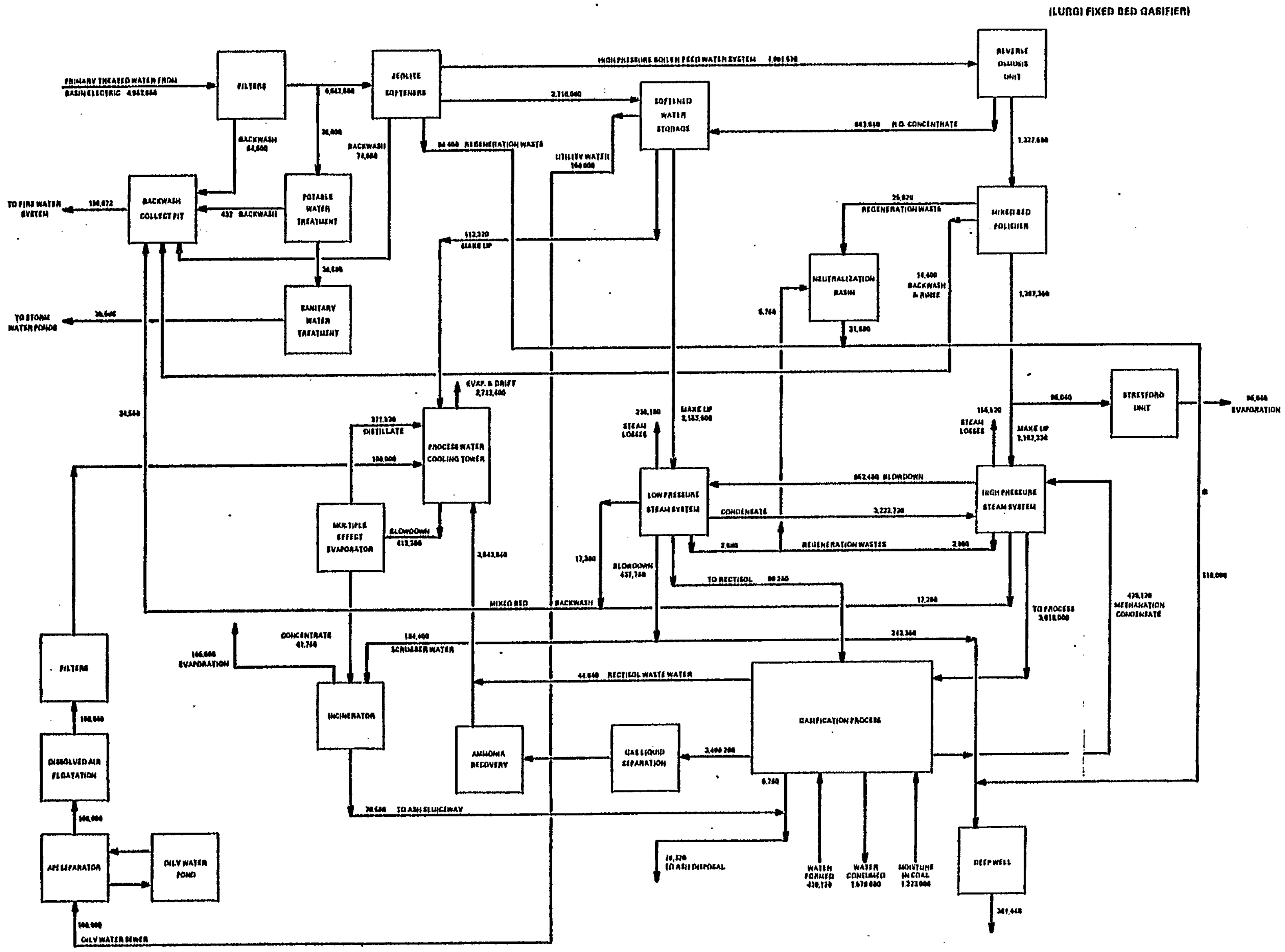


FIGURE 7. WASTEWATER TREATMENT SYSTEM — ICGG SNG DEMO PLANT



ALL FLOWS IN GALLONS/DAY

ALL FLOWS ARE FOR PHASE I ONLY — DOUBLE FLOWS FOR FULL PLANT

FIGURE 8. SCHEMATIC OF WATER SYSTEM FLOW ANG COAL GASIFICATION COMPANY
(REVISED OCTOBER 31, 1979)

One common characteristic of the wastewater systems that must handle an organically charged condensate water (Conoco, ICGG, and ANG) is that there is "zero discharge" for this stream. The rationale for the selection of the "zero discharge" alternative with respect to condensate waters is that while activated sludge tends to be a universal process for adequately treating condensate waters to effluent qualities reflective of current regulations, the nature of these wastewaters, i.e., high organic loading, toxicity of certain compounds, presence of refractory organics, heavy metals and trace elements, causes uncertainty with respect to the evolving Federal regulations resulting from the Toxic Substance Control Act (TSCA) and the Resource Conservation Recovery Act (RCRA). While the technical feasibility of additional steps to the conventional activated sludge train for controlling effluents to more stringent standards has been demonstrated, the treatment processes become more complicated and costly.

solid wastes -

The major solids produced by coal conversion facilities obviously result from the mineral content of the coal feedstock. The characteristics (state) of the slag or ash associated with the conversion process are dependent on the nature of the process per se, since high temperature entrained gasification produces a relative inert glassy material while non-slagging fixed bed gasifiers produce an ash. Preliminary leaching tests indicate that both forms have weathering properties similar to power plant bottom ash. Depending on the method of controlling SO_2 emissions, there may be considerable scrubber sludge from the auxiliary power plant which typically gets disposed of along with wastes from the conversion process. Wastewater sludges, salts from evaporator ponds and/or concentration equipment, spent catalysts and absorbents are representative of relatively low volume secondary wastes that are likely to require special treatment in order to be disposed in a manner consistent with RCRA requirements. The individual treatment and/or disposal methods must be tailored to the specific waste and site.

Integration of Multimedia Controls within Coal Synfuel Processes

In incorporating the afore discussed controls into a plant design, a number of trade-offs exist, e.g., situations where by-products, contaminated water, spent solids, waste heat, etc. can advantageously be used within the process and/or environmental control area (Figure 9). A number of these "options" have appeared in process designs and the literature. Others have been "conjured up" to give some indication where innovative engineering might lead to improve the efficacy of the process. In my judgement, this is an area that deserves further analysis to determine the more promising options and their respective incentives.

One might ask "What are the economic incentives for some of the synergisms which have been projected?" That is, are they really worth the undertaking of the development and associated risk in the application? The answer to this question is best satisfied by a detailed trade-off analysis. However, one can develop a "feel" for potential savings. A very approximate breakdown of costs of environmental controls for a major coal synfuels facility is given in Figure 10[2] Product costs are estimated to be in the neighborhood of $5-8/MBtu for SNG, thus environmental controls should typically account for 10-20% of the total product cost. Reducing overall environmental control costs by say 50% (which is highly unlikely) would result in a saving of merely 5-10% in product costs, not a large incentive

FIGURE 9. CANDIDATE SYNERGISMS FOR COAL CONVERSION PROCESS AND ENVIRONMENTAL CONTROLS

ENVIRO CONTROL	SECONDARY CONTROL/ UNIT OP	SYNERGISM	POTENTIAL BENEFIT
Wastewater Concentration	Cooling Tower	Wastewater Conc-Heat Rejection	Precludes or Reduces Effluent Release, Reduces Raw Water Requirements
Wastewater Treatment	Water Reuse	High Quality Effluent from Treatment Train-Boiler Water Makeup and Process Water Requirements	Reduces Raw Water Requirements
Oil/Tar Disposal	Aux Heat/ Power	Combustion of Organics-Heat Recovery	Maintains Potentially Hazardous Material Within Plant Boundary
Tail Gas Control	Aux Power Combustor/FGD	Existing Boiler and Flue Gas Clean-up Train Used to Control Tail Gas HC and Sulfur Releases	Avoids Special Controls and Insures High Quality Emission
Vent Gas Control	Aux Power Combustor	Existing Boiler Used to Control Vent Gas HC Release in Lieu of Flare	Potentially Better Control Especially if Stack Gas Clean-up Practiced
Wastewater Incineration	Entrained Gasifier	Destruction of Organics, Conc of Solids-Provide Steam Req'mts	Avoids Elaborate Treatment Train to Produce High Quality Effluent
Wastewater Concentration	Aux Power FGD	Wastewater Conc-Makeup to Flue Gas Scrubber	Reduces Effluent Release and Raw Water Requirements
H_2S Recovery	Regenerative FGD, i.e. Dual Alkali	H_2S and SO_2 Control Combined in Claus Unit	No Scrubber Sludge, By-product Elemental Sulfur
Ash/Slag Disposal	FGD Sludge Disposal	Mutual Disposal	Alkaline Sludge will Discourage Trace Metal Leaching from Ash/Slag
Wastewater Treatment	FGD Sludge/ Slurry Disposal	Flocculation/Clarification-Combined Wastewater/FGD Sludge Disposal	Reduction of Wastewater Lime Req'mts
Wastewater Treatment	Oxygen Production	Relatively Cheap Oxygen Used to Abet Bioxidation and/or Ozone Production	Improved, Cost-Effective Treatment
Wastewater Disposal	Ash Cool Down	Wastewater Further Concentrates While Quenching Hot Slag	Facilitates Disposal of Wastewater Concentrate
Wastewater Disposal	Wetdown of Ash Piles and Mine Tailings	Wastewater Disposal-Control of Fugitive Emissions	Facilitates Disposal of Wastewater Concentrate, Dust Control and Mine Restoration
Wastewater Concentration	Heat Rejection	Wastewater Conc by Evaporation and/or Freezing Adsorption System-Low Quality Steam Utilization	Improved, Cost-Effective Wastewater Desalination and Reduction of Organics
Wastewater Treatment	Wastewater Stripping	Addition of Lime to the Wastewater Abets NH_3 Stripping and Flocculation/Clarification	More Complete NH_3 Stripping and Cost-Effective Use of Lime

FIGURE 10. ESTIMATE OF ENVIRONMENTAL CONTROL COSTS COAL SYNFUEL FACILITY

Overall process efficency assumed to be 65%
Auxiliary power plant assumed to use 20% coal input
Coal: 10,000 Btu/lb, 10% ash, 3.5% S

	Cost basis	¢/MBtu synfuel output		
Auxiliary power plant		low		high
SO_2 scrubbing	5-10 mills/kwhr	15	-	30
NO_X burner control	nil			
Particulates - bag house	1-2 mills/kwhr	3	-	6
Solid disposal (ash and sludge)	$10/ton		2	
Conversion Process[1]				
Sulfur[2]	10-20 ¢/MBtu	10	-	20
Tail gas incineration	5-10 ¢/MBtu	5	-	10
Wastewater treatment	$10-20/1000 gal	10	-	40
Slag disposal	$3-10/ton	2	-	6
		47	-	114

MBtu = 10^6 Btu

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[1] excludes mining - environmental aspects included in cost of coal.

[2] in some instances high level removal required to preserve catalysis activity

from the perspective of the producer and potential risks incurred, if the control processes encounter difficulties and disrupt operations. However, if one looks at the incentive in absolute terms, for a single major facility, a 10¢/MBtu saving translates into \$7.5 M/yr. or \$200 M over the life of the facility. Savings of 10¢/MBtu in the environmental control area are not unrealistic. It is this driving force that has encouraged the study of the feasibility of improved environmental control options in DOE's Environmental and Safety Engineering Division (ESED).

Control Options Studied

As a result of a continuing assessment of environmental control adequacy within DOE/ESED, a number of candidate control options have become worthy of a determination of technical-economic feasiblity:

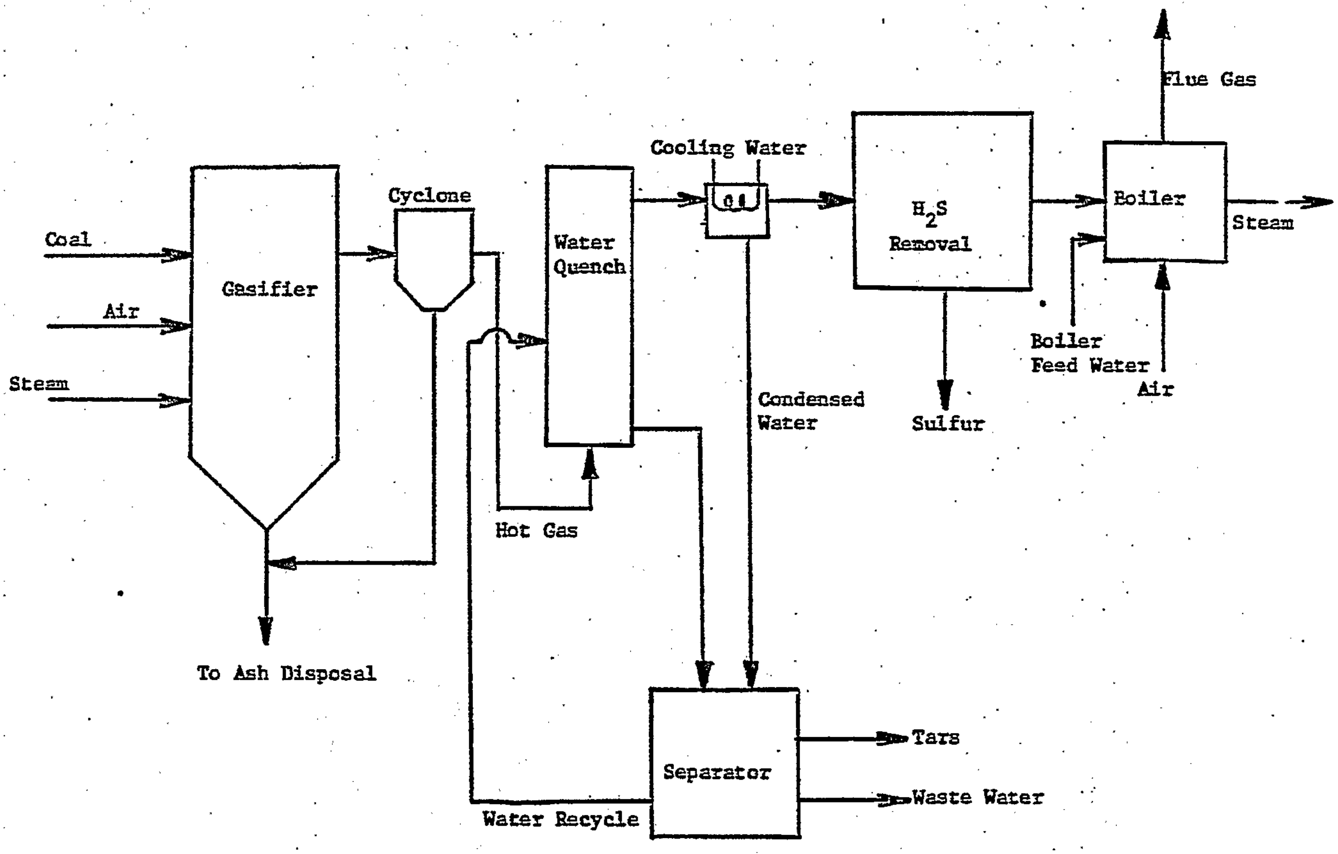
sulfur -

Sulfur absorption technology is well established and based on experience in the petroleum industry. There has been some minor concern for possible contamination of the absorption media with complex hydrocarbons, trace elements and dust; however, operating experience on coal gases indicate such effects can be accommodated.

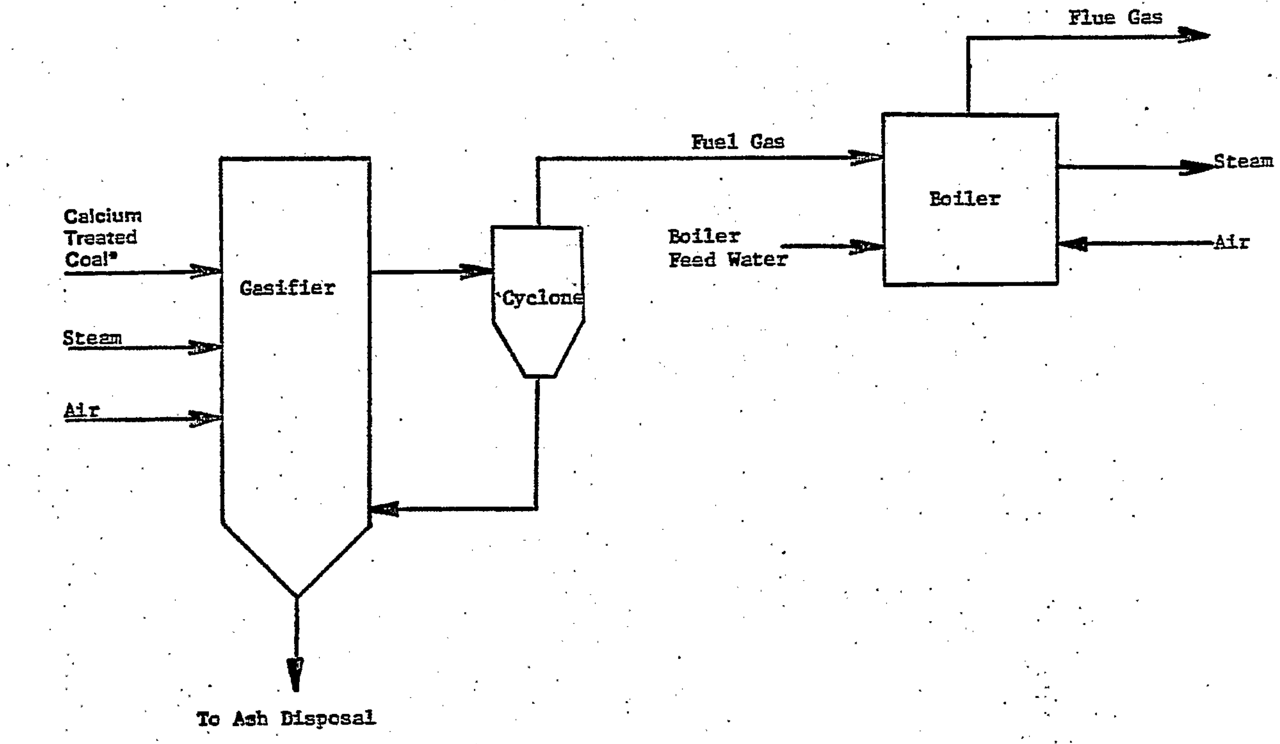
With the intent of simplifying the clean-up technology for an on-site industrial fuel gas producer, the control of sulfur within the gasifier proper using a calcium treated coal has been studied (Figures 11 and 12)[3] An important advantage of the use of a treated coal feedstock to small users is that it eliminates the environmental problems associated with the treatment and disposal of sludges and waste water generated from flue gas clean-up and fuel gas desulfurization. Another significant advantage to consider is the improved process reliability expected from this approach relative to product (fuel) gas cleanup and FGD options. The user simply needs a supply/inventory of treated coal to keep running or make a fuel switch. For those applications where intermittent operations are contemplated due to prime fuel curtailment, the use of treated coal would eliminate the need to operate and maintain a chemical scrubbing system.

Laboratory screening studies have demonstrated that a coal treated with CaO at ambient conditions can effectively remove sulfur and produce a low-sulfur fuel gas in a moving-bed, a fluidized-bed, or an entrained bed gasification system. The sulfur captured in the gasification ash is converted to essentially inert calcium sulfate for environmentally safe disposal. Sulfur removal efficiencies of calcium treated coal relative to untreated coal are shown in Figure 13.

A preliminary economic evaluation of "conversion to coal" (oil/gas backout) by typical industrial users has shown the treated coal to be competitive with the direct combustion of coal and with the gasification of untreated coal that require flue gas desulfurization and fuel (product) gas desulfurization respectively, for controlling sulfur emissions. Results of a preliminary cost evaluation of industrial steam generating systems with a peak load of 100,000 lb/hr steam and an average load of 60,000 lb/hr steam are presented in Figure 14 to compare various fuel-replacement/retrofit options.



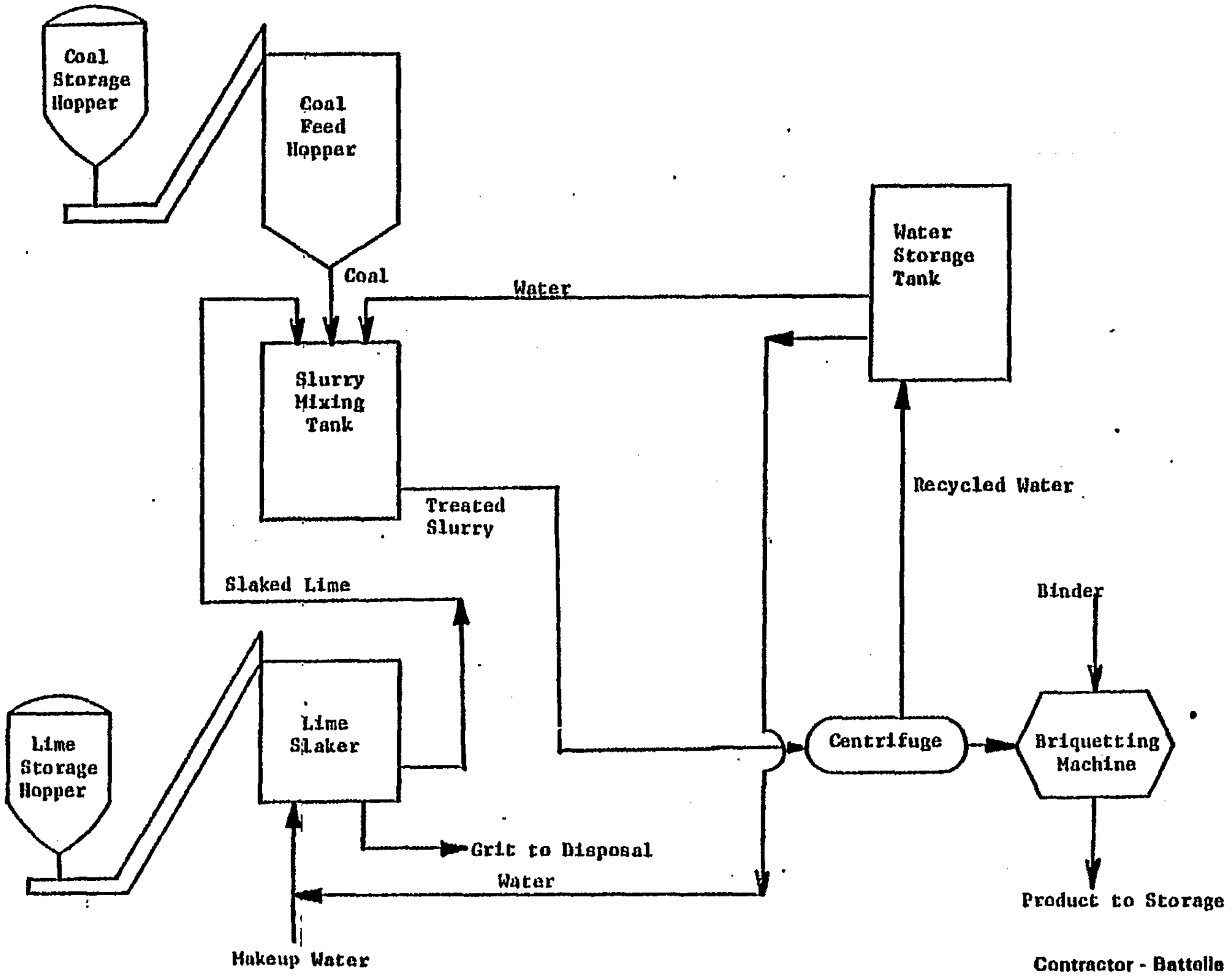
GASIFICATION OF UNTREATED COAL WITH H_2S REMOVAL



* Supplied by off-site, central treatment facility.

GASIFICATION OF CALCIUM TREATED COAL

FIGURE 11. PROCESS VARIATIONS FOR FUEL GAS RETROFIT APPLICATIONS



Contractor - Battelle

FIGURE 12. PRODUCTION FACILITY FOR CALCIUM TREATED COAL

FIGURE 13. NOMINAL SULFUR CONTROL LEVELS-CALCIUM TREATED COAL (LABORATORY SCREENING STUDIES)

	SULFUR REMOVAL, PERCENT	
	UNTREATED COAL	TREATED COAL
Moving-Bed Gasification	4[a]	80
Fluidized-Bed Gasification	[b]	85

Entrained Gasification	CONCENTRATION, PPM UNTREATED COAL	TREATED COAL
PRODUCT GAS		
H_2S	4500	370
HCN	33	10
SCRUBBER WATER FLASH GAS		
H_2S	5300	25
HCN	180	25
SO_2	8000	200

(a) Agglomeration occurred but gas flow through pellets allowed test to be completed.

(b) Test unsuccessful due to severe agglomeration of untreated coal in fluidized-bed gasification.

Contractor — Battelle

FIGURE 14. PROJECTED ECONOMICS FOR CONVERSION OF INDUSTRIAL GAS-FIRED BOILERS TO COAL

SYSTEMS	CAPITAL COST, $\$10^6$	OPERATING COST, $\$10^6$/YR	STEAM COST, \$/1000 LB STEAM
Coal-Fired Boiler with FGD (Boiler and Scrubber New)	9.1	2.8	10.7
Gasification with FGD (Boiler Retrofit, New Scrubber)	9.8	3.1	11.6
Gasification with H_2S Removal (Boiler Retrofit)	10.4	3.1	11.9
Gasification of Calcium Treated Coal (Boiler Retrofit)	7.7	3.0	10.3

tail gases -

The reference control technology for the tail gases associated with acid gas stripping operations is direct incineration at approximately 1,600°F with a clean fuel gas. Alternative control methods which showed promise in a preliminary assessment study were incineration in a coal fired boiler at 4¢/MBtu (product gas basis) and catalytic incineration at 5¢/MBtu, while tail gas incineration with clean fuel gas is projected to cost in the neighborhood of 10-12¢/MBtu.[4] Commercial catalyst have been screened to determine the effect of temperature, space velocity, and the presence of H_2S and COS on hydrocarbon and carbon monoxide conversion (Figure 15).[5] These bench scale studies indicate the most effective catalysts are precious metal catalyst on a monolith substrate and a non-precious metal oxide deposited as micro spheres on a solid substrate (Figure 16). The more promising catalysts H, G, and A are currently undergoing life tests. A detailed analysis of the coal-fired incineration option is to be made by a commercial incinerator/boiler manufacturer.

wastewater -

The control options for treating condensate wastewaters in a conventional mode have been demonstrated at bench scale. It appears that activated sludge is sufficient for coal wastewaters to meet existing discharge standards. Prior to biotreatment, gross ammonia and organic removal is required to render the feed non-toxic.[6]

Coal condensate waters contain dissolved ammonia, up to 2%. This NH_3 is usually neutralized by dissolved CO_2 that is produced in driving the conversion process; thus the condensate waters are strongly buffered and to change the pH via the addition of chemical reagents is normally quite expensive. Some coals contain high chloride which enters the condensate water and provides a strongly acidic anion to retain the NH_3 as NH_4Cl. In such instances, it is necessary to add a strong base (CaO) to enhance NH_3 strippability. Normally such coals occur in the East and the additional salt loading due to reagent addition presents no critical problem with effluent discharges.

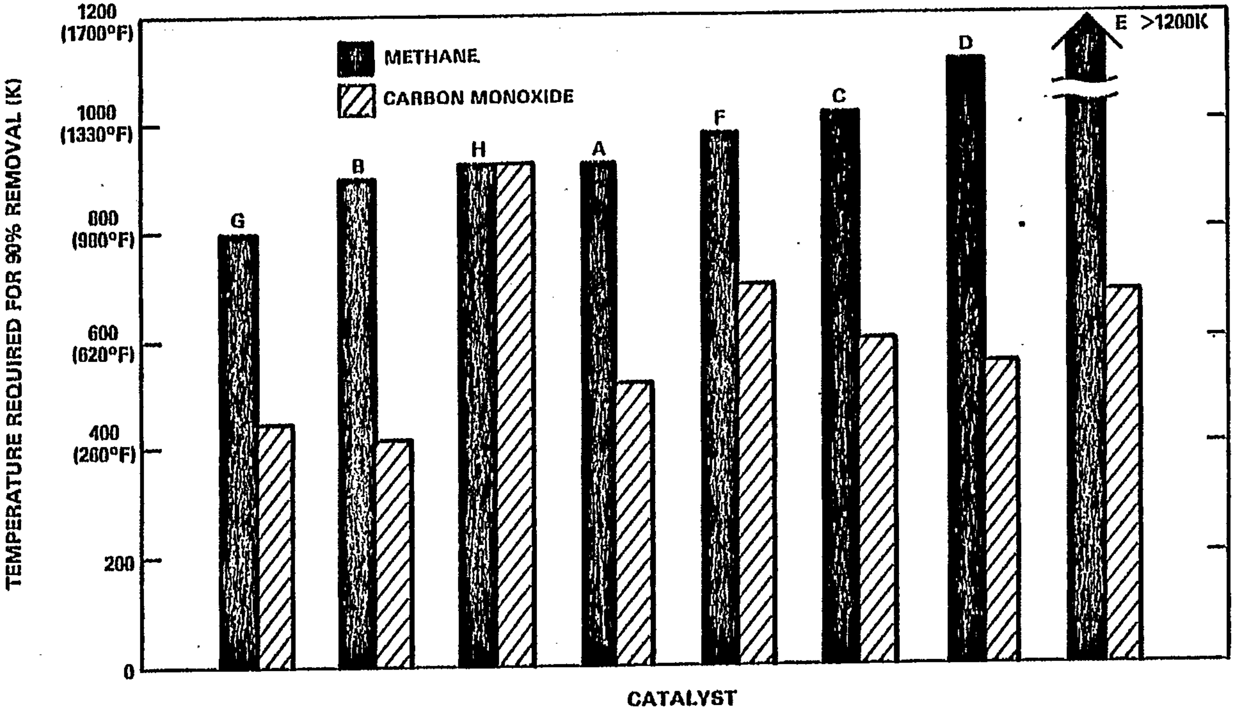
Phenolic compounds contribute to the bulk of BOD (5,000-10,000 ppm) and along with other organics, pose a severe stress on sludge microorganisms. One typically resorts to solvent stripping and/or dilution to bring the levels down to 1000-2000 ppm, at which level acclimated organisms can do a reasonable job. An on-going study is determining the trade-offs between NH_3 and organic stripping options attempting to conserve reagents and at the same time, reduce steam requirements.[7]

Coal wastewaters contain some ring structures, polynuclear aromatics (PNA's) and heterocyclics (1-10 ppm), some of which are biorefractory. The more refractory compounds are adsorbed on the sludge, with effluent concentrations running in the range of 10-50 ppb. Laboratory bench testing has indicated that a significant reduction of PNA type materials can be achieved if the effluent is subjected to partial ozonation followed by activated carbon adsorption.[8] It appears important that the ozonation precede the sorption step, lest the large ring-structure compounds be too large for the pores of the carbon. Current efforts are focused at determining the efficacy of regeneration techniques for the spent carbon. Another study is attempting to demonstrate the viability of powder activated carbon (PAC) to help stabilize the biooxidation of solvent stripped condensate waters and improve the efficacy of activated sludge systems.[5] Biological screening tests are being performed on the various intermediate process waters to help ascertain the completeness of the treatment with regard to mitigating any low level adverse biological impact that may result by the release or use of partially

FIGURE 15. SUMMARY OF INCINERATION CATALYSTS TESTED

CODE	COMPOSITION	COMMENTS
A,F	*Spherical and Extrudate Forms, Non-Precious Metal Oxide on Support Material	Inexpensive, ~640 $\$/m^3$ Not Poisoned by Pb, Zn, Halides. <10 ppm SO_3 in Effluent. Used for CO, H/C and Other Organic Removal.
D	0.1% Pt, 5% Ni	"Some" SO_3 in Effluent. No Experience with Similar Streams. An NO_x Removal Catalyst Via NH_3 Reduction.
C	0.1% Pt, 3% Ni	Same as D, a Hydrogenation Catalyst
E	Pd on Metal Lessing Rings	<10 ppm SO_3 in Effluent. Expensive, $\sim 1.4 \times 10^5$ $\$/m^3$. No Comment on Poisons. Can be Recycled 3 Times. Primarily Used for H_2 Removal.
H	Pt on Al_2O_3 Monolith Support	Favors SO_3 Production. Expensive, $\sim 5.3 \times 10^4$ $\$/m^3$. No Comment on Poisons. For Industrial Tailgas Cleanup.
G	Precious Metal on Ceramic Honeycomb	~100 ppm SO_3 in Effluent. Expensive, $\sim 6.4 \times 10^4$ $\$/m^3$. For Industrial Tailgas Cleanup.
B	Mn and Cu Oxides	Poisoned by S and Heavy Metals. Inexpensive ~710 $\$/m^3$. Designed Removal of H/C's and CO from Breathing Air.

Contractor - ORNL



Note: ethane oxidation found comparable to methane, while catalysts tended to oxidize ethylene at lower temperatures, 600-800°K

FIGURE 16. METHANE AND CARBON MONOXIDE REMOVAL AS A FUNCTION OF CATALYST

Contractor — ORNL

treated effluents (Figure 17).[8] Note that the toxicity after biotreatment is suspected to result solely from inorganic species, i.e., the conversion of thiocyanates to ammonia during biotreatment (laboratory unit not as fully aerated as a commercial operation) and conversion of trace, residual cyanates to cyanide on ozonation. In some instances, a color problem has been associated with the aging of trace polyhydric phenols which may be overcome with a carbon polishing step or the addition of PAC to the activated sludge system. Unit operations can be arranged in a condensate treatment train that would produce almost drinking quality water. Relatively high treatment costs are likely to bar such intensive treatment (Figure 18); however, it should be noted that the cost impact under current standards is considerably less, expecially since only 10-20 gallons of condensate water may be produced per MBtu.[10] Costs also can be reduced if it is practical to resort to PAC in lieu of ozonation and activated carbon.

As indicated in the plant designs, the trend for wastewater control is to perform some partial treatment on the wastewater stream (solvent extraction, activated sludge) and use cooling towers to concentrate the stream to a point where a reasonably sized blowdown stream can be fed to evaporation ponds or multiple effect evaporators. Ideally it is economically desirable to use as poor a quality of water as the reuse application will permit. An on-going study is evaluating water quality requirements for a number of reuse applications, such as cooling towers, many of these applications have been previously outlined.[11]

Special attention has been given to reducing the quantity of wastewater associated with the quench operation by instituting a two stage quench - the initial stage is a low volume recycled highly contaminated water while the second stage consists of a much larger volume of relatively clean water, the strong acid gases condensing out in the first stage. The incentive for such a system has been shown to reside with coals having a halide content greater than 0.15% Cl, i.e., generally Eastern coals (Figure 19).[12] It is likely that future plant designs will adopt water conservation measures and desalting technology to preserve the water balance within the plant so that a concentrated, highly contaminated, low volume waste stream will be produced. Thermal oxidation techniques, e.g., gasification (recycle to the conversion process), wet-air oxidation, and even incineration, are expected to become viable treatment practice for the concentrate.

solid wastes -

As indicated, it is desirable to dispose of solid wastes in a manner tailored to the specific properties of the individual waste. Studies have been supported to classify major gasification and liquefaction slags/ashes as hazardous or non-hazardous under EPA/RCRA protocols (Figure 20).[13] It appears that such material may be disposed in a conventional manner, which can mean landfilling during mine restoration for strip mining operations near to the conversion facility. With the intent of better defining the true environmental acceptability of waste disposal practice for such materials, a series of laboratory column leaching and lysimetric tests are being performed to develop an understanding of leaching/mobilization phenomena and identify viable control procedures. Preliminary studies have shown high initial sulfur releases from gasifier slags and their auto-oxidation to sulfuric acid, may preclude the natural capacity of geologic material to adsorb migrating trace heavy metals. Incorporating an alkaline material (limestone, spent scrubber sludge, etc.) with the slag ash would tend to discourage acid formation during these critical, early leach cycles (Figure 21).

FIGURE 17. ACUTE TOXICITY TO *DAPHNIA MAGNA* OF HYDROCARBONIZATION WASTEWATER BEFORE AND AFTER VARIOUS TYPES OF WASTEWATER TREATMENT

SAMPLE	APPROXIMATE 48-HR LC_{50} (%)
Raw Scrubber Water	0.65
Biofeed Water	2.3
Biotreated Water	≈70
Water After Ozonation	≈18
Water After Ozonation and Charcoal Adsorption	≈0.1
Water After Charcoal Adsorption and Ozonation	≈4.5

Contractor — ORNL

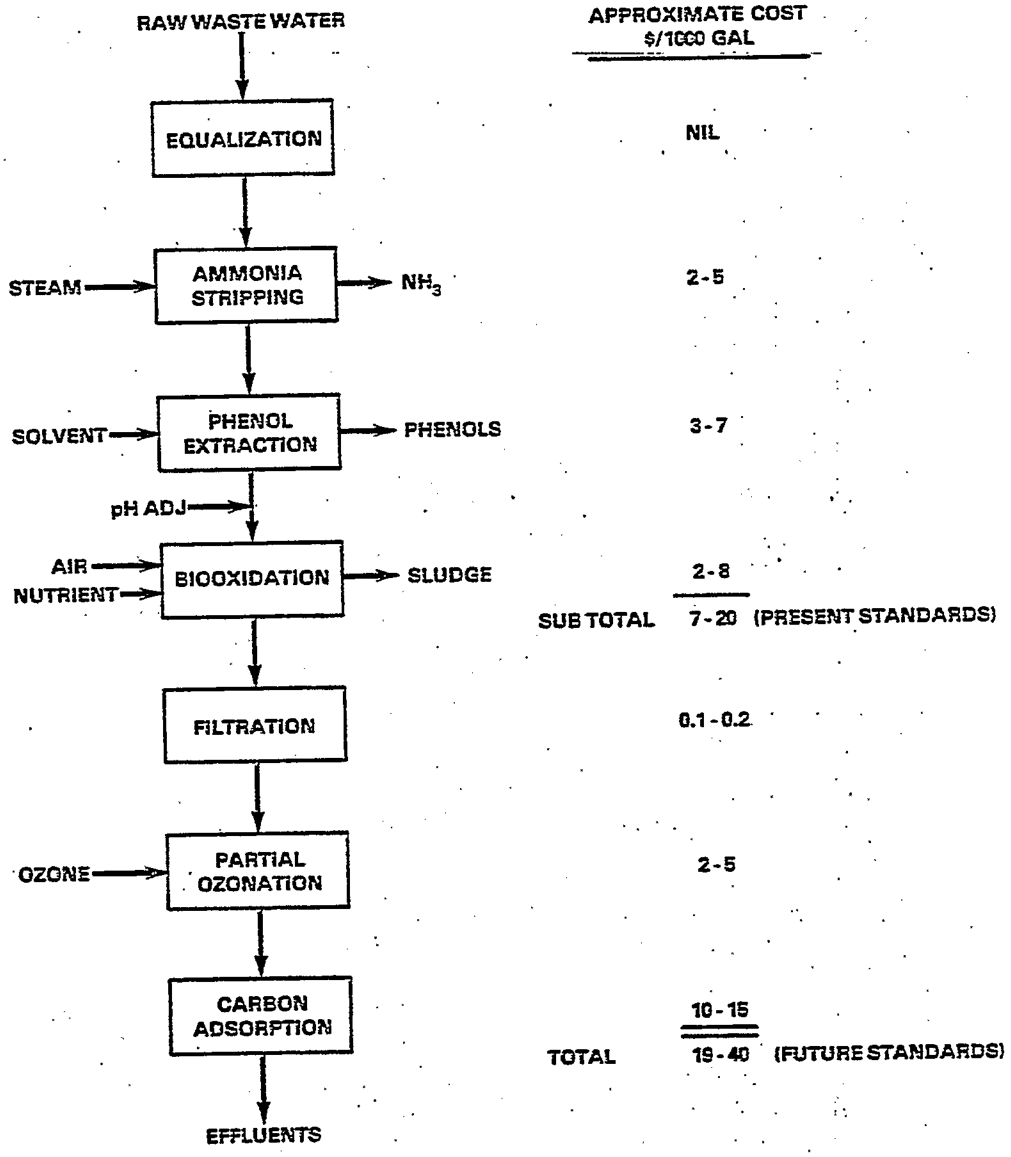
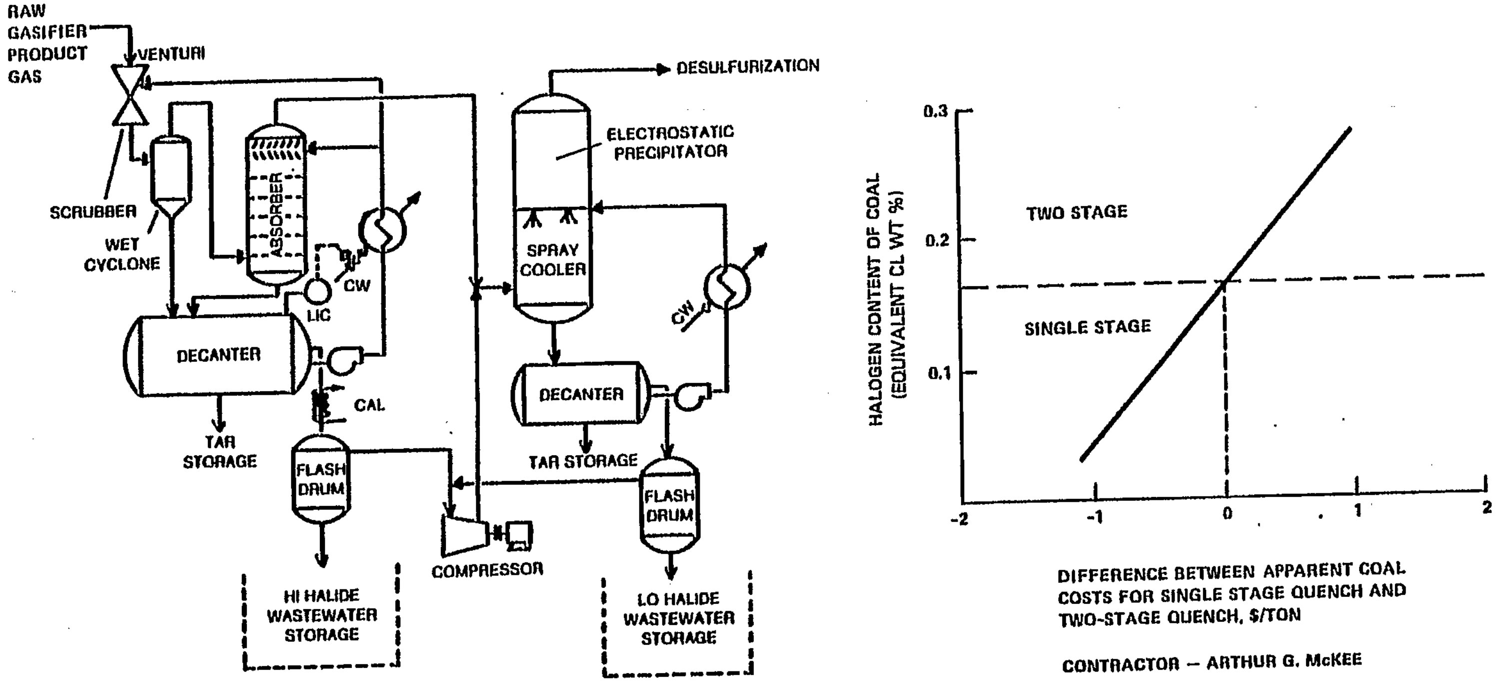


FIGURE 18. REPRESENTATIVE WASTE WATER TREATMENT PLAN FOR COAL CONVERSION EFFLUENTS

FIGURE 19. TWO STAGE QUENCH OPTION



CONTRACTOR — ARTHUR G. McKEE

FIGURE 20. EPA-EP LEACHING RESULTS FOR SIX GASIFICATION/LIQUEFACTION SOLID WASTES[1]

(All Concentrations in ppb)

ELEMENT	WASTE C	WASTE E	WASTE G	WASTE H	WASTE I	WASTE J	RCRA LIMITS[a]
Arsenic	0.27	0.06	<1	<1	0.53	4	5,000
Barium	<200	<500	20	80	<500	3.3	100,000
Cadmium	0.054	0.97	<1	28	3.4	0.098	1,000
Chromium	1.6	0.44	<5	<5	0.13	0.46	5,000
Copper	2.7	3.7	10	10	0.94	1.3	b
Lead	<0.3	0.26	<10	<10	1.6	1.1	5,000
Mercury	0.64	0.03	<1	1	0.191	0.022	200
Selenium	<5	2	<1	<1	<1	<5	1,000
Silver	<0.03	<0.03	<2	<2	0.07	<0.01	5,000
Nickel	281	219	30	540	758	100	b
Zinc	63	10	13	2240	385	12	b

[a] RCRA Criteria are 100 times the interim primary drinking water standards.

[b] No criteria have been established for these elements at this time.

[1] Boegly, et al 1980. "Disposal Characteristics of Solid Residues from Coal Gasification." Air Pollution Control Association, June 1980, Annual Meeting, Montreal, Canada

Contractor — ORNL

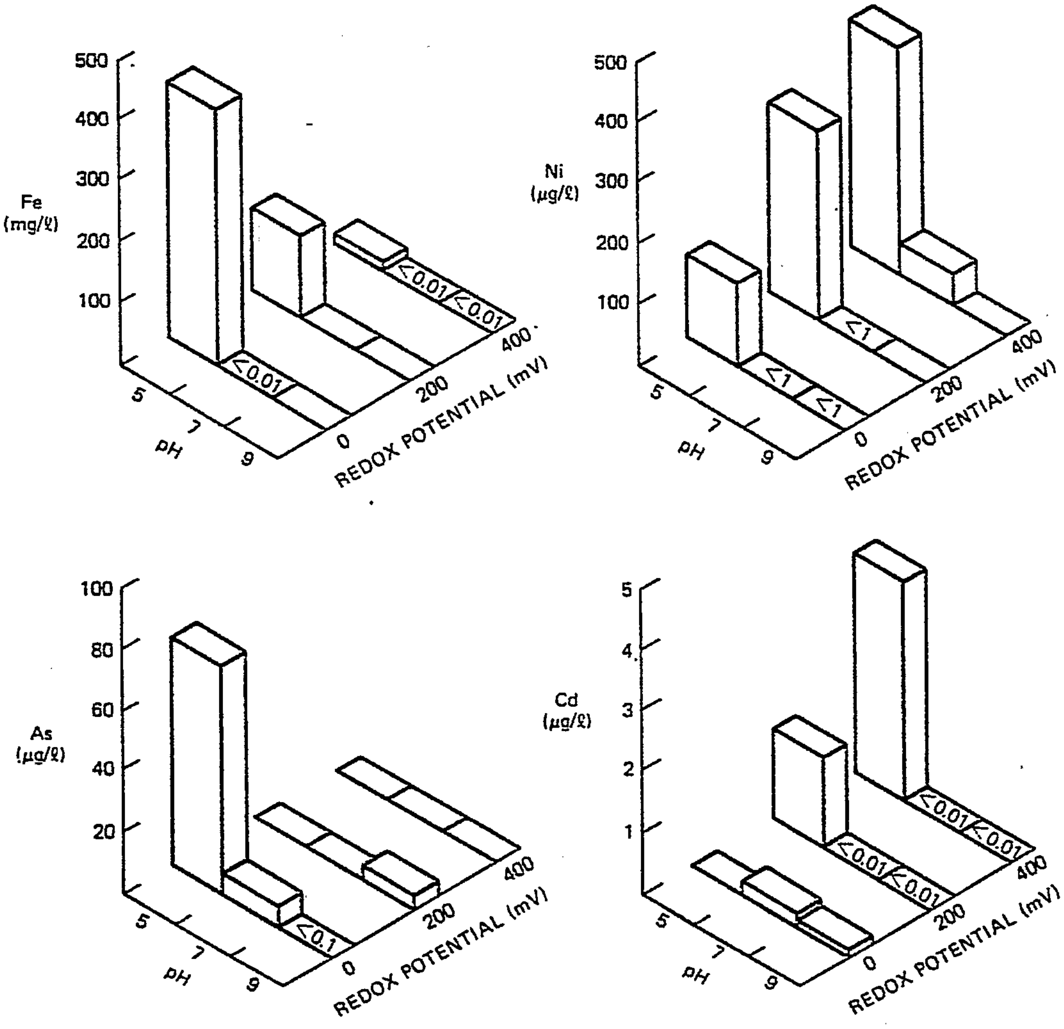


FIGURE 21. INFLUENCE OF pH AND REDOX POTENTIAL ON METAL CONCENTRATIONS IN WATER (GASIFICATION WASTE, SOLID:SOLUTION RATIO, 1:50)

Contractor — ORNL

CONCLUSION

Hopefully what has been conveyed by this broad-brush presentation is that a large number of environmental control options exist, that many of these control options are integrated into the process to improve the efficacy of the overall conversion process and lessen the concomitant environmental insults of the conversion process The inventory of viable control options are rapidly evolving: under such a dynamic situation where actual performance data on full-scale, environmentally acceptable facilities is lacking, it appears premature to develop firm BACT criteria. What would appear to be of greater service to the nascent industry would be a set of reasonable technology based emissions regulations or guidelines that would provide industry with the requisite freedom and flexibility and the incentive for innovation to operate within such bounds. In a nut shell, let's be prudent.

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TECHNICAL AND ENVIRONMENTAL ASPECTS OF THE GREAT PLAINS GASIFICATION PROJECT

Remarks of Gary N. Weinreich
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American Natural Service Company

Ladies and gentlemen, it's a pleasure to have this opportunity to speak before you today about the Great Plains Coal Gasification Project. Unlike our presentations during the last seven years, today we can talk about a synthetic fuels facility that is under construction, a facility that will be the first commercial-sized substitute natural gas (SNG) plant in the United States, and a facility that represents a signal to the world that this country is serious in its efforts to reduce its dependency on foreign countries for its crucial energy supply. While this plant is by no means a panacea, it most definitely represents a major and difficult first step on the part of industry and government that will eventually lead to a successful new synthetic fuels industry in this country. Synthetic fuels, coupled with energy conservation and successful developmental efforts in the areas of solar power, non-conventional and renewable energy sources, will enable the United States to enter the twenty-first century in a much better energy supply and national security posture than is maintained today.

We must give a great deal of credit to the US Department of Energy for their assistance in the form of a federal loan guarantee for the project. With DOE's pledge of assistance, Great Plains was able to maintain the 1980 construction start date and avoid further delays in this long overdue venture. As you may be aware, the Federal Energy Regulatory Commission approved the Great Plains Project in November, 1979, but General Motors Corporation and three state commissions opposed the consumer-backed financing arrangements approved by the FERC. The federal loan guarantee alleviates this situation and has permitted the project to proceed. Ground was broken in August and construction of the facility will continue through to the completion date in 1984.

I was asked to speak on the technical and environmental considerations involved in a coal gasification facility such as the Great Plains Project. As you can imagine, this is a very broad subject to cover in 25 minutes. I will try to address the highlights and the bases for some of the environmental decisions involved in our project.

A brief organizational description of the Great Plains Project might be appropriate for those of you who are unfamiliar with the project. Great Plains Gasification Associates is a consortium made up of subsidiaries of five major natural gas pipeline companies. The project was originally proposed by ANG Coal Gasification Company, a subsidiary of American Natural Resources Company of Detroit, Michigan. ANG is now an equal partner in the project as well as the project administrator responsible for the design, construction and operation of the facility for the consortium. The other members of the consortium are subsidiaries of the Peoples Energy Company, Transcontinental Gas Pipe Line Corporation, Tenneco, Inc. and Columbia Gas Transmission Co.

The project consists of a 275-million cubic-foot per day high-BT coal gasification plant which is being built in two half-size phases.

The project is located in Mercer County, North Dakota, six miles northwest of the town of Beulah (population approximately 3,000) and seven miles south of the plant's water supply, Lake Sakakawea. The plant is located immediately adjacent to an 880-megawatt steam electric generating plant currently being constructed by Basin Electric Power Cooperative of Bismarck, North Dakota. Together, the two plants will share common facilities such as water supply, railroad, plant access and coal mining. The power plant will supply electricity to the Great Plains facility while using the lignite fines which are unusable in the Lurgi gasifier. Together, the two plants complement each other and provide economic advantages while reducing the adverse environmental impacts of two separate plant sites.

The air pollution control systems included in the design of the Great Plains facility represent the largest single pollution control cost. The air emissions control system can be divided into four broad categories: 1) coal gasification, 2) steam generation, 3) coal handling, and 4) incinerators, flares and miscellaneous sources. Each category is unique and merits a brief explanation of the control alternatives.

The Great Plains' gasification system, like that of many other proposed SNG plants in the United States, will employ the Lurgi Rectisol process to remove acid gases from the synthesis gas stream. The Rectisol process uses a cold methanol wash to absorb CO_2, H_2S and other sulfur compounds from the product gas, and the methanol is then regenerated. Our engineers considered several options for treating the sulfur-containing off-gas streams from Rectisol. At first a Claus unit with tail-gas clean-up and a Wellman-Lord stack gas scrubber was considered. Detailed investigation, however, raised a number of questions about the operating reliability of the Claus system on a feed stream containing variable concentrations of H_2S. For this reason as well as high cost, a system utilizing the Stretford sulfur recovery process was selected for the Great Plains plant. The Stretford process is known to effectively reduce H_2S to less than 10ppmv; however, the Stretford process has not been proven on streams with as high a CO_2 content as that of the Rectisol off-gas.

For this reason, our plant includes a Stretford system designed to remove H_2S to a level less than 10ppmv, but our permit takes credit only for the vendor-guaranteed removal efficiency or 100ppmv. Of course, we are hopeful that the higher removal efficiency will be achieved and the plant-wide sulfur emission will be much lower.

The tail-gas from the Stretford unit will contain residual H_2S and virtually all the organic sulfur and hydrocarbons present in the feed from Rectisol. For this reason, incineration of the Stretford tail-gas is required. In the case of the Great Plains plant, this tail-gas will be incinerated in the plant boiler system, recovering the BTU value of the gas while converting the H_2S, organic sulfur and hydrocarbons to compounds acceptable for emission to the atmosphere. Although the Stretford tail-gas contains a very small BTU value on a cubic foot basis, it constitutes a major fuel source by virtue of its large volume. We, therefore, have found that combusting the Stretford tail-gas is preferable to flaring from an energy utilization, conservation and environmental standpoint. The environmental benefit results from increased energy efficiency which reduces the need to burn additional sulfur-containing fuel. In addition, with this boiler design, the gasification section of the Great Plains plant will comply fully with EPA's guidelines for the Control of Emissions from Lurgi Coal Gasification Plants (EPA-450/2-78-012).

This brings us to our second air emission source, the plant steam generation system. Several sources of steam generation are available to the designer of a modern SNG facility, including generation from coal fines or liquid by-products, recovery from exothermic processes (such as methane production), and recovery from gasifier steam jackets. The Great Plains plant will utilize plant byproduct tar, tar oil, naphtha, and phenols plus the Stretford tail-gas to generate the steam required above and beyond that recovered in an extensive in-plant steam recovery, reuse and conservation system. EPA's new source performance standards for steam generation apply to this section of the plant. However, the EPA emission standards are not suited to direct application in the case of Great Plains due to the innovative energy conservation approaches utilized. First, EPA has no sulfur emission standard for a sulfur-containing gaseous fuel such as the Stretford tail-gas. Further, EPA's NO_x emission standard does not consider NO_x emission from a liquid fuel (e.g. tar and tar oil) with a higher entrained nitrogen value than conventional liquid fuels. Fortunately, the North Dakota State Department of Health, from the time of our first project announcement, has been willing to evaluate our proposals in detail, carefully considering and balancing environmental, economic, energy conservation and safety criteria. After a thorough review with an invitation for public comments, the Health Department made determinations of 1) best available control technology for the project, 2) compliance with the federal guidelines for the Control of Emissions from Lurgi Coal Gasification Plants, 3) compliance with ambient air quality standards and 4) compliance with the Prevention of Significant Deterioration regulations at the Class I area 100 kilometers west of the plant site. The North Dakota State Department of Health, in their 167-page analysis of the Great Plains Project, found that the facility as proposed would comply with all federal, state and local air quality regulations. The EPA, Region VIII, then reviewed the state's analysis and congratulated the Health Department, stating that their technical effort "may well become the standard to which new source reviews of this office and the other Region VIII States are compared".

It is evident that in this case a very thorough evaluation of a new synthetic fuels facility was completed by means of a "case-by-case" review. The existence of new source performance standards, pollution control guidance documents or the like could very possibly have made permitting of the facility more difficult due to the inherent inflexibility of the regulations and the restrictions they impose when considering special situations and innovative techniques. A case in point is EPA's 1979 Environmental Assessment Report on Lurgi Coal Gasification Systems for SNG (EPA-600/7-79-120). This report contains an excellent overview of the environmental aspects of a Lurgi SNG facility. However, when applying the EPA guidelines and new source performance standards, the report incorrectly states that the Great Plains Project (refered to in the report as ANG) exceeds federal standards for SO_2 emission from the gasification section, exceeds the federal standards for SO_2 emissions from the steam and power generation section, and exceeds the federal standard for TSP emission from the steam and power generation section. This is after the Health Department and Region VIII certified that the facility is in 100% compliance with all regulations. The lesson to be learned is that hard-and-fast standards are not appropriate for complex emerging technologies such as those found in the synthetic fuels industry. A very thorough case-by-case review is highly preferable until such time as sufficient operating data on modern facilities have been compiled and verified and valid standards can be developed.

The other two sources of air emissions are 1) coal handling and 2) incinerators, flares and miscellaneous sources. Particulate emissions from the coal handling facilities will be controlled through the use of covered conveyors and baghouse collectors at all transfer points. EPA new source performance standards for Coal Preparation Plants applies to this section of the plant. The low-volume intermittent gaseous streams in the plant will be incinerated where such treatment is appropriate and does not represent a safety hazard. Start-up gases and expansion gases from gas-liquor separation will be routed to a start-up incinerator for controlled combustion. The majority of the coal lock-gas will be recovered, desulfurized and reused, resulting in a very small vent, less than 2% of the total lock gas volume. The flare system is the primary plant safety system and is capable of combusting the entire gas flow from either train of the plant in the event of an emergency shut-down of a gas processing unit.

The water pollution control systems included in the Great Plains Project are designed to eliminate the discharge of process wastewaters to surface streams. A complex recycle and reuse system will be employed within the plant followed by utilization of the plant cooling tower, multiple effect evaporators and a liquid incinerator to concentrate, then destroy all organic components of the plant wastewater. A brine solution from the regeneration of demineralizers and softeners will be disposed of via a deep well into an aquifer where the natural water quality is six times more brackish than the waste stream. Stormwater runoff will be collected in sedimentation ponds prior to discharge and the coal pile has been covered to minimize suspended particulate loading from that potential source. Sanitary wastewater will be treated in a package plant and the effluent will be discharged to the runoff pond which will provide tertiary treatment in the form of a polishing pond prior to discharge.

This system for handling liquid effluents was selected over other alternatives such as solar evaporation ponds, activated carbon adsorption and biological treatment after detailed engineering, economic and environmental review revealed that the present system is the best suited for our particular plant design and location.

Solid waste from the gasification plant consists primarily of coal ash from the gasifiers and from the liquid incinerator. Approximately 2200 tons per day of ash will be generated by the full plant.

This waste does not qualify as hazardous under the EPA's extraction procedure toxicity test and is further exempted as a coal combustion waste. Nonetheless, care will be taken in selecting and developing disposal areas within the mine. Disposal will be limited to dry locations where natural or emplaced clay barriers will prevent the formation and migration of ash leachates. In west-central North Dakota, the natural soil and groundwater conditions exhibit a relatively high pH and acid formed by the oxidation of pyrites is quickly buffered. Acid conditions and the resulting leachate problems evidenced in other parts of the country are not encountered in the Northern Great Plains region.

The in-mine disposal technique proposed to be used at the Great Plains Project represents a considerable improvement over the primary alternative which is ash sluice ponds. In-mine disposal eliminates four problem areas that occur with sluice ponds: 1) the commitment of large acreages for ponds, 2) the need to dispose of decanted water, 3) the need to reclaim the filled pond to a useful end-use and 4) the need to protect the groundwater from infiltration of sluice water. For these reasons, it is felt that proper in-mine disposal represents state-of-the-art in solid waste disposal.

In the area of employee health and safety, the Great Plains Project is designed to protect the worker from the potentially hazardous substances that are present in all synthetic fuels facilities. Containment of these substances and a good work practices control program coupled with a thorough medical surveillance program, are the essential elements of the occupational health and safety program. Our consulting agreements with the South African Coal Oil and Gas Corporation, Ltd. of South Africa enabled our engineers to discuss possible solutions to various air, water and process emissions and to select the most efficient means of control based on years of operating experience. As you may know, the Sasol plant was visited by an investigative team from the National Institute for Occupational Safety and Health (NIOSH) in 1977. The plant was given a clean bill of health by that group, a remarkable achievement for a facility that has been in operation for over 25 years.

In summary, we are confident that the Great Plains Coal Gasification Project can be built and operated in compliance with all requirements for environmental, health and safety control. In additi our monitoring and surveillance programs will go beyond that required by regulation and will include data gathering programs necessary to develop a data base for future synthetic fuels projects. As always, we pledge our cooperation and assistance to the EPA and the other federal and state agencies wherever possible and we look forward to sharing the non-proprietary portions of our operating data so that sound substantiable regulations may be developed.

On behalf of the partners of the Great Plains Gasification Associates, I appreciate the opportunity to speak before you today and wish to extend an invitation to each of you to come to Beulah, North Dakota in 1984 and visit the first operating commercial-sized synthetic fuels plant in the United States.

Thank you.

Session II: ENVIRONMENTAL ASSESSMENT; DIRECT LIQUEFACTION

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Preliminary Results of the
Fort Lewis SRC-II Source Test

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Introduction

The SRC pilot plant was designed to convert coal into a low sulfur and ash product in either solid or liquid form. The process that yields the solid product is called SRC-I, while the liquid product mode is referred to as SRC-II. This paper deals with the SRC-II operation.

The primary objective of this study is to evaluate environmental implications of the SRC-II technology on the basis of data obtained from the Fort Lewis SRC-II pilot plant. Efforts were made to sample and analyze non-site-specific streams that could be scalable to a full-size commercial plant. Although the characteristics of some of the streams collected may differ somewhat from their commercial counterparts, they may provide general qualitative information on pollutants expected from a commercial facility. Data obtained from this pilot plant must be carefully evaluated in order to determine their applicability and scalability to a commercial-size facility.

This paper first establishes basic similarities and differences in process and operation between the Fort Lewis SRC-II pilot plant and an expected commercial SRC-II facility. It then discusses an SRC-II sampling and analytical program being conducted by Hittman Associates, Inc. (HAI), and provides the data obtained thus far.

SRC-II Process Description

The SRC-II process involves non-catalytical treatment of coal with hydrogen at an elevated temperature (454°C) and pressure (13.8 MPa). In this process, a dried, pulverized coal is mixed with a process-produced recycle slurry to form a coal slurry. The coal slurry is then mixed with hydrogen and pumped through a preheater to a reactor where coal is dissolved and hydrocracked, liberating gases such as H_2S, H_2O, NH_3, CO_2, and hydrocarbons. The reactor effluent enters a series of pressure let-down vessels where process gases and liquid are separated. The gases are sent to an acid-gas absorber unit for the removal of H_2S and CO_2. The H_2S is further processed into a salable sulfur product. Light hydrocarbons and unconverted excess hydrogen leaving the absorber are cryogenically separated; the hydrogen gas is recycled to the process and the light hydrocarbons are processed into salable product gases. The light liquid stream is fractionated into naphtha and fuel oil. The product slurry is split into two streams. One of the streams is sent to the front end as recycle slurry to be mixed with feed coal, while the other stream passes to vacuum distillation where fuel oil is further recovered. The high-ash and low-sulfur residue (referred to as vacuum bottoms) from the vacuum distillation tower is sent to a gasifier for the production of make-up hydrogen or synthetic gas.

The Fort Lewis SRC-II pilot plant (Figure 1) does not have some of the process features described above. Many of the processes it employs are unique to the pilot plant and therefore would differ from those of an anticipated commercial facility. These differences are given in Table 1. Only if and when these differences are fully understood, can the data obtained be successfully extrapolated to the commercial operation to provide pollutant characterization and control technology information.

Sampling and Analysis Program

Background

HAI, under contract to the U.S. Environmental Protection Agency, began an SRC-II sampling and analysis effort in March 1978. The purpose of this effort was to evaluate the SRC wastewater treatment system and characterize the SRC-II products. Because of the important role of coal liquefaction to our nation's energy self-sufficiency and the environmental implications of this technology, this initial effort soon evolved into a comprehensive environmental assessment program to measure pollutants associated with the SRC-II operation. This program uses the EPA phased sampling and analytical approach to characterize emission and effluent streams from various processes and control units.

The first phase (Level 1) environmental assessment began in February 1979, and is now completed. Environmentally significant streams and their chemical components were identified, screened, and prioritized for more detailed second phase (Level 2) analysis. However, the SRC-II pilot plant underwent major system modifications and since then experienced start-up problems, which delayed the planned phase 2 sampling program. Meanwhile, the original SRC-II operation schedule was altered and the feedstock used (Powhatan No. 5) during the Level 1 sampling period was replaced with Powhatan No. 6. As a result of the process modifications and coal type change, the original Level 2 test plan was revised to include Level 1 and Level 2 sampling to be performed simultaneously to obtain the required sequential data. This combined Level 1/Level 2 sampling and analytical effort began in March 1980. Analyses of these samples are

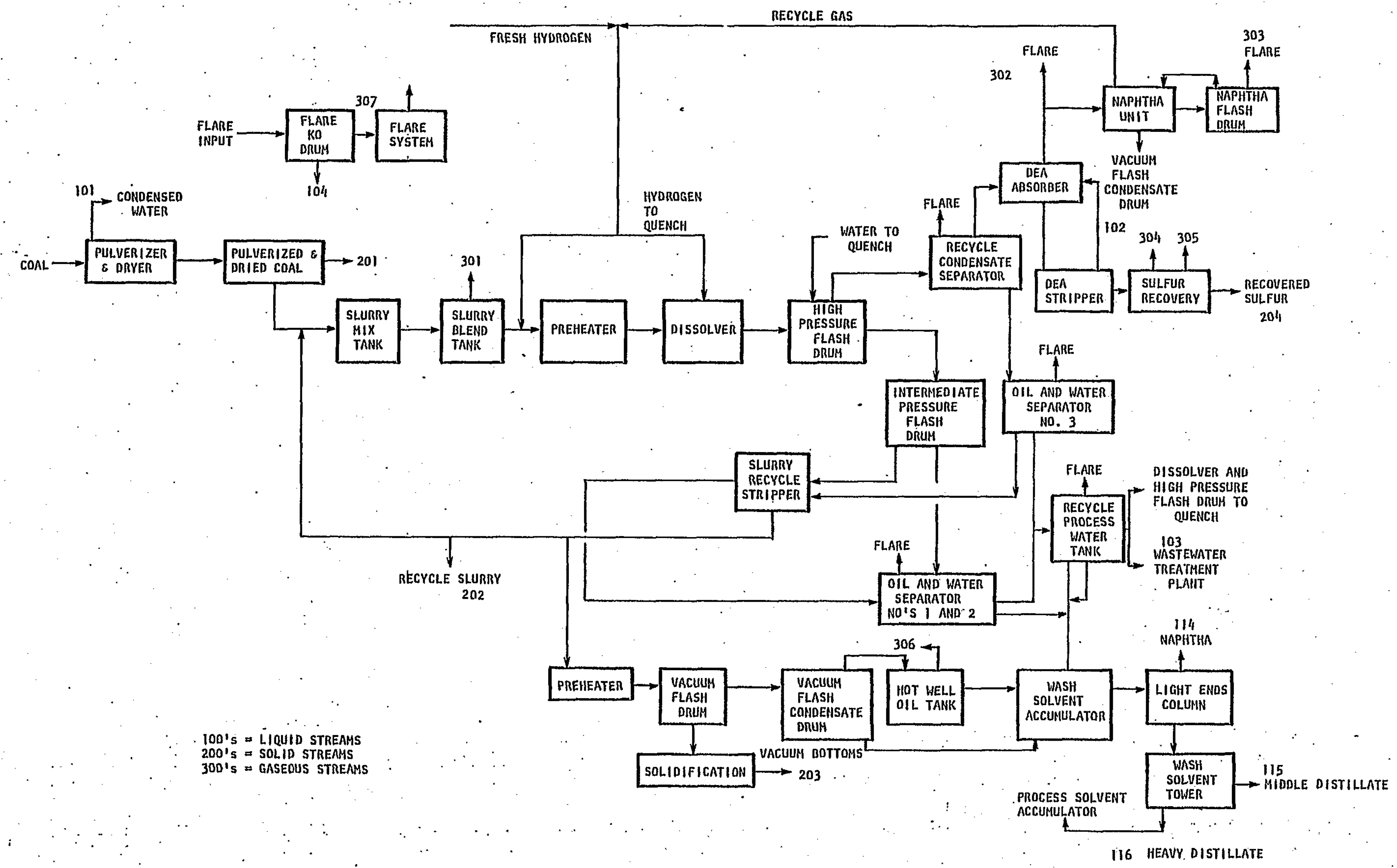


Figure 1. Overall process flow diagram of the Fort Lewis SRC-II pilot plant.

TABLE 1. THE FORT LEWIS SRC-II PILOT PLANT Vs. COMMERCIAL SRC-II FACILITIES

Fort Lewis Facility	Commercial Facility	Affected Stream Characteristics
No gasification of Vacuum Bottoms. Vacuum Bottoms currently stored for outside disposal.	Vacuum Bottoms will be gasified, and resultant slag will be landfilled.	No emissions and waste discharge associated with Vacuum Bottoms solidification. However, in commercial practice slag and quenching water from gasification may pose disposal problem.
A portion of Sour Water is being recycled to provide a quenching stream.	Oil quenching is currently under consideration.	Alteration in process sour water characteristics expected.
Middle and Heavy Distillates produced separately.	Blended to yield fuel oil.	Will not affect overall pollutant balance. However, chemical constituents in the fuel oil may vary depending on the blend ratio.
Sour Water is not treated but diluted with non-process water prior to treatment.	Sour water will be pretreated to recover NH_3, H_2S, and phenols.	The pretreatment of sour water will affect the stream entering the wastewater treatment system. Consequently, different treatment process may have to be considered.
Fuel gases and purged hydrogen are being flared.	Fuel gases will be recovered. Cryogenic hydrogen separation obsoletes hydrogen purge.	Flare input stream is not representative of that of commercial facilities.
No hydrotreating of product fuels including Naphtha.	Products may have to be upgraded.	Lower heteroatomic compounds in the hydrotreated products.

still in progress. Preliminary data obtained from selected sampling streams are presented in this paper.

With the exception of analyses which called for non-composite sampling, such as volatile organic analysis, each aqueous or solid stream was sampled three times per day, 8 hours apart, for six sampling days, and was composited to constitute a single representative sample for a given stream. All aqueous samples were preserved according to EPA procedures, by organic extraction, or by refrigeration. Product streams were sampled once a day for six sampling days. In addition, a total of 36 samples were collected from four streams - wastewater treatment plant influent and effluent, and middle and heavy distillates - in order to perform a comprehensive statistical evaluation of process variability, sampling and analytical variability.

Gaseous streams were sampled once or twice per stream during the entire sampling period. Inorganic and organic species were collected in evacuated glass flasks, teflon bags, and Tenax GC and XAD-2 sorbent columns. Impinger bottles were used for species such as ammonia, cyanide, and volatile elements which could be collected and analyzed more effectively by wet-chemical or other methods. Collected volatile species such as H_2S, CO, COS, SO_2, and mercaptans were analyzed immediately using onsite GC columns equipped with species-specific detectors. Tenax GC columns were thermally desorbed and analyzed on a GC/MS system for the volatile species lost during extraction. Higher boiling organic compounds were extracted with methylene chloride in a Soxhlet extraction apparatus and subjected to GC/MS analysis. Table 2 presents the environmental source tests being performed on the collected SRC-II stream samples.

Table 3 shows metals present in dried coal (2 percent moisture) with their distribution among various products/by-products and their recycle process water (process sour water). As expected, most of the non-volatile metals present in the feed coal find their way into the vacuum bottoms. Use of the vacuum bottoms for a commercial gasifier will generate slag material which consists primarily of inorganic elements. Leaching characteristics of this material must be thoroughly investigated for the development of a safe method of disposal. This slag contains high levels of metals such as aluminum, iron, and titanium (see Table 3). The recovery of these elements may provide a potential disposal alternative. High levels of vanadium, sodium, iron, and other elements present in the elemental sulfur do not originate in the feed coal, but rather in the Stretford solution. Currently, the Fort Lewis plant produces unwashed sulfur which is transported for outside disposal. The

TABLE 2. SUMMARY OF TESTS TO BE PERFORMED ON THE SRC SAMPLES

STREAM NO.	STREAM IDENTIFICATION / ANALYSIS	Ammonia	Cyanide	Sulfide	COD	VOA	Metals	RCRA Leachate Analysis	Priority Pollutant Analysis	On-site Gas Analysis	Gas and Vapor Analysis (Organics trapped onto Tenax GC)	Vapor Analysis (Organics trapped onto XAD-2)	Level 1/Level 2 Organic Analysis	Level 1 Bioassay (Total Sample)	Level 2 Bioassay (Fractionated Sample)
101	Condensed water from coal dryer	●	●	●	●	●	●		●				●	●	●
102	Lean DEA Solution	●	●	●	●	●	●		●				●	●	●
103	Recycle Process water	●	●	●	●	●	●		●				●	●	●
104	Flare Knockout Condensate	●	●	●	●	●	●		●				●	●	
105	Solvent Fractionation Area Runoff	●	●	●	●	●	●		●				●	●	●
106	Dissolving and Separation Area Runoff	●	●	●	●	●	●		●				●		
107	Stretford Pad Runoff	●	●	●	●	●	●		●				●		
108	Feed Cooling Water	●	●	●	●	●	●		●				●		
109	Cooling Water	●	●	●	●	●	●		●				●		
110	Wastewater Treatment Plant Influent	●	●	●	●	●	●		●				●	●	●
111	Bio-unit Influent	●	●	●	●	●	●		●				●		
112	Bio-unit Effluent	●	●	●	●	●	●		●				●		
113	Sand Filter Effluent	●	●	●	●	●	●		●				●	●	●
114	Naphtha					●	●						●	●	●
115	Middle Distillate					●	●						●	●	●
116	Heavy Distillate						●						●	●	●
201	Pulverized & Dried Coal						●	●							
202	Recycle Slurry						●								
203	Vacuum Bottoms						●	●							
204	Elemental Sulfur						●	●							
205	Flottazur Skimmings						●	●					●	●	
206	Clarifier Sediment						●	●					●	●	
207	Digester Contents						●						●	●	
301	Slurry Blend Tank Vent						●			●	●	●	●		
302	Purge Hydrogen to Flare						●			●	●	●	●		
303	Light Hycrocarbons from Naptha Flash Drum to Flare						●			●	●	●	●		
304	Off Gas from Stretford Unit						●			●	●	●	●		
305	Stretford Oxidizer Tank Vent						●			●	●	●	●		
306	Hot Well Tank Vent						●			●	●	●	●		
307	Input Stream to Flare System						●			●	●	●	●		

TABLE 3. METALS PRESENT IN FEED COAL, PRODUCT/BY-PRODUCTS, AND PROCESS SOUR WATER

	Feed Coal (Pittsburgh Seam,) Powhatan #6	Vacuum Bottoms	Elemental Sulfur	Heavy Distillate	Middle Distillate	Naphtha	Process Sour Water
Aluminum	1.3%	2.8% (12%)**	1.4	7.7	<0.4	<0.4	<0.15
Antimony	<15	<15	0.3	<0.3	0.003*	2×10^{-4}*	5×10^{-4}*
Arsenic	11	23	<0.6	0.006*	0.004*	0.006*	0.007*
Barium	44	96	0.12	0.04	0.02	<0.002	0.008
Beryllium	< 0.3	<0.3	<0.006	<0.006	<0.006	<0.006	<0.003
Bismuth	-	-	<1.0	<1.0	1.0	<1.0	<0.5
Boron	-	-	<0.02	0.34	0.1	<0.04	230
Cadmium	2.5	<2.5	<0.05	<0.05	<0.05	<0.05	<0.025
Calcium	0.26%	0.53%	14.5	2.1	0.35	0.18	1.1
Chromium	18	52	0.3	11	0.39	<0.06	<0.03
Cobalt	3.1	7.6	<0.04	<0.04	<0.04	<0.04	<0.02
Copper	12	45	2.0	0.17	<0.03	0.18	0.015
Iron	2.3%	4.9% (21%)**	110	51	0.69	0.44	2.1
Lead	<0.1	<0.1	2.1	<0.16	<0.16	<0.16	<0.08
Magnesium	460	0.1%	0.7	0.35	0.35	0.08	0.08
Manganese	34	74	0.8	0.86	0.04	<0.006	0.03
Mercury	-	-	-	-	-	-	-
Molybdenum	5.8	17	0.8	0.77	<0.08	<0.08	<0.04
Nickel	12	35	0.4	4.1	<0.05	<0.05	<0.025
Phosphorus	310	660	1.2	<0.8	<0.8	<0.8	<0.13
Potassium	0.13	0.27	20	0.9	0.19	<0.02	0.4
Selenium	-	-	-	0.003	0.002	6×10^{-5}	3.4×10^{-4}
Silicon	-	-	2.5	3.7	1.75	2.3	3.4
Silver	-	-	<0.06	<0.06	<0.06	<0.06	<0.03
Sodium	410	730	0.1%	1.1	5.1	0.84	1.0
Strontium	69	150	0.1	0.05	<0.002	<0.002	0.004
Tin	<3	<3	<0.06	<0.06	<0.06	<0.06	<0.03
Titanium	630	0.14% (0.6%)**	0.1	0.35	<0.012	<0.012	<0.006
Tungsten	-	-	-	-	-	-	-
Uranium	-	-	-	-	-	-	-
Vanadium	34	77	34	0.07	<0.02	<0.02	<0.01
Zinc	13	39	4.0	0.1	0.03	0.35	0.03

*Determined by flameless AAS. All other elements were determined by ICP.
**Expected concentrations present in commercial gasifier slag.

Concentrations in μg/g, unless otherwise designated.

levels of metals found in the products are generally related to product volatility. Generally, levels of trace elements present in the heavy distillates are high when compared with either the middle distillate and naphtha. Heavy distillates are least volatile, middle distillates are next, and naphtha is most volatile. Process sour water contains low levels of metals, with the exception of boron. High pH and sulfide appear to be responsible for low metal concentrations in this stream.

Table 4 shows the reductions in various water quality parameters and trace elements from the wastewater treatment system. The wastewater treatment system is depicted in Figure 2. On the average, a 20 to 93 percent reduction in metals was accomplished by the treatment process. The table also shows trace elements found in the clarifier sediment and flottazur skimmings. Trace element analyses on RCRA extracts of these streams are currently being performed. Table 4 reveals that a high level of phosphorus is entering the treatment plant. The high level of phosphorus is attributed primarily to the blowdown from the cooling tower and boiler systems.

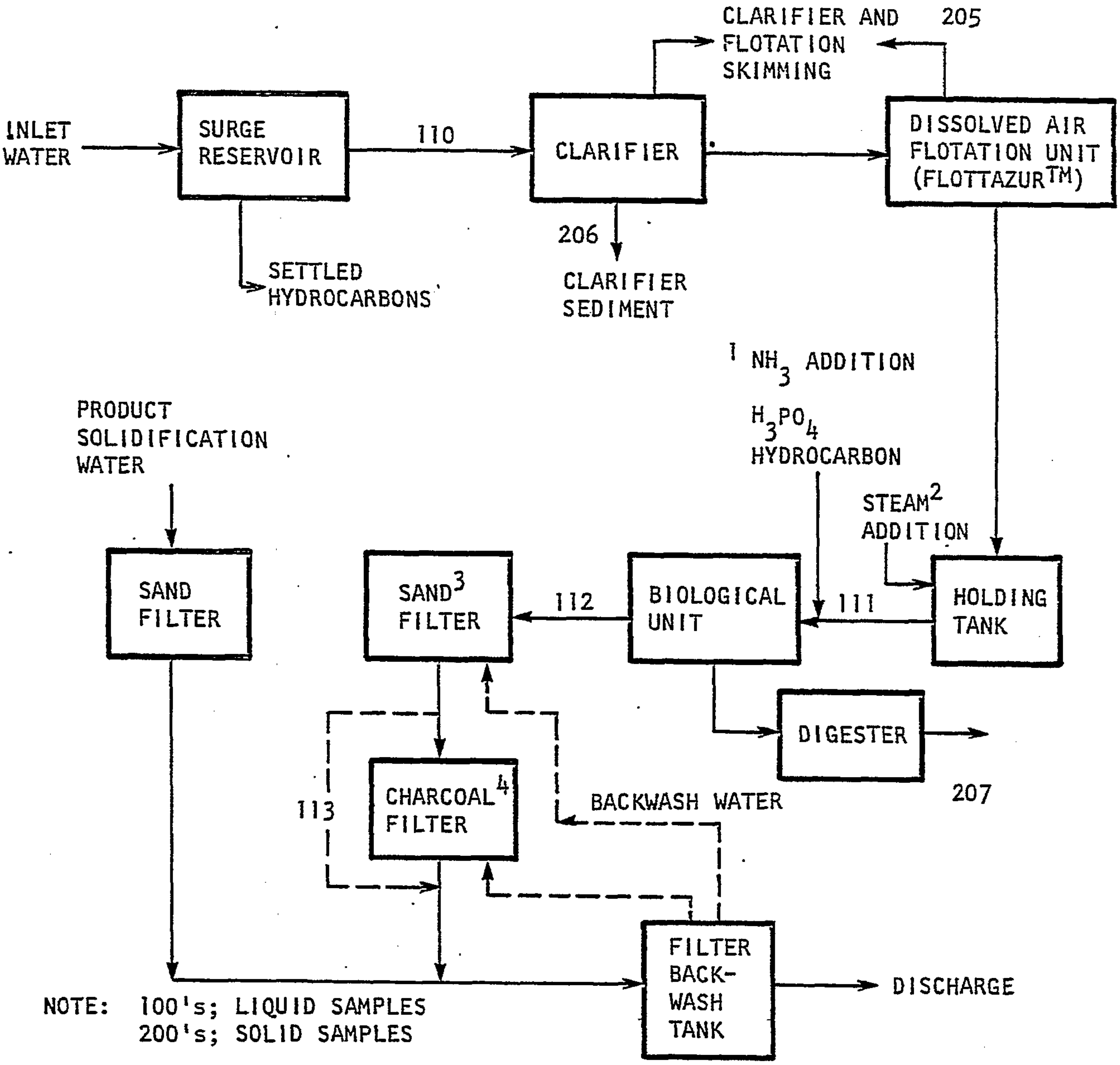
Figure 3 shows the effectiveness of this treatment in reducing organic class compounds. This figure, which was derived from the previous Level 1 data from the SRC-II operation with Powhatan No. 5 coal, indicates that the treatment system appears to be effective in lowering levels of organics such as aliphatic hydrocarbons, benzene and substituted benzenes, and fused polycyclic hydrocarbons. The effectiveness of the treatment system in reducing biological toxicity is shown in Figure 4. This figure was also derived from the previous Level 1 data. Neither the influent nor effluent demonstrated toxicity on the Ames or the rodent tests.

Analytical results of the SRC-II gaseous streams are shown in Table 5. While the slurry blend tank vent, the oxidizer tank vent, and the hotwell tank vent are emission streams discharged directly into the atmosphere, the Stretford offgas stream is sent to the flare system. Although the existing flare system receives emissions from the various pressure relief vessels, major input sources are the purged hydrogen, offgas from the Stretford unit, and light hydrocarbons from the naphtha scrubbing unit. Since fuel gases were not recovered but were being flared at this pilot plant, the characteristics of these flared gases would be quite different from those of a commercial facility. From an operational standpoint, the pilot plant flare unit is very similar to a commercial flare system operating under plant upset conditions.

TABLE 4. CHARACTERISTICS OF WASTE STREAMS FLOWING THROUGH THE WASTEWATER TREATMENT SYSTEM

	Influent	Sand Filter Effluent	Treatment Efficiency (%)	Primary Clarifier Sediment	Flottazur Skimmings
				mg/g dry base	
Ammonia	61	46	25		
Sulfide	5.1	0.4	92		
Cyanide	0.12	0.1	17		
COD	950	300	(68)	1770	1860
Aluminum	22	1.6	93	51	29
Antimony*	0.002	2×10^{-4}	90		
Arsenic*	0.03	0.006	80		
Barium	0.09	0.04	56	0.04	0.02
Boron	1.9	0.6	68	-	-
Calcium	19	15	21	5.7	3.3
Chromium	0.03	<0.03	-	0.12	0.07
Copper	0.2	0.04	80	0.4	0.2
Iron	45	8.5	81	72	44
Magnesium	5.4	4	26	1.1	0.7
Manganese	0.06	0.04	33	0.07	0.04
Nickel	0.025	0.025	-	0.06	0.04
Phosphorus	9.1	0.9	90		
Potassium	4	2.5	38	0.4	0.26
Selenium*	3×10^{-4}	2×10^{-4}	33		
Silicon	23	12	48		
Sodium	140	100	29	4.6	3.1
Strontium	0.11	0.07	36	0.06	0.04
Titanium	0.06	<0.006	>90	0.2	0.12
Vanadium	1.2	0.12	90	2.1	1.2
Zinc	0.9	0.1	89	1.8	1.1

*Determined by flameless AAS. All other elements were analyzed by ICP.



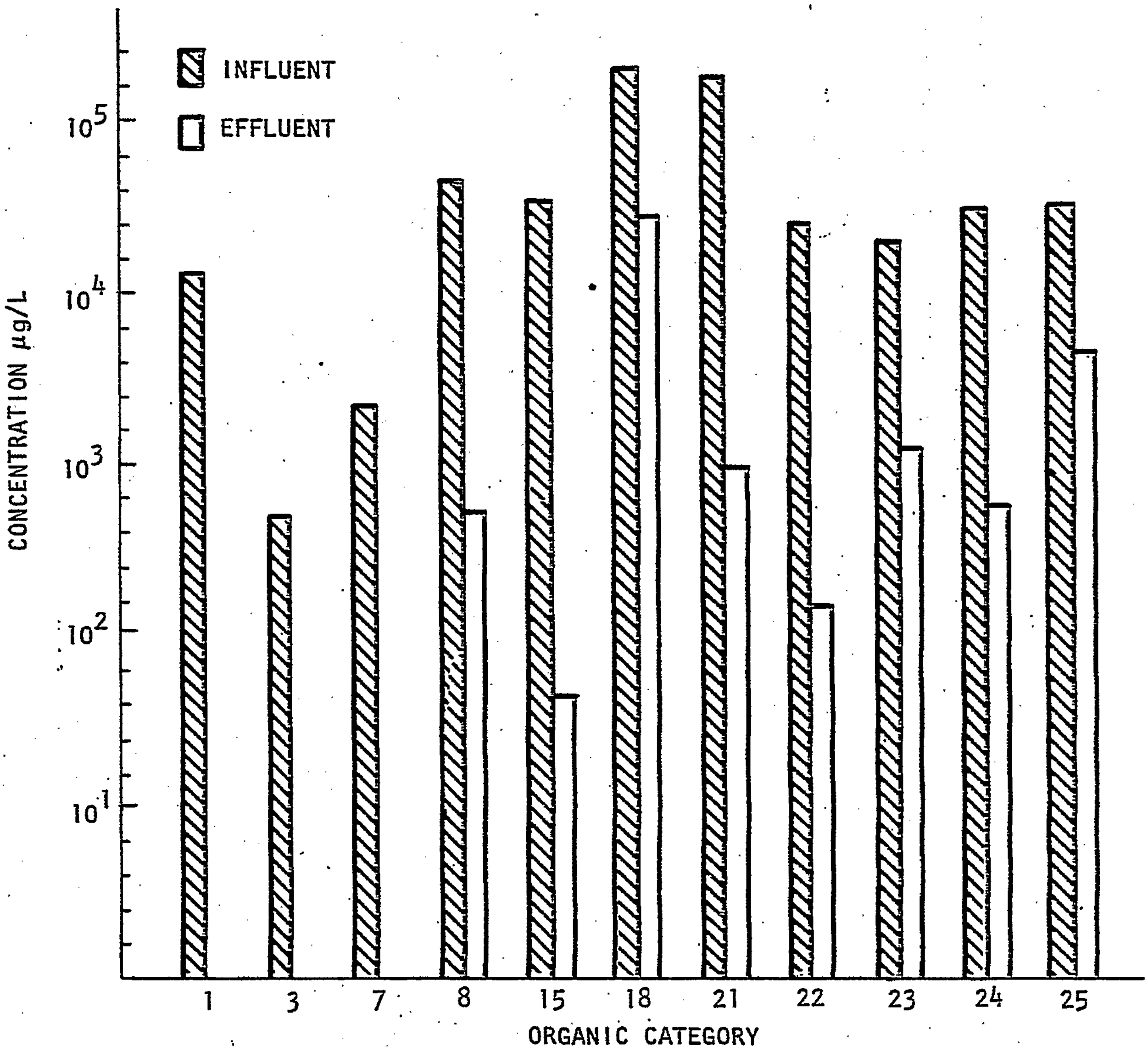
[1] WHEN WASTEWATER IS LOW IN NUTRIENTS DURING THE SRC PROCESS PLANT SHUTDOWN

[2] WHEN THE TEMPERATURE OF WASTEWATER IS LOW FOR NORMAL BACTERIA ACTIVITY

[3] THE SPENT BACKWASH WATER IS ROUTED TO THE SURGE RESERVOIR

[4] CHARCOAL FILTER WAS NOT IN USE DURING THIS SAMPLING

Figure 2. Overall flow schematic of the SRC pilot plant wastewater treatment system showing sampling points.



1 - ALIPHATIC HYDROCARBONS
3 - ETHERS
7 - ALDEHYDES, KETONES
8 - CARBOXYLIC ACIDS AND DERIVATIVES
15 - BENZENE AND SUBSTITUTED BENZENE HYDROCARBONS
18 - PHENOLS
21 - FUSED POLYCYCLIC HYDROCARBONS
22 - FUSED NON-ALTERNANT POLYCYCLIC HYDROCARBONS
23 - HETEROCYCLIC NITROGEN COMPOUNDS
24 - HETEROCYCLIC OXYGEN COMPOUNDS
25 - HETEROCYCLIC SULFUR COMPOUNDS

(Based on the average concentrations of three independently taken grab samples on February 11, 12, and 16, 1979, for the influent, and 2 independent grab samples taken on February 12 and 16, 1979, for the effluent).

Figure 3. Levels of organics present in the treatment plant influent and effluent.

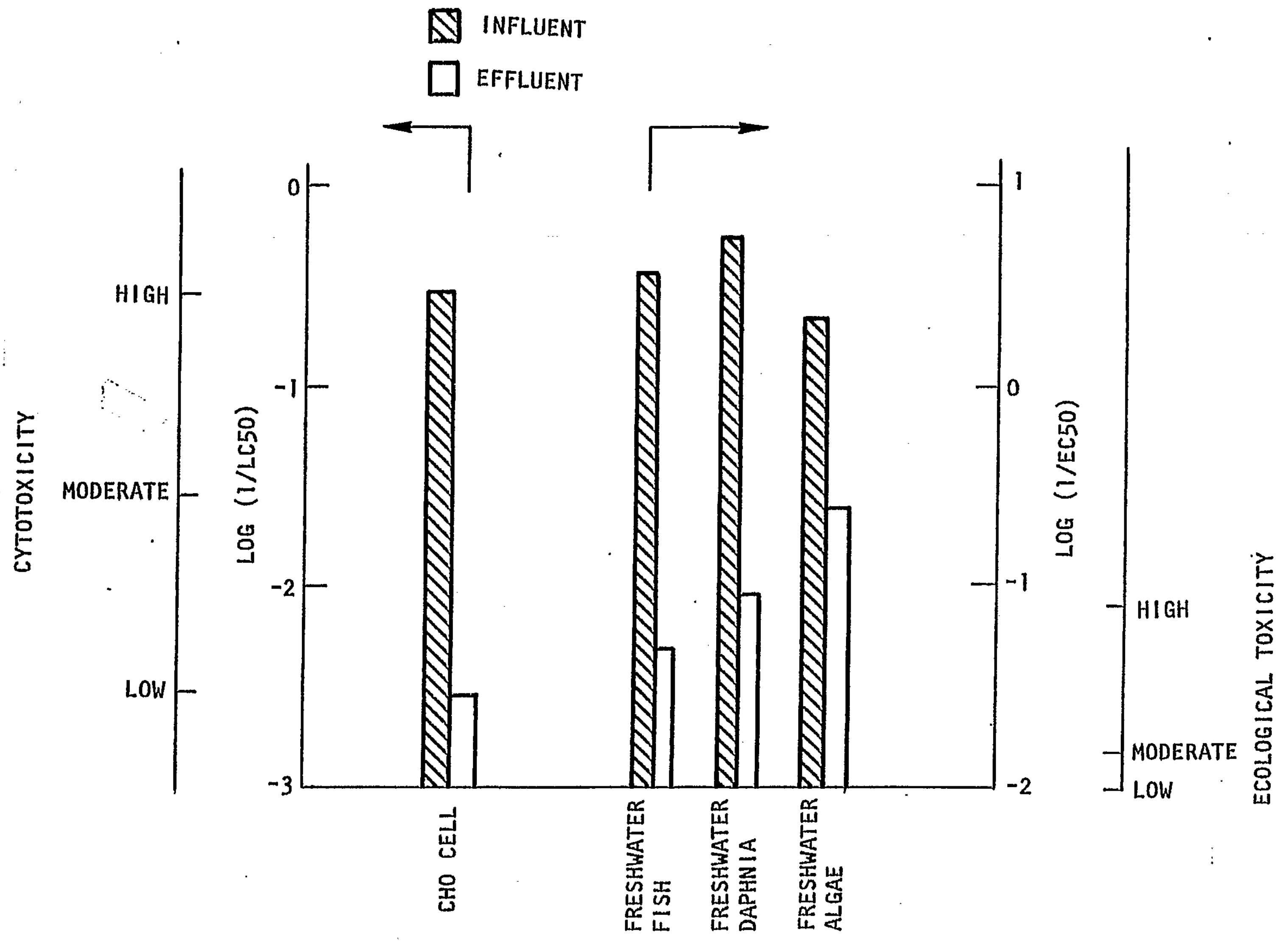


Figure 4. Reduction in biological toxicity by wastewater treatment.

TABLE 5. COMPOSITION OF THE SELECTED SRC-II GASEOUS STREAMS

Parameter	Slurry Blend Tank Vent (2-Day Average)	Stretford Offgas	Oxidizer Tank Vent	Hotwell Tank Vent	Input to Flare
C_1's	360	1.4×10^4	ND	2	1.8×10^4
C_2's	280	6,200	ND	290	2.9×10^4
C_3's	230	5,000	ND	50	3.6×10^4
C_4's	280	1,300	ND	50	1.3×10^4
C_5's	1,400	ND	ND	29	5,000
C_6's	1,400	ND	ND	12	3,000
H_2S	1,020	5,900	ND	ND	4.2×10^4
COS	3	40	ND	ND	40
Methyl Mercaptan	23	400	ND	ND	40
Ethyl Mercaptan	ND	40	ND	ND	220
Nos. of unidentified Sulfur Species	ND	3	ND	ND	3
CO	ND	2.5×10^4	ND	ND	5×10^4
NH_3	11	120	8	ND	88
HCN	ND	0.1	ND	ND	0.04
Species identified by GC/MS	phenol xylenes (O, M, & P-) Benzenes (C_2, C_3 & C_4-) benzofurans (methyl-) naphthalenes (C_1, C_2 & C_3-) phenanthrene/anthracene pyrene/fluoranthene	xylene benzenes (C_3 & C_4-) naphthalene (C_1, C_2-) tetralin phenanthrene/anthracenes (methyl-) pyrene/fluoranthenes (methyl-)	methyl benzofuran naphthalene (C_1, C_2, & C_3-) fluorenes (C_1 & C_2-) phenanthrene/anthracene (methyl-) pyrene/fluoranthene	benzene (C_3, C_4-) naphthalene (C_1, C_2, & C_3-) tetra/methyl benzofuran methyl teralin/ C_2-benzofuran	cyclopentene cyclohexanes phenols cresols xylenols xylenols benzenes (C_2, C_3 & C_4-) toluene furan xylenes (O, M, & P-) benzofuran naphthalenes (C_1, C_2, C_3, & C_4-) fluorenes (methyl-) phenanthrene/anthracene pyrene/fluoranthene tetralin

The Stretford offgas and the oxidizer tank vent are the Stretford process-related streams. The slurry-blend tank vent was designed to remove various fumes and vapors generated during the slurry/coal mixing. These pollutants are cooled and further condensed by a steam ejector prior to atmospheric release. Because sampling occurred at a point before the steam ejector, the information on pollutant characteristics shown in Table 5 is of limited value. For the hot well tank vent, the sampling probe was not placed in the vent duct, but rather, over the open end of the vent. Furthermore, the vent cycle could not be determined; thus, the concentration data shown in Table 5 provide only comparative quantitative information on the identified pollutant species. Table 5 shows the organic species identified by GC/MS. Compounds present in the streams did not vary greatly. Quantitative information on the identified species is not yet available, but is expected to be in the $\mu g/m^3$ range. It should be noted here that accurate sampling of high molecular weight compounds was difficult because samples could only be taken from existing sampling valves which were connected through a long, unheated sampling line to the main process streams. As a result, many high boiling organic compounds probably condensed out, and therefore, were not collected at the outlet.

For the selected liquid stream samples, volatile organic compounds were identified by GC/MS using the purge and trap technique (Table 6). Although the treatment plant influent contained volatile compounds which were collected from various sources, no detectable amounts of these compounds were present in the effluent. This probably resulted from atmospheric loss in the aeration unit rather than actual biological degradation of these substances.

Table 7 shows several important water quality parameters of the recycle process water. This stream was characterized by extremely high alkalinity with very low hardness and low levels of alkali metals. Actual COD for this stream should be somewhat higher than the value shown in the table. Volatile organic substances, including some phenolic compounds, were believed to be lost by purge gases (mostly H_2S) formed during acidification for sample preservation. The phenol level shown in the table was somewhat higher than expected (normally about 0.7 percent). Since a portion of this stream is recycled to the process, the phenol level at a given time is dependent on the recycle ratio, assuming that all other process conditions are constant.

TABLE 6. VOLATILE ORGANIC COMPOUNDS PRESENT IN THE SELECTED FORT LEWIS SRC-II STREAMS

	Recycle Process Water	Condensed Water From Coal Dryer	Solvent Fractionation Area (Fugitive Effluent)	Wastewater Treatment Plant Effluent	Sand Filter Effluent
Pyrroles	8.6 (4.2-16)		0.005 (0-0.03)	0.02 (0-0.1)	
Furans	0.3 (0-0.8)				
Pyridines	0.21 (0.05-0.3)	0.007 (0-35)		2.1 (0.04-3.7)	
C_4 Hydrocarbons	1.8 (0.4-4.2)		0.05 (0-0.08)	0.08 (0.02-0.2)	None Detected
C_5 Hydrocarbons	0.98 (0.2-1.4)		0.06 (0-0.1)	0.05 (0.02-0.1)	
C_6 Hydrocarbons	1.1 (0.5-2.0)			0.03 (0-0.06)	
Benzene	ND	0.21 (0.04-0.5)	0.21 (0.08-0.4)	0.06 (0-0.1)	
Ethyl Benzene	ND	0.3 (0-0.7)	0.26 (0.07-0.2)	0.06 (0-0.1)	
Toluene	11 (5-17.3)	0.33 (0.1-0.5)	1.3 (0.34-3.7)	0.24 (0.15-0.3)	
Xylene	0.64 (0-1.5)		0.13 (0-0.5)		
Unidentified - CN	8 (4.6-11.3)				
Chloroform				0.01 (0-0.06)	

NOTE: Concentrations in mg/L.
The numbers in parentheses represent the ranges of concentration variation over a 6-day sampling period.

ND = Not Detected

TABLE 7. CHARACTERISTICS OF RECYCLE PROCESS WATER (SIX-DAY AVERAGE)

pH	9.0
Alkalinity (as $CaCO_3$)	97,000 mg/L
Hardness (as $CaCO_3$)	10 mg/L
Ammonia (as N)	36,000 mg/L
Sulfide (as S)	30,000 mg/L
Cyanide (as CN)	1.3 mg/L
Chemical Oxygen Demand (as O_2)	26,000 mg/L
Phenol	7,600 mg/L
Cresols	2,850 mg/L
Xylenols & C_2 phenols	1,250 mg/L
C_3 Phenols	2,200 mg/L

Conclusions

More detailed analytical data and plant process information are still forthcoming. The results discussed herein are preliminary in nature, and require further confirmation and expansion as more data become available.

Most of the metals present in feed coal were almost entirely recovered in the vacuum bottoms. Use of this material for a commercial gasifier will generate slag, consisting almost entirely of inorganic elements. Detailed leaching characteristics must therefore be investigated in order to develop a safe method of disposal. The recycle process water contained mostly ammonia, sulfide, and phenols, and was essentially free of metals, except for boron. The boron level in this stream was over 200 mg/L. Because at levels exceeding 1 mg/L, boron has deleterious effects on the human body and the ecosystem, it may be necessary to remove it, along with ammonia, sulfide, and phenols, from this stream. In the coal drying process at the Fort Lewis pilot plant, moist air from the coal dryer is cooled with a dehumidifier and the condensed water is sent to wastewater treatment. This stream contains a number of pollutants of environmental significance. Although their levels are relatively low, these pollutants may have to be controlled since, in commercial facilities, the moist air resulting from coal drying is expected to be discharged as vapor into the air.

Due to several process upsets, the wastewater treatment samples may not fully reflect normal operating conditions.

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CHEMICAL/BIOLOGICAL CHARACTERIZATION OF SRC-II PRODUCT AND BY-PRODUCTS

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ABSTRACT

Biological and chemical tests in concert with engineering analyses of plant operations have been used to provide data for the assessment of health and environmental effects of a mature coal liquefaction industry. In this report, we describe the methodology whereby biological testing is used to guide the chemist in the analysis of fractions of selected pilot plant materials. The principal components of an unmodified distillate blend from the SRC-II process are two-and three-ringed aromatic and heteroatomic species. Phenolic and polynuclear aromatic components are generally present at higher levels than expected in petroleum crudes. Biotesting, with the Ames test as the primary first tier method, revealed mutagenic activity. Chemical fractionation in conjunction with Ames testing implicates the primary aromatic amines as the compound class of primary concern. Chemical biotesting of a hydrotreated distillate blend showed a significant reduction of the primary aromatic amines as well as polynuclear aromatic hydrocarbons. Hydrotreating also can result in the reduction of sulfur- and oxygen-containing compounds, e.g., thiophenes and phenols.

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CHEMICAL/BIOLOGICAL CHARACTERIZATION OF SRC-II PRODUCT AND BY-PRODUCTS

Dependency of the United States upon foreign oil has led to the rapid implementation of programs oriented toward the development of new energy technologies. Simultaneously with the development of these synfuel processes, it is necessary to perform studies which will determine the potential health and environmental effects associated with the given technology. The purpose of this paper is to discuss the method and approaches used at the Pacific Northwest Laboratory in providing chemical and biological data dealing with SRC (Solvent Refined Coal) materials. The approach we have taken is designed to provide meaningful health effects data to the technology developers within the time frame which permits technology changes to be made optimally to ameliorate potential problem areas.

In evaluating the health effects associated with a coal conversion industry, it is essential that the chemist and biologist coordinate their research efforts toward a common goal. The usual scenario, however, results in the biologist asking the chemist to give him the compounds or materials with which he should be performing his assays. The chemist, on the other hand, asks the biologist which compounds are biologically active in order to orient his analyses toward these selected materials. The end result is usually one of utter frustration and mutual distrust leading to the confirmation as far as the chemist is concerned that the biologist doesn't really know what he is doing. The biologist, of course, already knew that about the chemist.

The problem is that the chemist is oriented toward the precise measurement of specific elements or compounds. Given a defined compound, a chemist, in many cases, can measure to femtogram levels. However, in the early stages of a developing technology such as coal liquefaction, the given compounds of concern have not yet been identified by the chemist nor has the biologist defined those materials which are biologically active. The chemist is thus faced with a horrendous task. He has in front of him what amounts to Beilstein's bucket of compounds and the effects with which the biologist is concerned may involve compounds whose toxicity or biological effects are so potent that miniscule quantities in this milieu of compounds may indeed be important. On the other hand, the engineer, who is concerned about the development of the process, usually doesn't give serious consideration to the problems of controlling his processes at micro levels. Yet, as we'll see in this paper, changes in the process will significantly affect the biological and chemical response of end products present at extremely low concentrations. The evaluation, therefore, of the biological impact of a given process requires effective coordination among the activities of the biologist, the chemist, and the engineer. In this paper, we will describe how this interaction has led to the definition of specific compounds of probable concern within the SRC process. Interaction with engineering personnel has led to the logical investigation of process parameters which may directly impact biological activity in coal liquefaction materials. One of the results of such interaction at Pacific Northwest Laboratory has been the identification of primary aromatic amines as compounds of principal concern. Hydrotreating, as will be seen, leads to a reduction of the biological activity of the SRC materials.

Chemical and biological characterization studies at the Pacific Northwest Laboratory have included GC, GC/MS, LC/MS analyses, specialized separations procedures for providing biological testing materials, microbial mutagenesis, in vitro mammalian cell toxicity and transformation assays, epidermal carcinogenesis (skin painting), acute and subchronic oral toxicity, developmental toxicity, dominant lethal assays, inhalation toxicity, and dosimetry and metabolism studies.

The approach to the study of SRC materials proceeds in basically three steps: in the first step, an engineering analysis defines the process and effluent streams in the pilot plant which are expected to be important in the final developed technology or to which there are expected to be high levels of occupational or populace exposure; in the second phase, materials selected in Phase 1 are subjected to biological screening tests and chemical characterization. Biological activity is usually detected using microbial assay systems. On evidence of activity, the material is chemically fractionated and the fractions subjected to bioassay. On the basis of the results of the microbial assay and the chemical characterization studies, materials are then selected for further study using mammalian cell cultures. The combination of results from cellular and microbial systems along with chemical characterization are then used to select materials which will be extensively analyzed by animal assays in the third phase. In this phase, materials are entered into animal systems for study of acute, subchronic, mutagenic and developmental effects. Certain long-term effect studies are also designed. Obviously, at each level of testing, other materials are employed including shale oil, petroleum crudes, other fossil-derived materials and pure known chemical mutagens and carcinogens for comparative purposes.

Material used in the studies described were obtained from the SRC pilot plant at Ft. Lewis, Washington. This pilot plant is operated by the Pittsburg and Midway Coal Mining Company for the Department of Energy. Materials from the pilot plant were selected on the basis of engineering design data for the projected demonstration plants of both the SRC-I and SRC-II processes. The selection of materials was based upon one or all of the following criteria:

a) The material is produced in significant quantity;

b) The material has potential for occupational and/or ecological enviornmental exposure;

c) The material can be obtained in a form which is considered by the best engineering estimates to be representative of demonstration or commercial level plant operations;

d) The material contains components which are already of known biological concern.

Consequently, the following process streams in the SRC pilot plant have been investigated: light oil, wash solvent and process solvent from the SRC-I process; and light, middle and heavy distillates from the SRC-II process. The boiling point ranges and specific gravity ranges for these materials are given in Table 1. The materials in all cases were obtained during equilibrium run conditions when the process was being operated for material balance determination. Given the conditions of pilot plant operations and pilot plant design objectives, these materials are probably not fully representative of materials expected from a commercial or demonstration plant.

However, the materials do provide information that may be of use in evaluating areas of toxocological concern whthin a given proposed process slate of products and effluents.

TABLE 1. Boiling Point Ranges of SRC Materials Used in Biological Experiments

Process	Material	Boiling Range (°F)	Density
SRC-I	Light oil	ambient to 380	0.72
	Wash solvent	380 to 480	0.96
	Process solvent	480 to 850	1.04
SRC-II	Light distillate	134 to 353	0.82
	Middle distillate	366 to 541	0.99
	Heavy distillate	570 to 850	1.10

CHEMICAL AND BIOLOGICAL STUDIES

The Ames mutagenesis assay provides a low cost method for the analysis of large numbers of samples in preliminary screening activities. In our laboratory, tests are carried out by mixing the test material with the Salmonella TA98 strain in the presence of mammalian liver microsomal enzymes (S9). By counting the number of revertants (from dependency on histidine in the media to nondependency on histidine) an index of mutagenicity induction is obtained for various test materials. As seen in Table 2, the heavy distillate and process solvent streams exhibit substantial mutagenic activity whereas the light oil, wash solvent, light distillate and middle distillate show no detectable activity.(1) By comparison, raw shale oil showed limited activity, and a crude petroleum (Prudhoe Bay) does not show activity in the Ames system.

To further define the response from the heavy distillate and process solvent materials, two fractionation procedures were employed: an acid-base scheme and a method based on LH20-Sephadex coupled with HP/LC. These schemes are diagrammed in Figures 1 and 2. While the acid-base sequence produces larger quantities of materials in a short period of time, the LH20-Sephadex method, when coupled with HP/LC, ultimately produces more refined cuts of

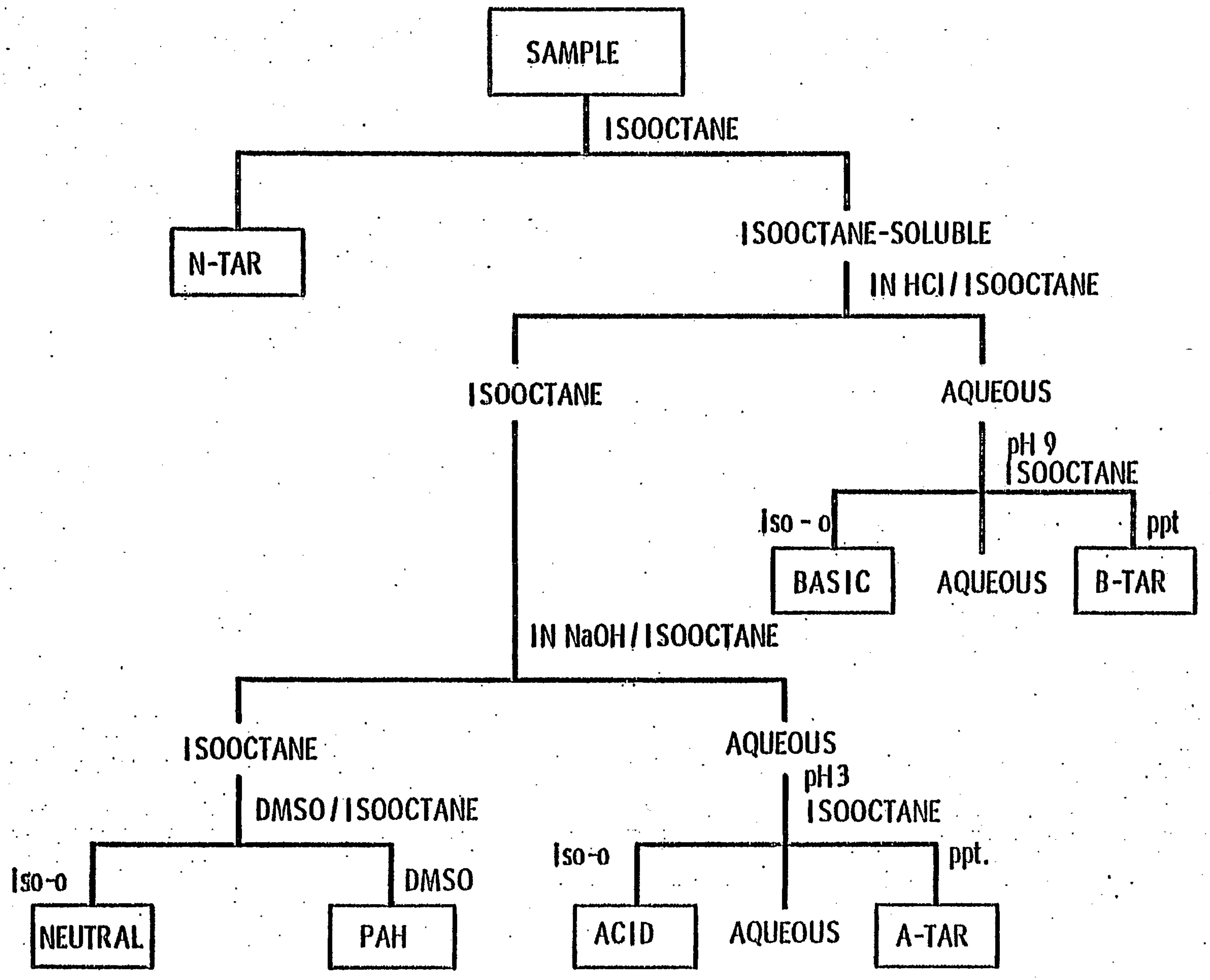

FIGURE 1. Acid-Base Fractionation Scheme

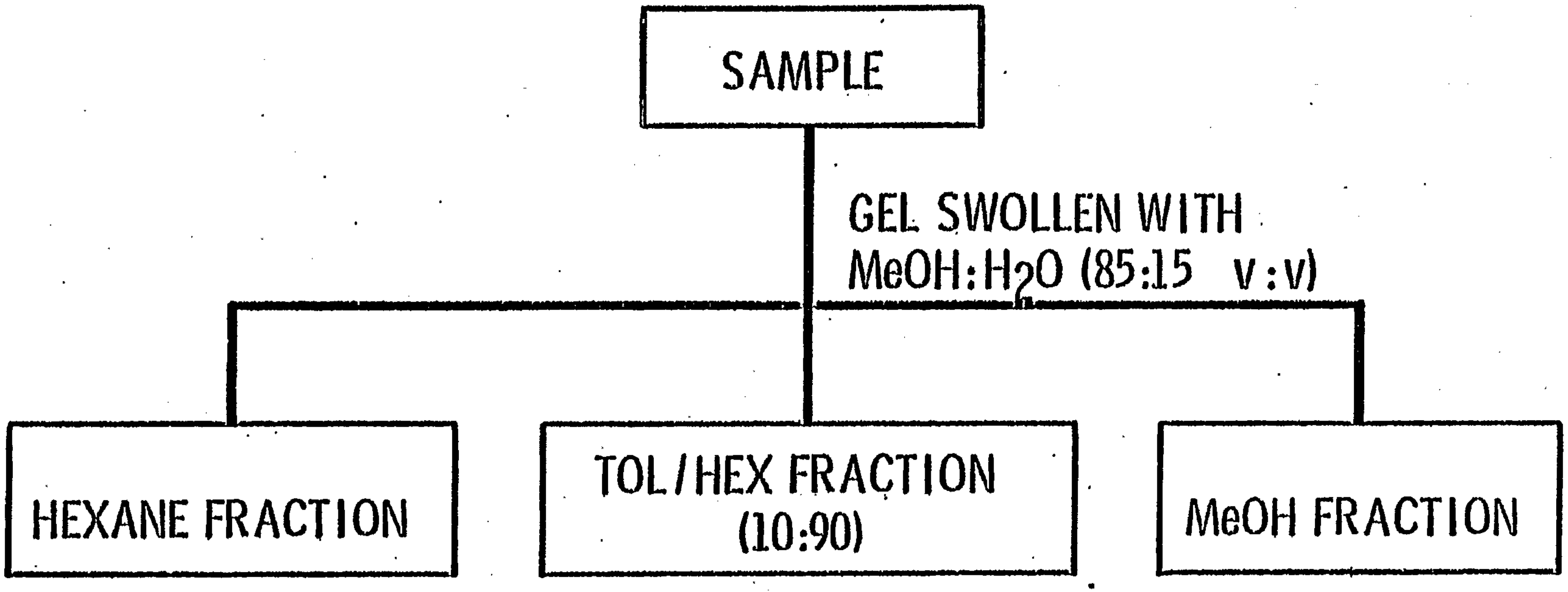

FIGURE 2. Sephadex LH-20 Fractionation Scheme

material with less crossover among fractions. Fractions for biological testing are collected from HP/LC separations made on reverse phase NH_2 columns. Where minimal amounts of materials are required for biological testing, thin-layer chromatography has been effectively used to provide both separation and material for analysis. Acid and neutral fractions derived from HD by using the acid-base separation scheme showed relatively little response to the Ames test whereas the basic, basic tar and neutral tar fractions were mutagenically active.(2) The data for the basic and tar fractions yielded essentially linear dose-response data as seen in Table 3. While the specific activity was about one-half that of the basic fraction, the total mutagenic activity in the basic tar and neutral tar fractions was greater than that in the basic fraction because of the substantially greater mass of the tars. It is interesting that the neutral (non-tar) fraction which contains most of the PNAs exhibited little activity. This is probably due to the large number of compounds in this material which potentially prevent metabolic activation of the PNA components.

TABLE 2.(1) Comparison of the Mutagenicity of Solvent Refined Coal Materials, Shale Oils, and Crude Petroleums in Salmonella Typhimurium TA98

Materials	Revertants/µg of Material
SRC-I	
Process solvent	12.3 ± 1.9
Wash solvent	<0.01
Light oil	<0.01
SRC-II	
Heavy distillate	40.0 ± 23
Middle distillate	<0.01
Light distillate	<0.01
Shale Oil	
Paraho-16	0.60 ± 0.19
Paraho-504	0.59 ± 0.13
Livermore L01	0.65 ± 0.22
Crude Petroleum	
Prudhoe Bay	<0.01
Wilmington	<0.01
Pure Carcinogens	
Benzo(a)pyrene	114 ± 5
2-Aminoanthracene	5430 ± 394

TABLE 3.(2) Mutagenicity of Basic and Tar Fractions from SRC-II Heavy Distillate (HD)

Sample	a	b	ϕ
Basic fraction	198	7	1.00
Basic tar fraction	88	4	0.9
Neutral tar fraction	78	10	0.89

Controls

2-Aminoanthracene	14,000 rev/μg/μℓ DMSO
benzo(a)pyrene	406 rev/5 μg/5 μℓ DMSO
DMSO only	41 ± 15 rev/5 μℓ

Data for HD is in form $Y = ax + b$ in rev/μg where a is the slope, b is the interrupt, and ϕ is correlation coefficient, x is the amount of material in μg.

Analysis by TLC using a solvent system designed to preferentially separate the polar compounds from less polar constituents is presented in Figure 3 for the heavy distillate (HD) basic fraction. The TLC chromatograms were cut into strips, extracted with hexane/acetone mixtures and the extractant subjected to Ames assay using an S9 enzyme system. The activity associated with each of the separated fractions is shown in the section of Figure 3 designated S9. The chromatographic behavior of the materials shown here corresponds very closely to that expected for polar compounds such as aromatic amines. Similar results were obtained with the basic and neutral tar fractions of heavy distillate. High resolution mass spectrometry and GC/MS studies on the materials also indicated the presence of nitrogen containing compounds and, specifically, aromatic amines including aminonaphthalenes, aminoanthracenes, aminophenanthrene, aminopyrenes and aminochrysenes.

High resolution MS data also allowed a tentative identification based on elemental compositions for aminofluorenes and aminocarbazoles; confirmation of these assignments will require further work with adequate standards.(2) Isomers of the various amines were separable by capillary GC as

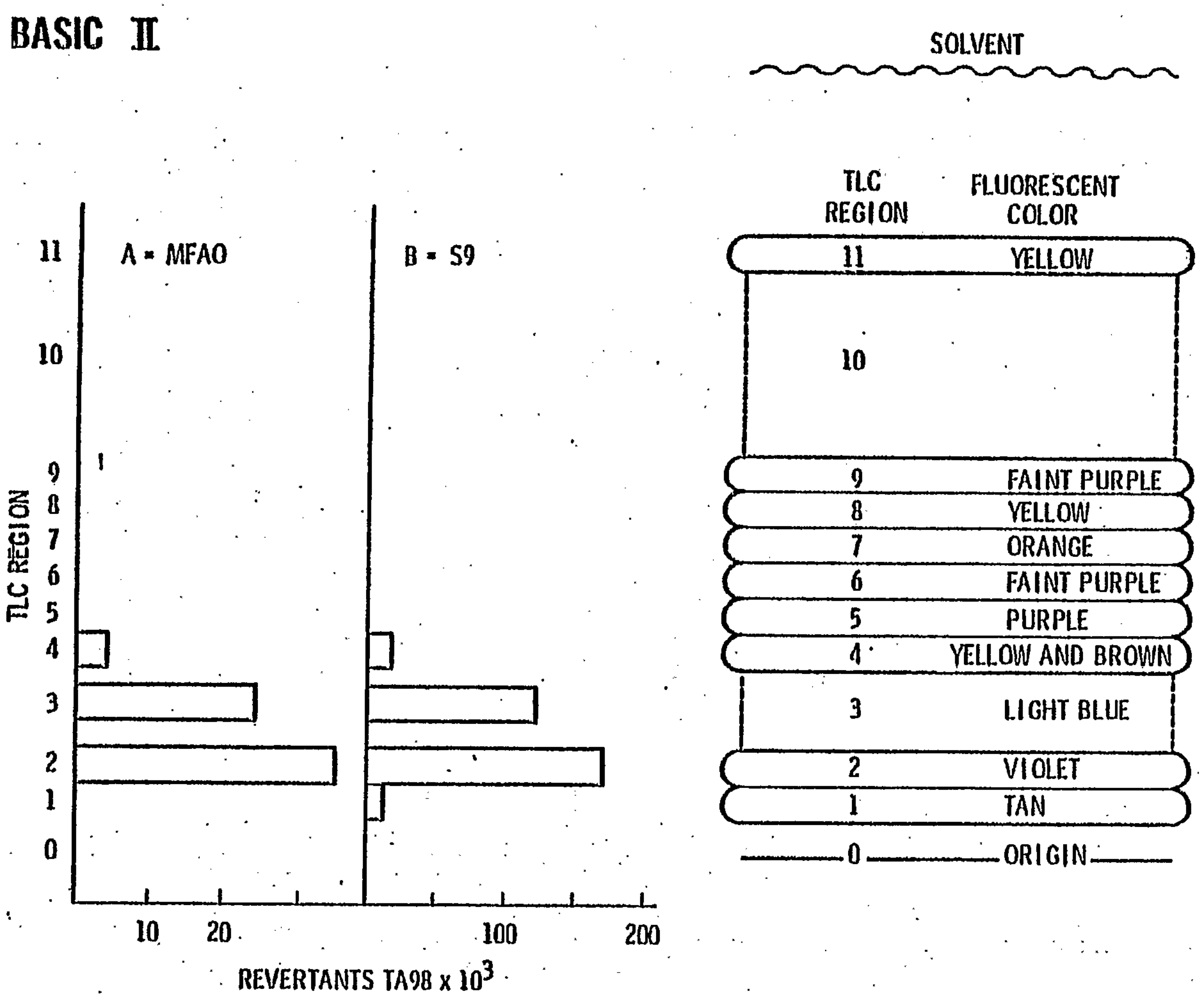

FIGURE 3. Ames Mutagenicity Analysis of Materials Eluted from Thin Layer Chromatogram of the Basic Fraction of SRC-II Heavy Distillate.

shown in Figure 4. Assignments specifically indicated in the figure were made on the basis of retention times of authentic standards.(2)

The correlation of the aromatic amine content with the biologically active regions from TLC of the heavy distillate basic fraction is shown in Figure 5. The relative concentrations of aminoanthracenes, aminophenanthrenes, aminopyrene and aminochrysene are seen to be highest in the regions with the strongest mutagenic activity. With the exception of aminonaphthalene, primary aromatic amines were not found in regions that lacked mutagenic activity. Aminofluorenes and aminocarbazoles have also been tentatively identified in the active regions. Analyses of these materials indicate that three and four ring primary aromatic amines are important mutagens, but that two ring aminonaphthalenes contribute little to mutagenic activity.

Since both GC/MS analyses and Ames results from the TLC fractions implicated the aromatic amines as the mutagenically active agents in the basic, basic tar, and neutral tar fractions of HD, a series of experiments were performed to further support this conclusion. One approach used the unique catalytic properties of mixed-function amine oxidase (MFAO), a purified liver enzyme system. This enzyme is specific for the matabolic transformation of primary aromatic amines to a mutagenically active state but is inactive with BaP and other polycyclic aromatic hydrocarbons. The 2-aminonaphthalenes are also not activated probably due to instability of the enzyme product. Mutagenic activity after activation of the HD basic fraction with S9 appears primarily in TLC regions with rf's of approximately 0.08 to 0.20. When activation was performed using MFAO, the same distribution of mutagenic activity among the TLC regions was found as with S9 as is seen by referring again to Figure 3 and comparing the MFAO with the S9. These results thus provide further evidence that aromatic amines are both present and capable of expressing their mutagenic activity in the basic fraction of HD.(1,3)

The above data were considered as presumptive for the involvement of the primary aromatic amines as causative agents in the mutagenic activity of the basic fraction and of the heavy distillate. Another more direct approach is also available to support this premise. Treating HD and its basic fraction with nitrous acid diazotizes aromatic amines and renders them nonmutagenic

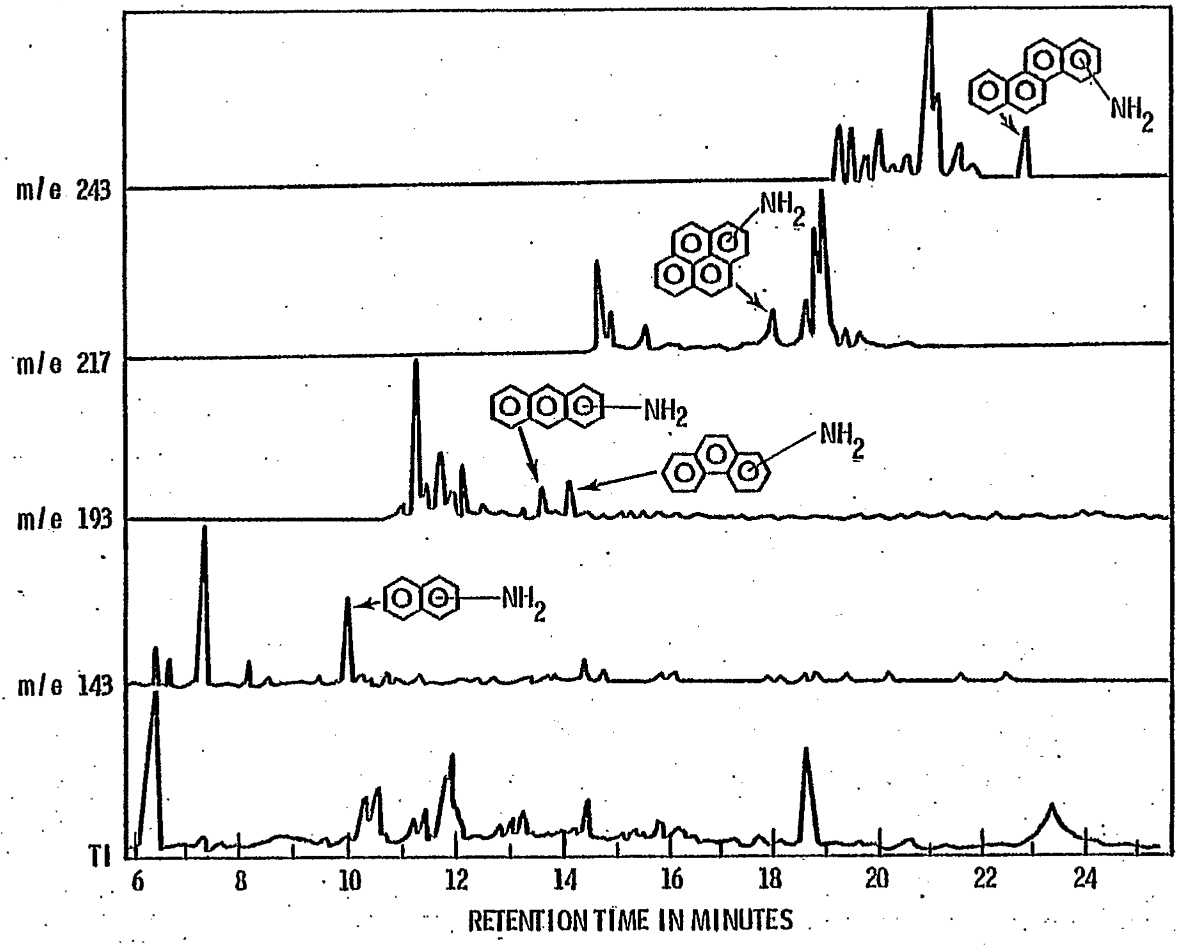

FIGURE 4. Single-ion chromatograms for the m/e 143 (M^+ for AN), the m/e 193 (M^+ for AA and APH), the m/e 217 (M^+ for AP) and m/e 243 (M^+ for AC) shown above the total ion current chromatogram of a mutagenic neutral tar subfraction of HD. Groups of peaks preceding the amino compounds arise from the methyl homologs of the corresponding nitrogen heterocyclic (e.g., methylacridine precedes aminoanthracene).

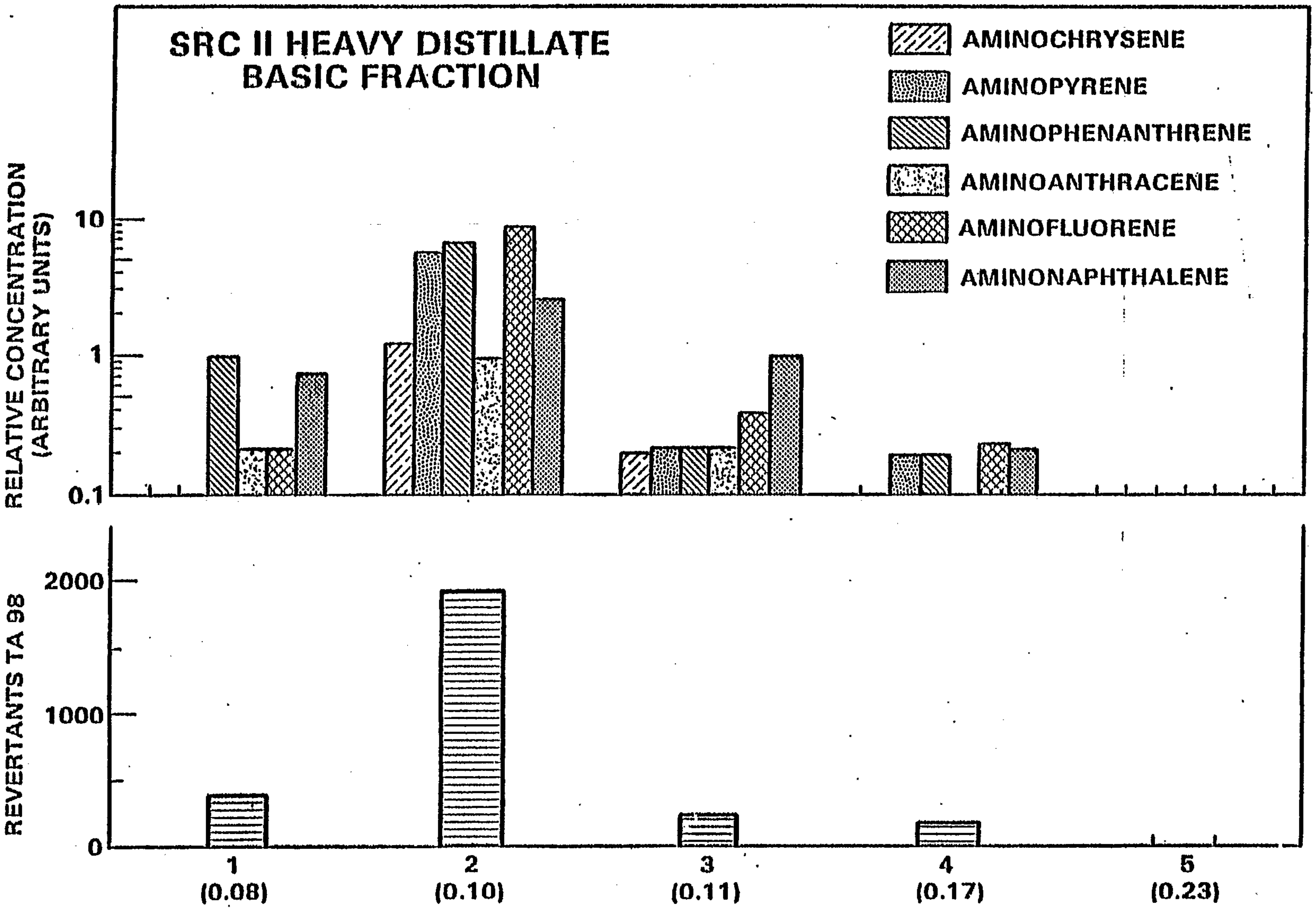

FIGURE 5. Identification and Relative Concentrations of Primary Aromatic Amines in Thin-Layer Chromatography Regions from SRC-II Heavy Distillate Cut, Basic Fraction

in the Ames system. Thus, disappearance of mutagenic activity in the basic fraction or in the heavy distillate after nitrous acid treatment would provide direct evidence for the mutagenic importance of this class of compounds. In Figure 6, it can be seen that the mutagenic activity of a pure aromatic amine 2-aminoanthracene is almost completely lost while the activity of benzo(a)pyrene or benzacridine is not affected by the nitrous acid treatment. Activity seen in heavy distillate, process solvent and their basic fractions is also mostly eliminated by nitrous acid treatment. As shown in Figure 6, activity of these materials after treatment with nitrous acid, is reduced to less than 10% of the original activity. It thus appears that much of the mutagenic activity is probably due to the presence of primary aromatic amines in both the crude material and in the basic fractions.(3)

HYDROTREATING

Since materials from coal liquefaction processes may at some point be used for chemical feedstocks or for further refining, it is possible that hydrotreating processes may eventually be employed in commercial SRC based plants. Hydrotreating, however, may also be expected to significantly impact nitrogen-containing compounds, particularly on deamination of the primary aromatic amines. Carbon-carbon bond cleavage will also occur which will also result in destruction of larger ring systems to form lighter weight alkylated and/or hydrogenated species. Loss of sulfur, nitrogen and oxygen in the form of H_2S, NH_3, and H_2O is also expected in heterocyclic compounds. Materials from the Ft. Lewis pilot plant which had been subjected to hydrotreatment were therefore examined.

While the hydrotreated samples were generated under process conditions which represent current commercial practice, final demonstration scale designs are not yet available. Thus the results of the hydrotreatment processing can be evaluated only in general terms.

Material obtained from tankage accumulated over a series of pilot plant runs extending from October 1978 into the early part of 1979 was subjected to hydrotreating by Universal Oil Products. A middle distillate to heavy distillate blend ratio 2.9 to 1.0 was determined from the average yield ratios of runs during this period. Obviously because of the long-term

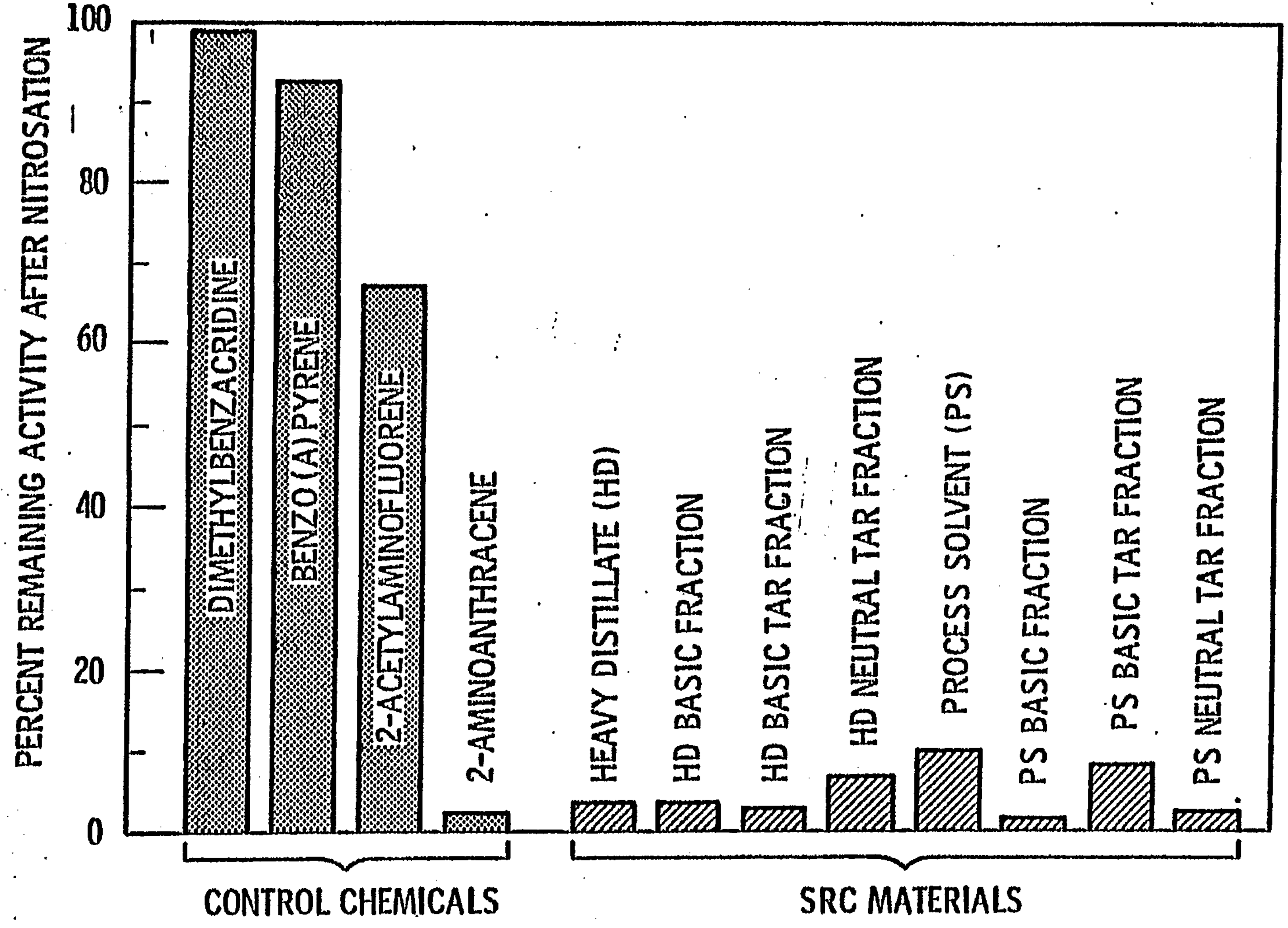

FIGURE 6. Effect of Nitrosation on Mutagenicity of SRC Materials

accumulation period, there are some difficulties in assessing sample representativeness and processing history due to the numerous modes ranging from steady state to upset conditions of operation and to the unavoidable product variability from one run to another. Materials were hydrotreated in standard research fixed bed reactors using a commercial UPO catalyst. Analysis of the materials of the distillate plant before and after hydrotreatment showed dramatic differences in gross chemical composition. GC/MS runs were made with SE2250 or SE52 coated capillary columns. Examples are given in Figure 7. The reconstructed total ion chromatograms of the materials show that there is a dramatic reduction of multiring compounds and phenols with subsequent conversion into hydroaromatic materials, specifically tetralins and their alkylated homologs. Table 4 summarizes the GC and GC/MS data and gives the concentrations in ppm for various compound classes before and after hydrotreatment. Severe hydrotreatment resulted in the reduction of total phenols from 130 ppm to 17 ppm in the total distillate blend. Aromatics and N-heterocyclic compounds show significant reduction. Introduction of hydrogen to the rings is obviously demonstrated by the appearance of compounds such as tetrahydroquinoline, tetrahydrocarbazole and tetrahydrozapyrene, tetralins and other hydrogenated multiring compounds. Primary aromatic amines, initially present at a total concentration of 1.9 ppm, are below the detectable range of GC and GC/MS following hydrogenation under the conditions employed. Figure 8 gives a graphic summary of the results for the compound classes affected.

Biological activity associated with the basic, base-induced tar, acid-induced tar and isooctane-induced tar fractions of the distillate blend followed the trend shown by chemical characterization in loss of the primary aromatic amines (Figure 9). Moderate hydrotreatment, for example, reduced the mutagenic activity of the basic fraction from 16.2 to 2.2 revertants per microgram (Table 5). This is a reduction in the weighted contribution to total mutagenicity from .86 to .03 revertants per microgram feedstock. The tar fractions were reduced in potency to levels below the limits of detection. While the specific effects of hydrotreatment upon chemical composition and biological activity of a given coal-derived fuel product will depend upon reaction conditions, catalysts, and starting material composition, it nonetheless appears that hydrotreatment will, in general, result in products with reduced mutagenic activity. This is probably due to the reduction of

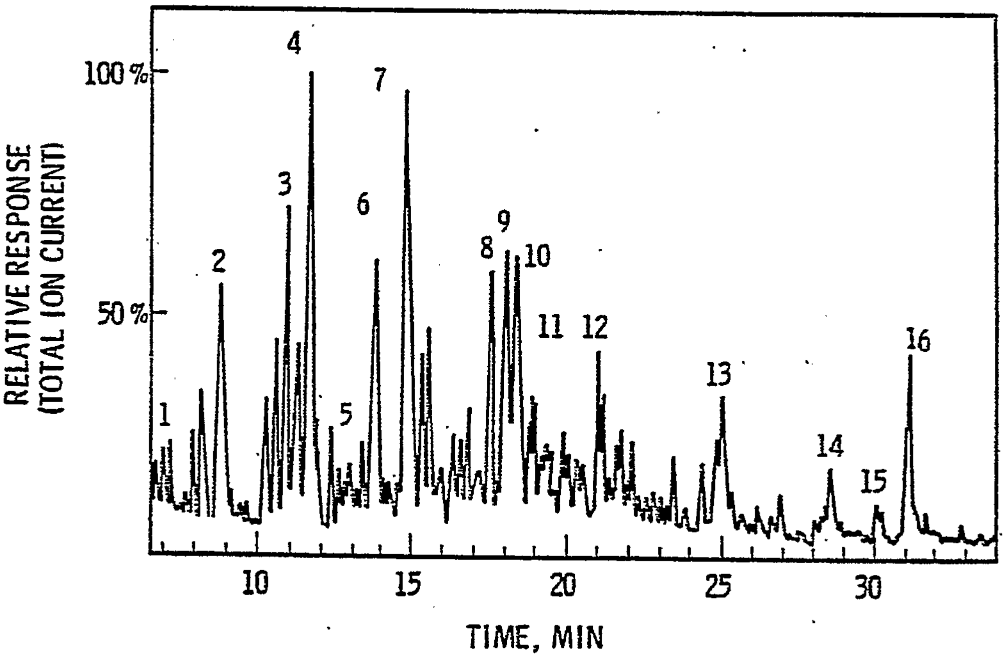

FIGURE 7a. Reconstructed Total Ion Chromatogram of SRC-II Distillate Blend(4)

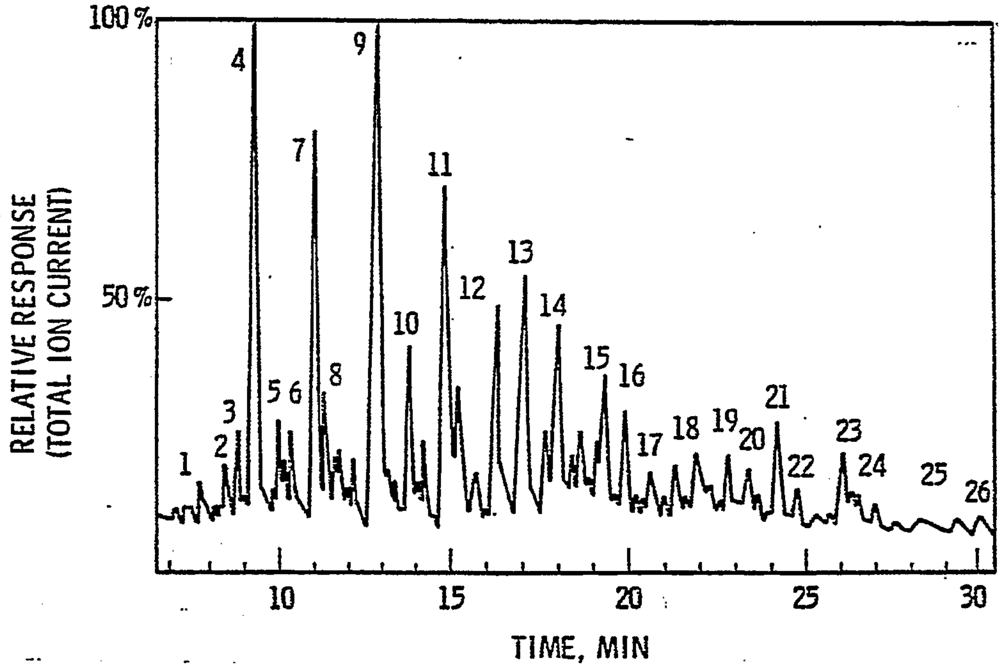

FIGURE 7b. Reconstructed Total Ion Chromatogram of Severely Hydrotreated SRC-II Distillate Blend(4)

(See legend on page 158)

LEGEND TO FIGURE 7

Reconstructed total ion chromatograms comparing unfractionated SRC-II feedstock, Figure 7a, with the severely hydrotreated material, Figure 7b. Principal peaks are identified in both chromatograms: (a) 1: phenol, 2: C_1 phenol, 3: tetralin, 4: naphthalene, 5: indole, 6: C_3 phenol, 7: C_1 naphthalene, 8: biphenyl, 9: C_2 naphthalene, 10: phenylether, 11: dibenzofuran, 12: acenaphthene, 13: fluorene, 14: C_1 fluorene, 15: dibenzothiophene, 16: phenanthrene. (b) 1: methyldecalin, 2: methylindan, 3: methyltetralin, 4: tetralin, 5: dimethylindan, 6: dimethylindan, 7: methyltetralin, 8: dimethylindan, 9: methyltetralin, 10: ethyltetralin + dimethylbenzofuran, 11: ethyltetralin, 12: ethyletralin, 13: biphenyl + hexahydroacenaphthene, 14: phenylether, 15: C_4-indene, 16: C_4-tetralin, 17: C_3-dihydronaphthalene, 18: tetradecahydroanthracene, 19: tetradecahydrophenanthrene, 20: C_3-dihydronaphthalene, 21: C_4-tetralin, 22: C_5-indan or C_4-tetralin, 23: C_5-indan or C_4-tetralin, 24: C_4-dihydronaphthalene, 25: hexadecahydropyrene, 26: octahydroanthracene.

TABLE 4. Alteration in Chemical Composition of SRC-II Distillate Due to Hydrotreatment for Five Compound Classes[(d,e)](4)

Material	Phenols[(a)]		N-heterocycles[(b)]		Primary Aromatic Amines[(b)]		Aromatics and Hydroaromatics[(a)]		Polynuclear Aromatics[(c)]	
Feedstock	$\sum$phenols	130	$\sum$N-heterocycles	20	$\sum$primary aromatic amines	1.9	$\sum$aromatics + hydroaromatics	450	$\sum$polynuclear aromatics	110
	C_1 phenols	41	quinoline	3.6	aminonaphthalenes	0.09	naphthalene	97	$C_{14}H_{10}$	38
	C_2 phenols	35	C_1 quinoline	1.4	aminoanthracene/ aminophenanthrene	0.07	C_1 naphthalenes	82	$C_{16}H_{10}$	9.2
	phenol	27	carbazole	1.3	aminobiphenyls	0.03	C_2 naphthalenes	65	$C_{18}H_{12}$	3.5
	C_3 phenols	16	C_2 quinoline	0.8	aminopyrene/ aminofluoranthene	0.03	tetralin	57	benzo(a)pyrene	0.041
	o-cresol	9	acridine	0.1	aminochrysene	0.02	C_1 tetralin	26	benzo(e)pyrene	0.077
					aminocarbazoles	trace	biphenyl	24		
Moderately Hydrotreated	$\sum$phenols	30	$\sum$N-heterocycles	1.2	$\sum$primary aromatic amines	≤0.005	$\sum$aromatics + hydroaromatics	660	$\sum$polynuclear aromatics	18
	C_1 phenols	5.5	tetrahydroquinoline	0.08			tetralin	71	$C_{14}H_{10}$	2.5
	C_2 phenols	2.6	tetrahydrocarbazole	0.06	none detected	≤0.005	C_2 tetralins	51	$C_{16}H_{10}$	0.8
	phenol	1.6	carbazole	0.04			C_1 tetralins	48	$C_{18}H_{12}$	0.4
	C_3 phenols	1.2	C_1 quinoline	0.03			C_1 naphthalenes	41	benzo(a)pyrene	≤0.010
			tetrahydroazapyrene	0.02					benzo(e)pyrene	≤0.010
Severely Hydrotreated	$\sum$phenols	17	$\sum$N-heterocycles	1.0	$\sum$primary aromatic amines	≤0.005	$\sum$aromatics + hydroaromatics	780	$\sum$polynuclear aromatics	7.5
	C_1 phenols	4.3	tetrahydrocarbazole	0.07	1		C_1 tetralins	120	$C_{14}H_{10}$	1.9
	C_2 phenols	2.1	tetrahydroquinoline	0.05	none detected	≤0.005	C_2 tetralins	41	$C_{16}H_{10}$	0.5
	phenol	1.2	carbazole	trace			tetralin	34	benzo(a)pyrene	≤0.010
	C_3 phenol	0.8	C_1 quinoline	trace			C_3 tetralins	27	benzo(e)pyrene	≤0.005

(a) Estimated directly in the unfractionated material by GC and GCMS.
(b) Estimated in the basic fraction by GCMS. Concentrations given have been calculated for the unfractionated material.
(c) Estimated in the unfractionated material and in the PAH fraction by GC and GCMS. Concentrations given have been calculated for the unfractionated material.
(d) The contributions listed do not total 100% due to the presence of compound classes not listed (e.g., aliphatics) and losses during extraction. Specific compounds listed under each heading are those found in the highest concentrations within that class.
(e) Concentrations are given in parts per thousand.

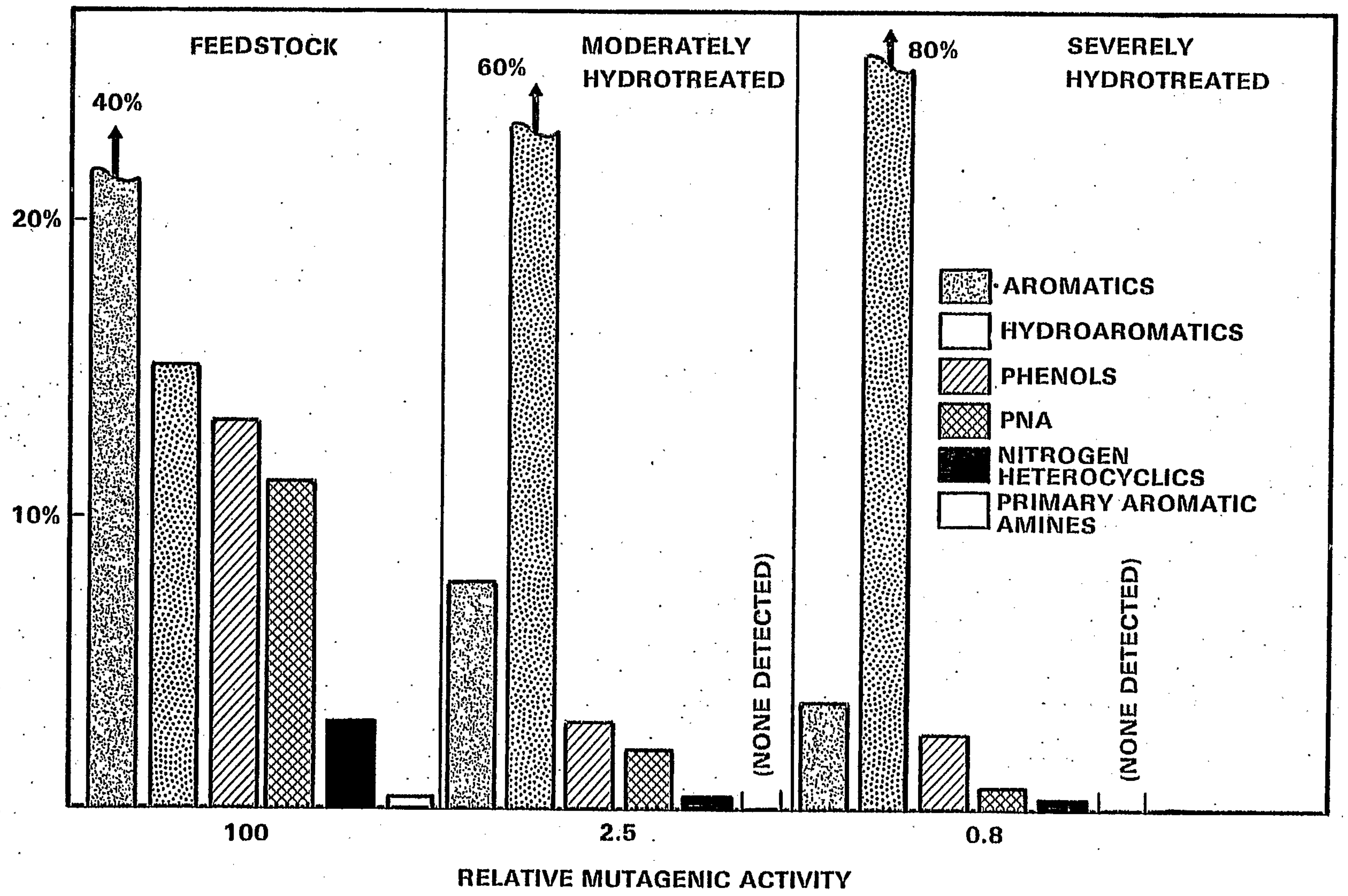

FIGURE 8. Gross Chemical Composition Related to Severity of Hydrotreatment(4)

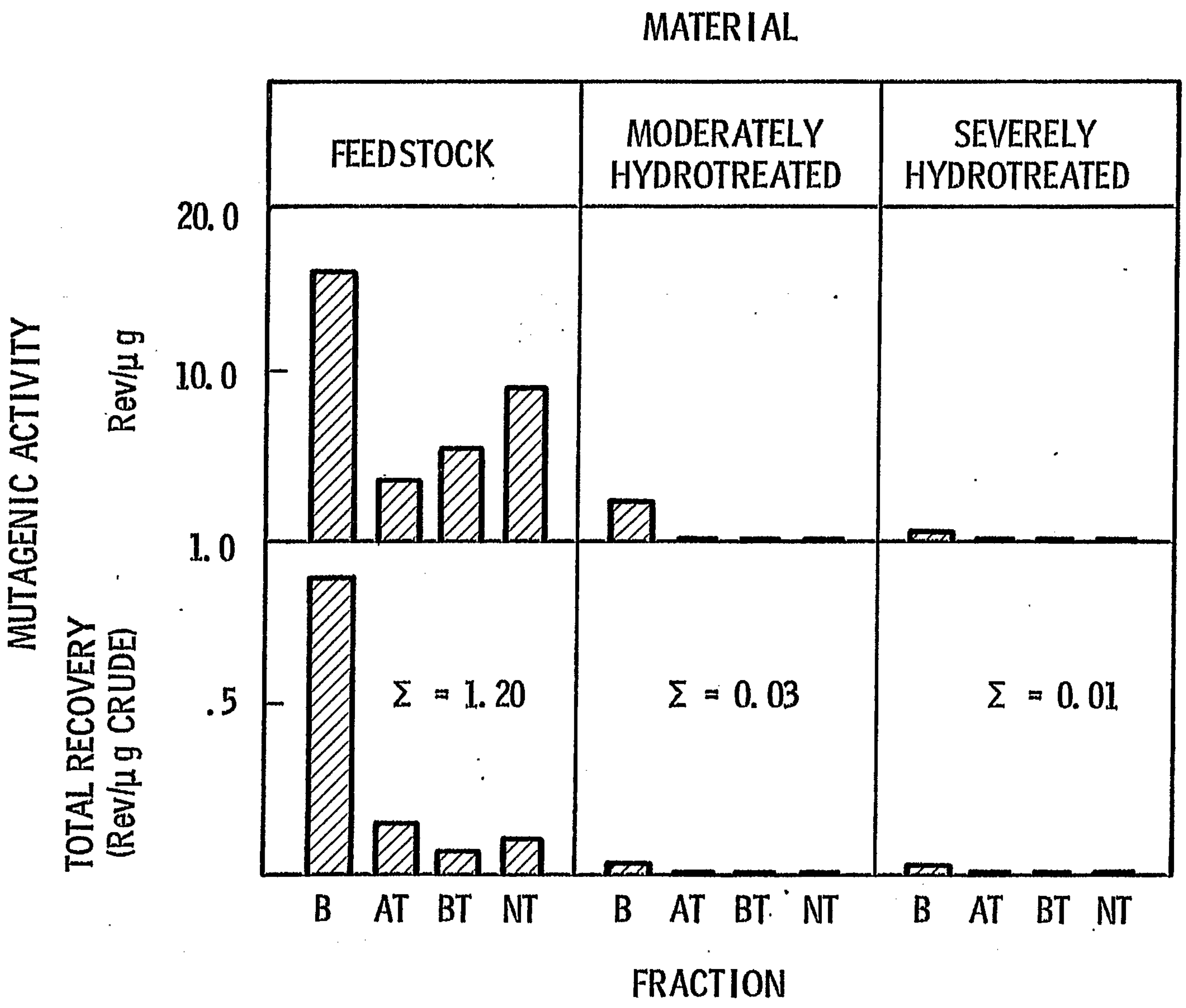

FIGURE 9. Specific and Weighted Activity Test Results for the Basic (B), Base Induced tar (AT) acid induced tar (BT) and isooctane induced tar (NT) from Raw and Hydrotreated SRC-II Distillate Blend. (a) Strain TA98 with S9 enzyme activation. (b) Specific activity weighted by the gravimetric yield of the fraction.[4]

TABLE 5. The Effect of Catalytic Hydrogenation on the Mutagenicity of SRC-II Coal Liquid(4)

Material	Chemical Fraction[(b)]	Percent of Total Wt.	Revertants per μg Fraction[(c)]	Weighted Response, rev/μg[(a)]	Total Weighted Response, rev/μg	Total Revertants Unfractionated Material, rev/μg
Feedstock	Basic	5.37	16.2	0.86	$\sum = 1.20$	2.54
	Acid Induced Tar	5.97	2.7	0.16		
	Base Induced Tar	1.40	5.6	0.08		
	Isooctane Insoluble Tar	1.16	8.9	0.10		
Moderately Hydrotreated	Basic	1.44	2.2	0.03	$\sum = 0.03$	None detected above backbround
	Acid Induced Tar	0.06	0	0		
	Base Induced Tar	0.03	0	0		
	Isooctane Insoluble Tar	0.44	0	0		
Severely Hydrotreated	Basic	0.99	0.79	0.01	$\sum = 0.01$	None detected above background
	Acid Induced Tar	1.31	0	0		
	Base Induced Tar	0.03	0	0		
	Isooctane Insoluble Tar	0.44	0	0		

(a) (Revertants per μg) x (percent total weight)/100.
(b) Other fractions were not active.
(c) Strain TA98 with S9 enzyme activation.

those compound classes in coal liquids which are primarily responsible for induction of mutagenic activity, namely, the nitrogen containing aromatics and especially the primary aromatic amines as well as reduction of the concentrations of polynuclear aromatic hydrocarbons. Other biological assays including mammalian cell culture and skin painting studies are also under way but are not reported in detail here. Generally, there has been relatively good agreement among the assays used. Table 6, a comparison of data from three biological assays, demonstrates this agreement. Differences do show up, however, in the results from 2-aminoanthracene and for heavy distillate. The mutagenic activity of 2-aminoanthracene is very high whereas tumorigenic activity is only moderate. The reverse is true for heavy distillate; tumorigenicity is high whereas mutagenicity is moderate relative to standard control compounds.(3)

Information such as reported here will obviously have some impact upon the development of a liquefaction industry. Samples used were selected with engineering guidance. Criteria included suitability and relevance to future demonstration or commercial design and operation. However, since one can, in practice, only anticipate or scale up to a limited number of the conditions in a final design configuration, caution must be applied in the application of pilot plant derived data. Certainly further data is required. But more important, interaction between chemists, biologists, ecologists and process engineers must be on a continuous basis such that pertinent and meaningful data is prepared within a time frame commensurate with the process development.

TABLE 6. Comparison of Mutagenic and Carcinogenic Activity for Several Crude Fossil-Derived Materials

Material	Ames Assay	Mammalian Cell Culture	Skin Tumorigenesis
Light distillate	---	---	---
Heavy distillate	++	++	++++
Shale oil	+	+	++
Crude petroleum	--	slight	+
Benzo(a)pyrene	++	++	+++
2-Aminoanthracene	++++	+++	++

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