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CONTROL SYSTEMS FOR AIR EMISSIONS FROM COAL GASIFICATION

By: Sid Thomson
Fluor Corporation
Irvine, CA 92730

ABSTRACT

This paper discusses control systems somewhat unique to coal conversion processes. The main subjects covered will be the control of emissions resulting from both the loading of gasification reactors and from the removal of acid gas from the raw process gas. Alternate control systems will be identified and difficulties in establishing Best Available Control Technology (BACT) will be addressed.

GASIFICATION REACTORS

Gasification reactors consist of primarily two types with regard to coal feeding: continuous and intermittent.

With continuous feeding, a coal slurry is usually the feedstock. Coal gasifiers utilizing slurry feeds are fed under pressure, thereby eliminating the need for a coal lock hopper. Air emissions from the gasifier feeding operation are eliminated, since the process occurs in a totally enclosed system.

With intermittent feeding, dry coal is usually the feedstock. This type of feeding requires the use of a coal lock hopper (Figure 1). The various operations required in intermittent dry coal feeding produce emissions that necessitate control to mitigate their environmental impact.

The sequence of the coal lock hopper operation consists of loading, isolating, pressurizing, unloading, isolating, depressurizing, and restarting the cycle. This cycle operates continuously, even though the coal is fed into the gasifier intermittently. To demonstrate this operation and the resultant emissions, assume that Step 1 begins when the coal dump has been completed and the bottom valve has been closed. At this point, the coal lock hopper is filled with reactor gas at reactor pressure. The next step in the cycle is the depressurizing of the coal lock hopper. These gases can be accumulated in a low-pressure vessel from which they may be transferred by compression to the product gas or fuel gas systems (Figure 2). When the vented gas is utilized as fuel gas, it must be treated to remove sulfur compounds before or after combustion due to its high sulfur content.

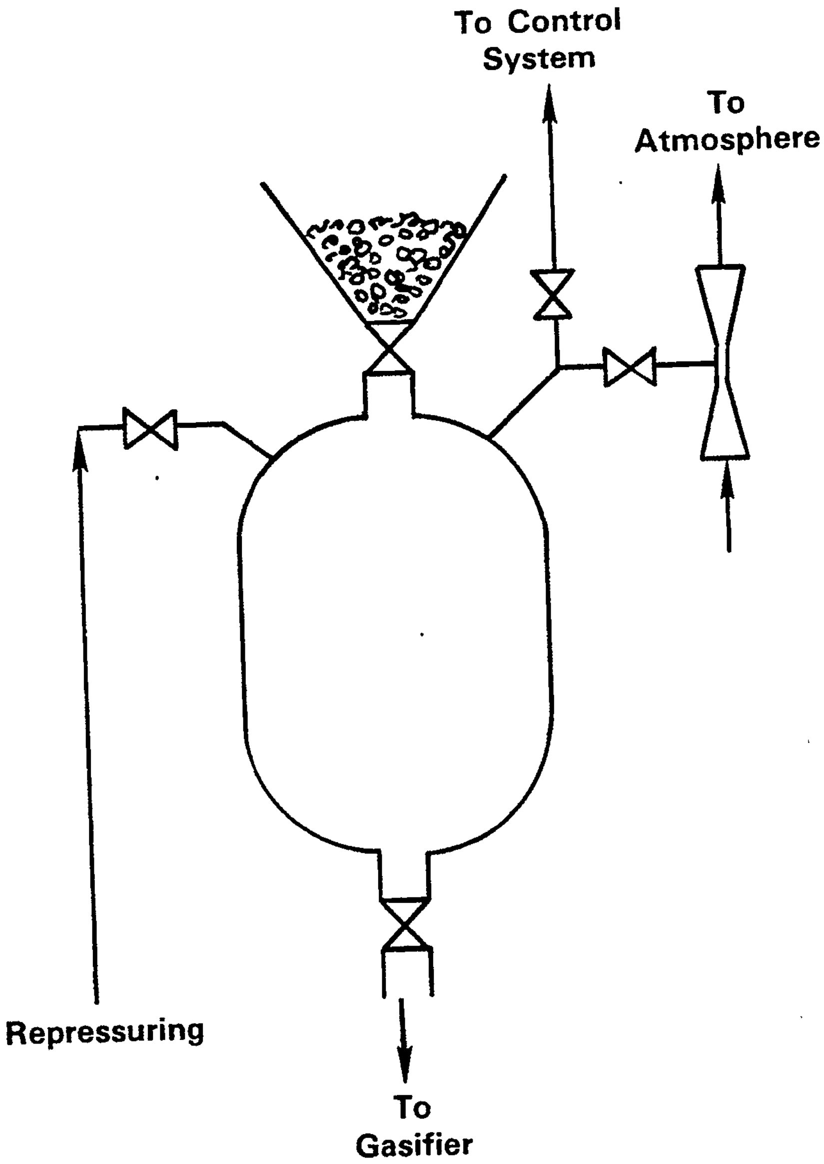

Figure 1. Coal Lock Hopper

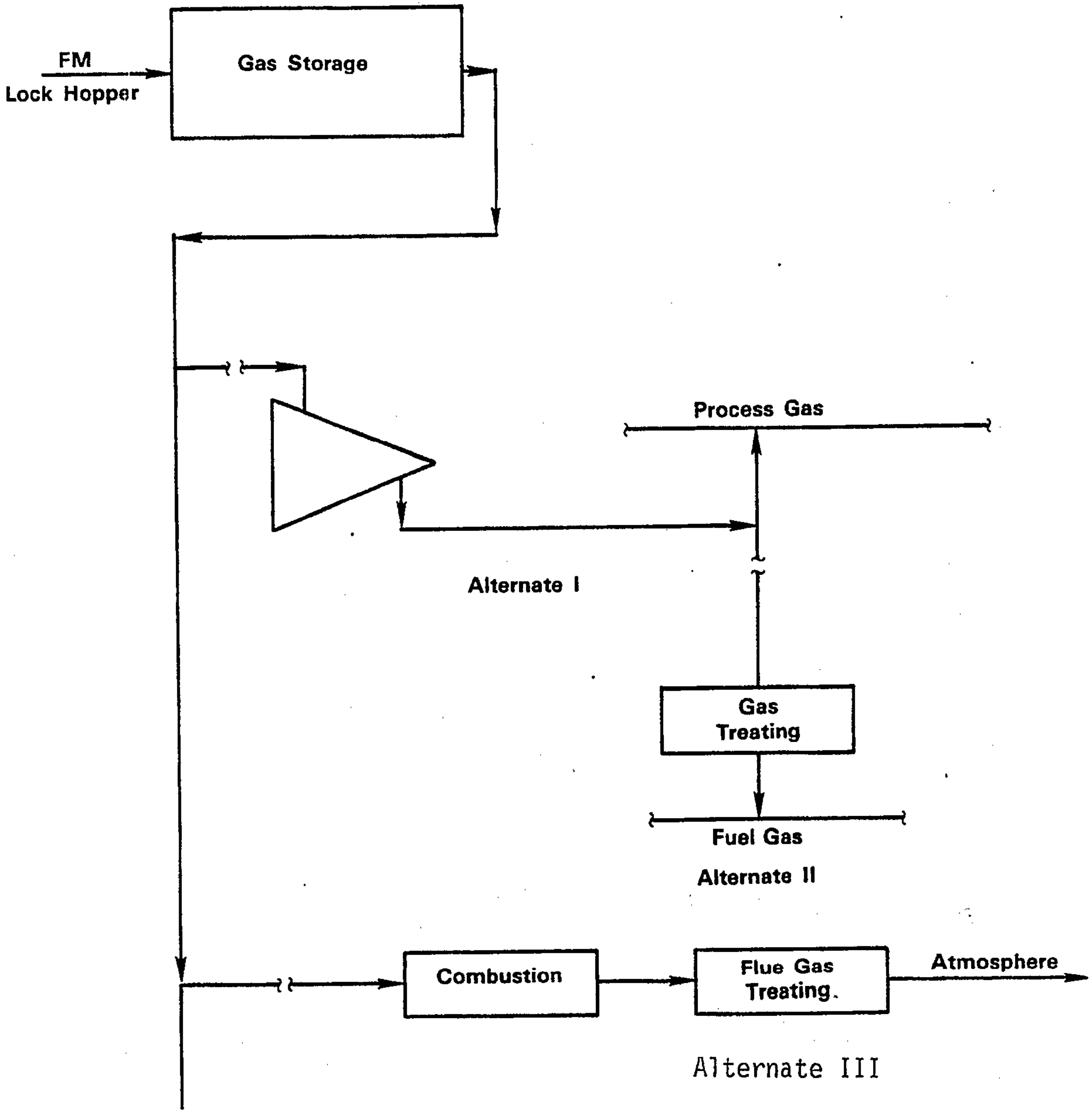

Figure 2. Coal Lock Hopper Vent Gas Treating

An evacuation step is essential since the coal lock hopper can only be depressurized to slightly above atmospheric pressure. This step depletes the amount of gas remaining in the coal lock hopper and ensures that gas does not flow from the hopper when the upper coal feed valve is opened. Evacuation is continued throughout the coal loading operation to ensure that no explosive mixture occurs as the coal is introduced.

Three methods of air emission control have been proposed for handling the evacuated material. The first, and most popular, method is direct venting of the gas through an evacuation jet, since this stream would contain very little total contaminants. A second method is routing the discharge of the evacuation jet through a scrubber for removal of the contaminants (Figure 3). A loss of evacuation jet motive force can cause an explosive mixture to occur in the system, thereby creating an explosion hazard. Care must be take to prevent the risk of creating this hazard when evacuating gas from the coal lock hopper. The protection against this hazard creates expenditures which are difficult to justify due to the small amount of contaminants prevented from entering the atmosphere. The third method is pressurizing the coal lock hopper with inert gas and maintaining the pressure in the hopper above reactor pressure during the reactor coal feed cycle. This method necessitates an extensive system to compress the gas and introduce it into the coal lock hopper as required. Additional raw gas feed processing is needed to remove the recycled inert gas required to guarantee that reactor gas does not diffuse into the coal lock hopper.

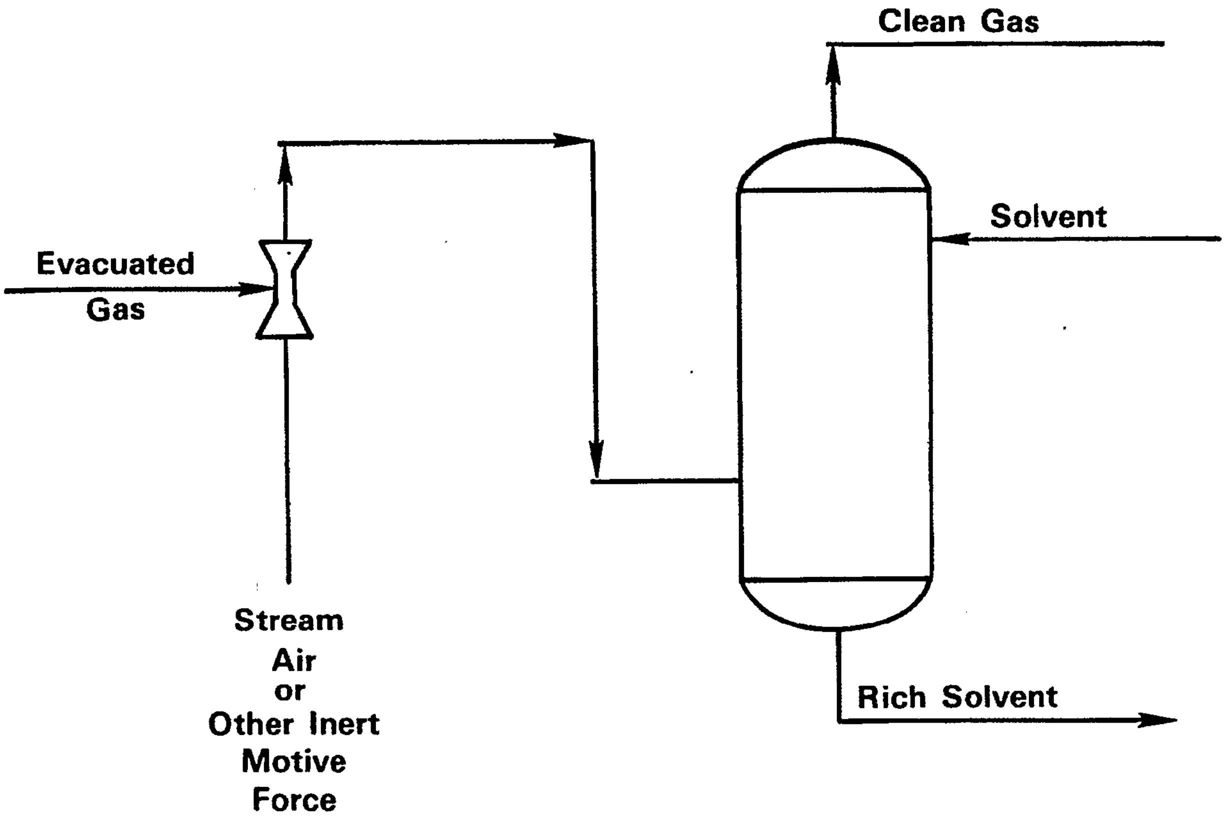

Figure 3. Treatment of Evacuated Gas

Table 1 compares the differences in emissions between the control system utilizing raw gas pressurizing and the control system utilizing inert gas pressurizing.

TABLE 1. EMISSIONS FROM COAL LOCK HOPPER

PRESSURIZING MEDIUM	RAW GAS		INERT GAS(1)
COAL TYPE:	NO. 6 ILLINOIS		NOT STATED
PLANT SIZE:	270 BILLION BTU/DAY		250 BILLION BTU/DAY
CONTROL SYSTEM:	UNCONTROLLED	98% RECOVERY	RECOVERY 400 PSIG→250 PSIG
EMISSIONS: (T/D)			
SULFUR	1,930	35	25
C_2 + HYDROCARBONS	3,160	70	4,000(2)
METHANE	21,160	429	

(1) EPA 450/2-78-012 Guideline Series.
(2) Listed as hydrocarbons.

RAW GAS TREATING

Competitive gas treating processes for H_2S and CO_2 removal from the raw gas stream are shown in Table 2.

TABLE 2. ACID GAS REMOVAL PROCESSES

Physical Absorption Processes	Solvent Used
• Rectisol	Methanol
• Purisol	N-methyl-2-pyrrolidone
• Selexol	Dimethyl ether of polyethylene glycol
• Fluor Solvent	Propylene Carbonate
• Estasolvan	Tri-n-butyl phosphate
Chemical Absorption Processes	**Solvent Used**
• MEA	Monoethanolamine
• Fluor Econamine	Diglycolamine
• Benfield	Potassium Carbonate Solution

The three processes receiving the most attention in the treating of raw gas from coal gasification are Rectisol, Purisol, and Selexol (Figure 4). Rectisol has the advantage in that it uses a methanol solvent which is

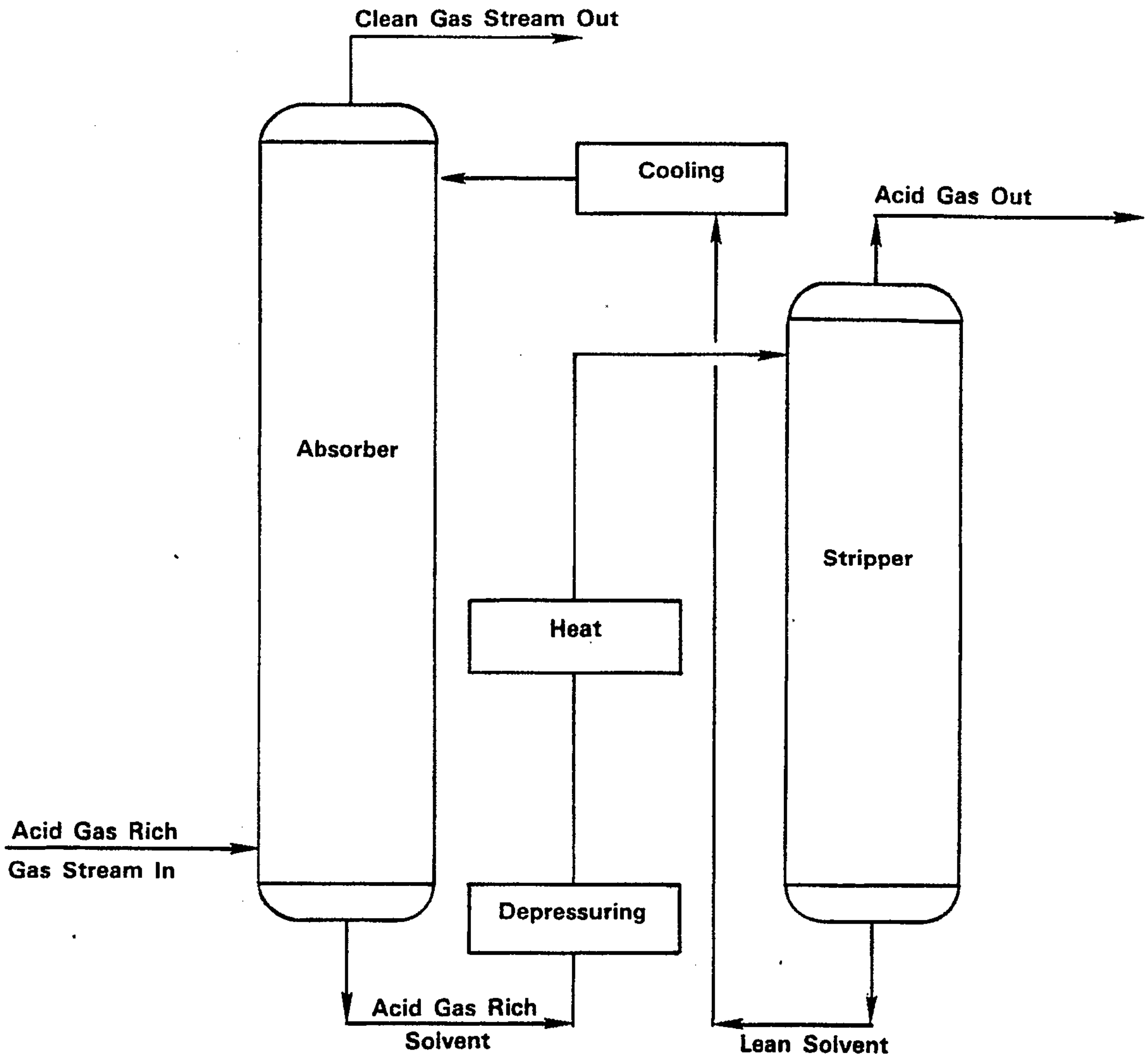

Figure 4. Typical Gas Treating Process

manufactured in plants that produce synthol liquids and methanol. Results of research continuously being conducted improve the performance of existing processes and are used to derive new processes for the removal of acid gas. This research work may change the favorability of the processes.

These acid gas removal processes can be operated in two modes: selective and nonselective. In the selective mode, the acid gas is removed in two streams. One stream of CO_2 is highly concentrated with H_2S and the second stream contains small amounts of H_2S in the CO_2. The selective operating mode is accomplished by the use of either two absorption steps and two stripping steps or in one absorption step with two stripping steps. Unfortunately, at different operating conditions, none of the solvents removes all of the H_2S without a large amount of the CO_2 also being removed. For this reason, numerous processing operations must be considered for removal of sulfur compounds to prevent their escape to the atmosphere. Figures 5 through 14 demonstrate ten methods of removing sulfur compounds from the acid gas streams based on selective and nonselective modes of operation for the Rectisol Process. By utilizing the Selexol and Purisol Processes, 20 additional processing operations can be drawn and by shifting the processes into different positions, a number of other operations can be devised.

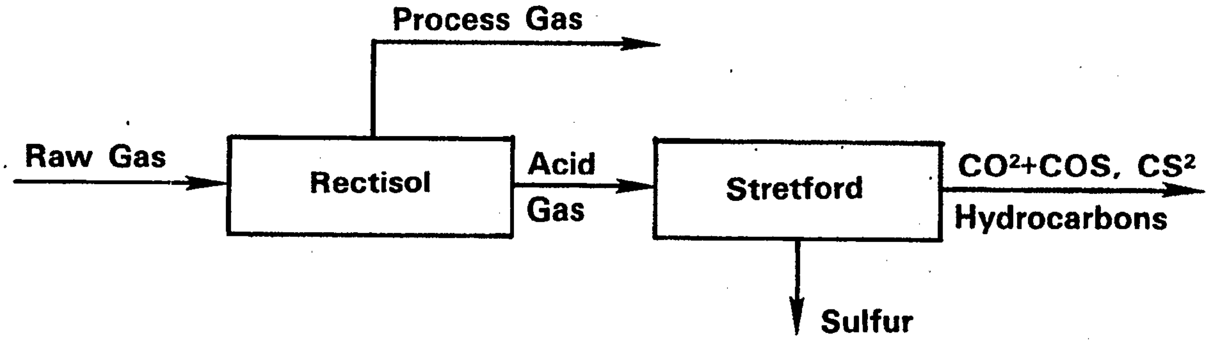

Figure 5. Raw Gas Treating Alternate I

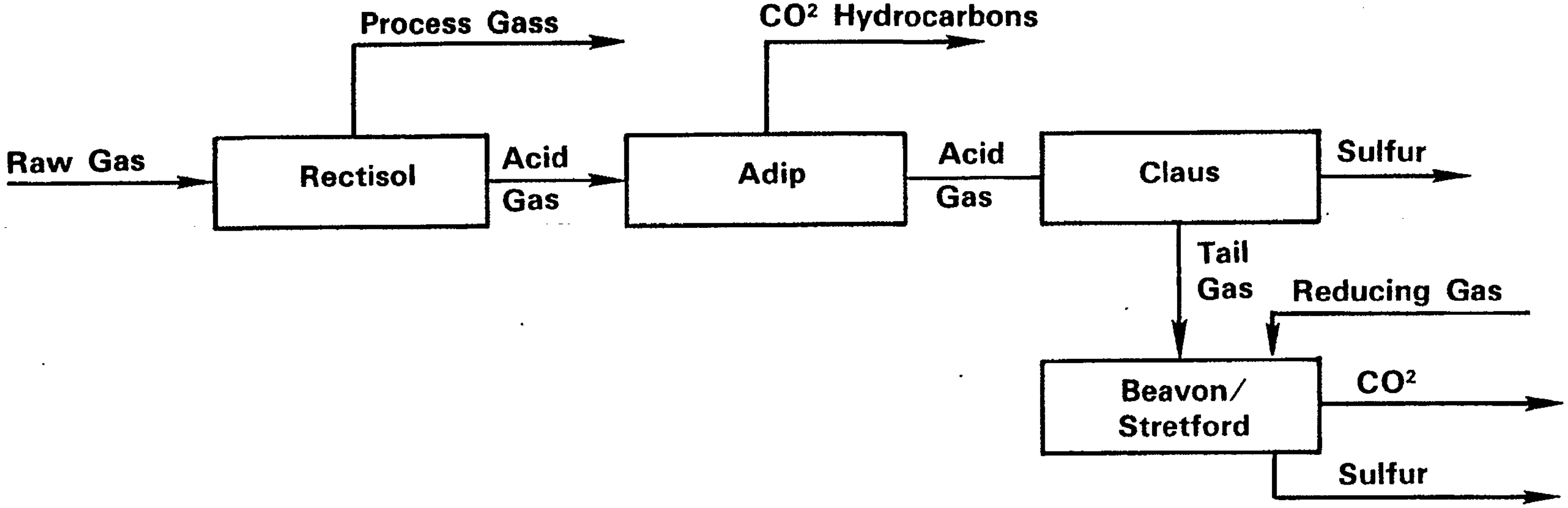

Figure 6. Raw Gas Treating Alternate II

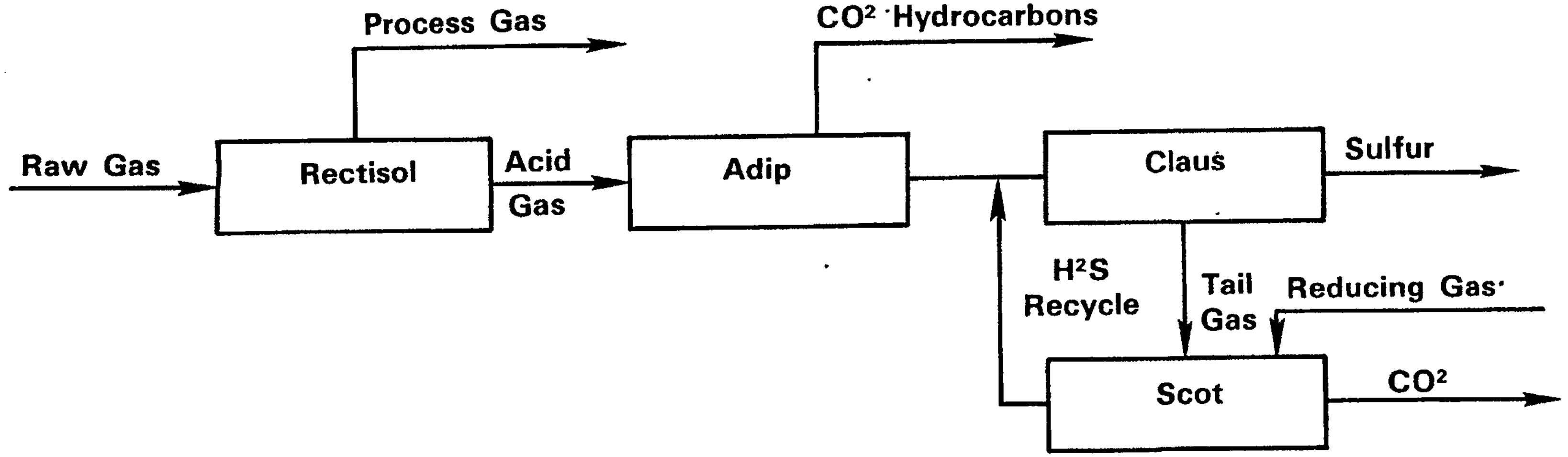

Figure 7. Raw Gas Treating Alternate III

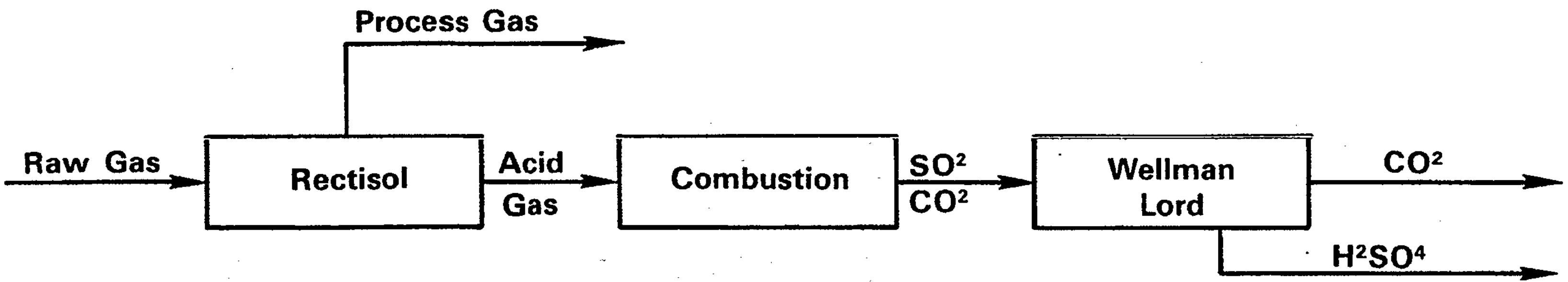

Figure 8. Raw Gas Treating Alternate IV

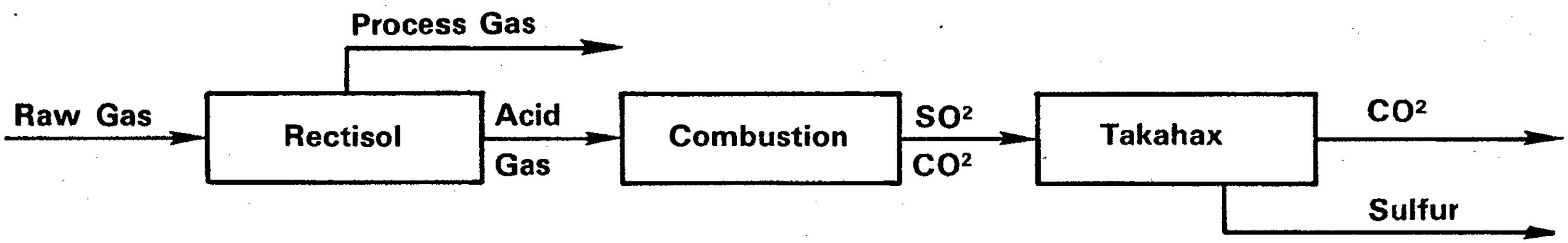

Figure 9. Raw Gas Treating Alternate V

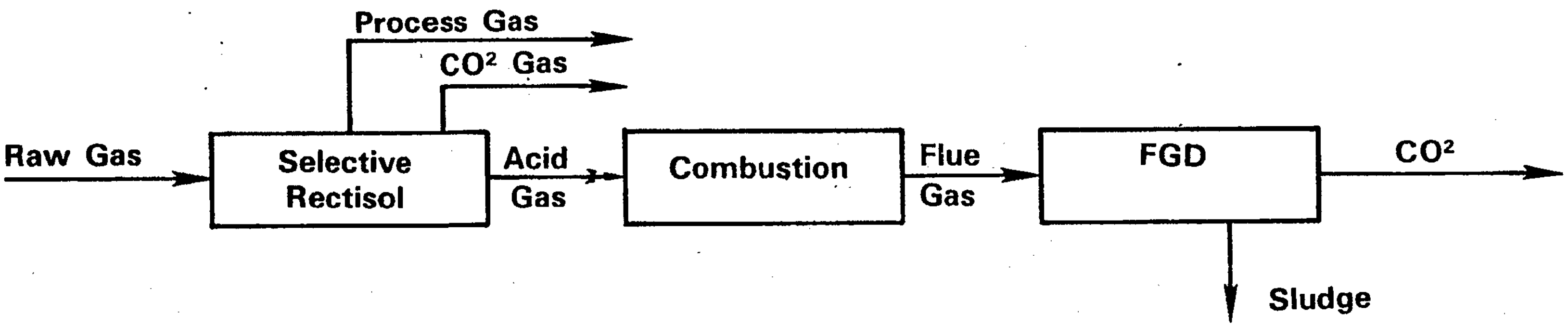

Figure 10. Raw Gas Treating Alternate VI

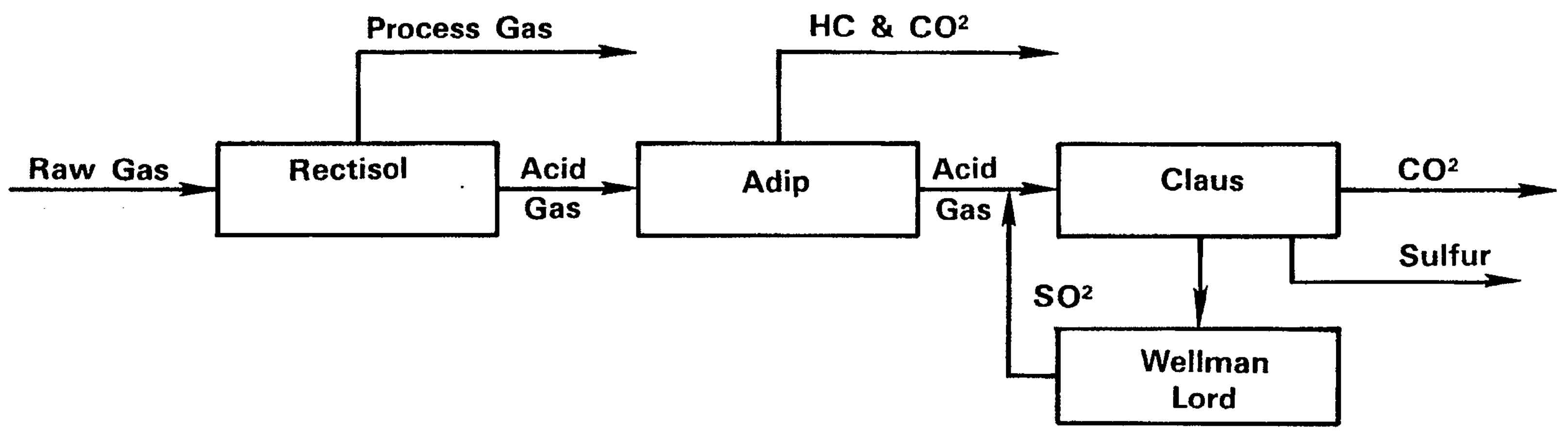

Figure 11. Raw Gas Treating Alternate VII

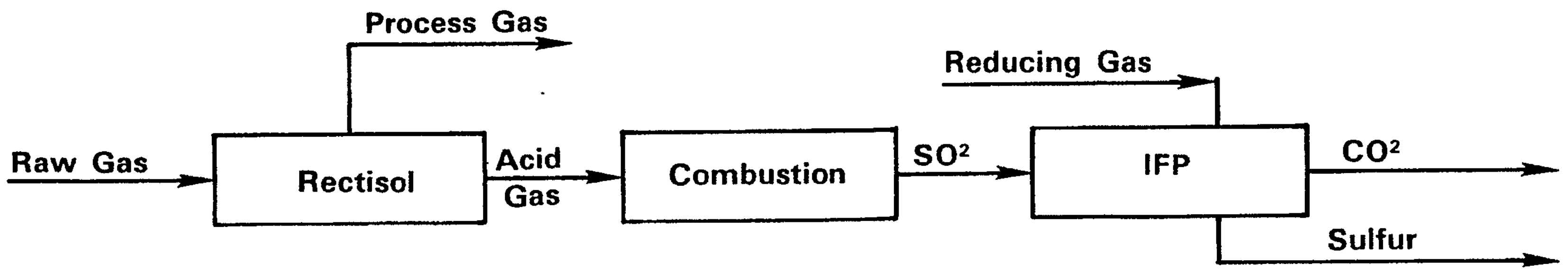

Figure 12. Raw Gas Treating Alternate VIII

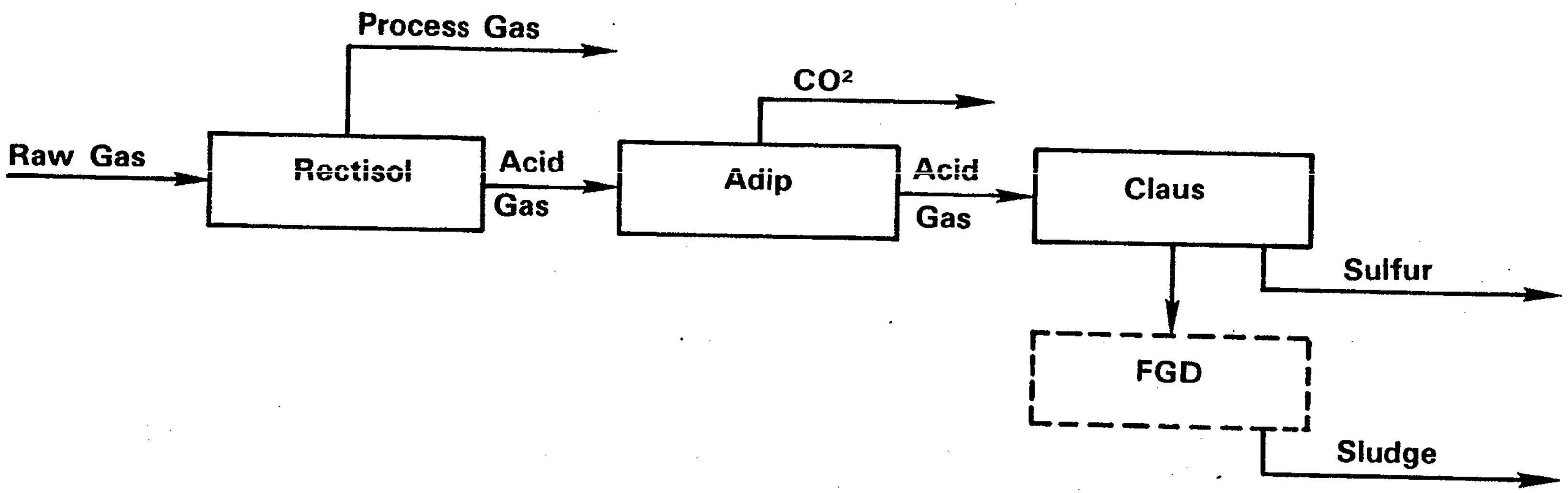

Figure 13. Raw Gas Treating Alternate IX

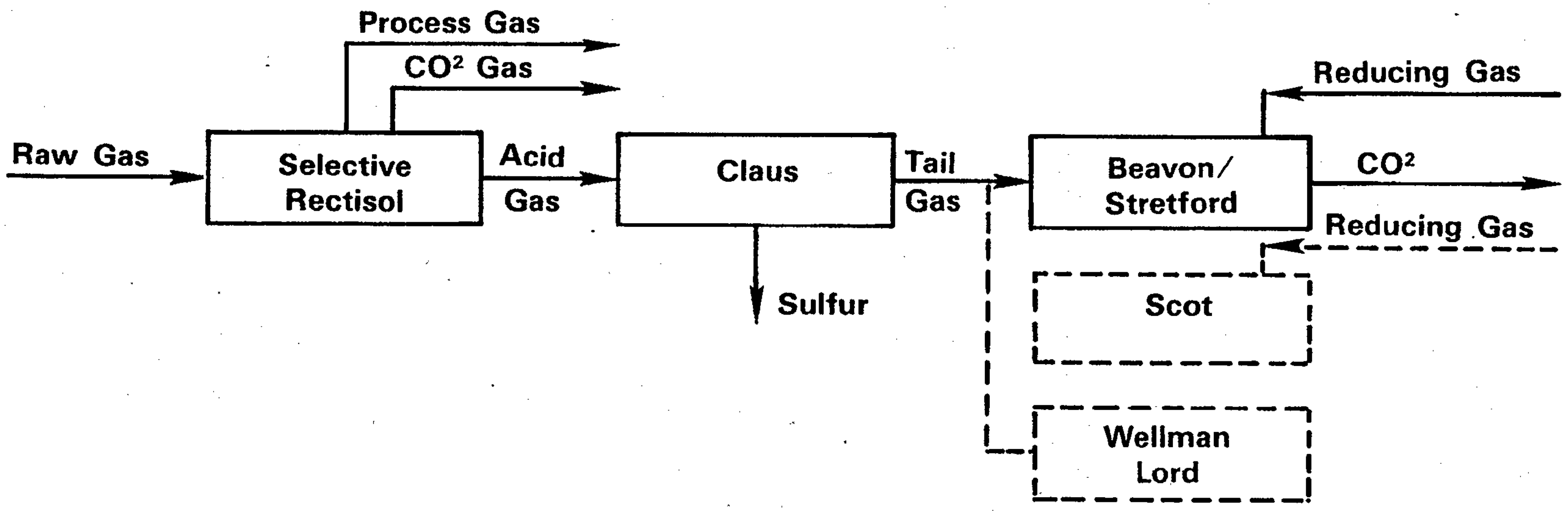

Figure 14. Raw Gas Treating Alternate X

Some prescreening must be done before designs and estimates proceed to perform BACT analysis in a reasonable period of time. The first prescreening step is the elimination of the processing operations which will not meet the emission regulatory requirements of New Source Performance Standards (NSPS) or Prevention of Significant Deterioration (PSD).

It is under the PSD regulations that modeling of the air dispersion characteristics of the plant site are required to estimate the amount of allowable emissions. Once this estimate is determined, those process operations which will not comply with these regulations can be eliminated from consideration.

The next prescreening step is the elimination of those processing operations that have been determined unable to meet the cost-effective demands on previous studies. Following this step, the remaining processes are reviewed to determine if they have special requirements which cannot be satisfied (e.g., availability of the required solvent, difficulty in obtaining equipment, excess delivery time for custom-made equipment, etc.). Finally, a review is conducted regarding the commercial applicability of the remaining processes to determine whether they have been proven in pilot plant, semicommercial, or commercial operations. A cost estimate is made for the two or three remaining process operations resulting from the prescreening steps. The most cost-effective operation that satisfies the regulatory requirements is then selected.

BEST AVAILABLE CONTROL TECHNOLOGY (BACT)

There have been numerous studies made for the Environmental Protection Agency (EPA) and Department of Energy (DOE) to determine the best control scheme for given conditions or plant sites. A list of these studies and the selected acid gas removal and treatment schemes follows:

1. EPA 650/2-74-009-b, June 1974, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification: Section 1: Synthane Process," by Esso Research and Engineering Company. The Benfield Process was selected for acid gas removal with the Stretford Process for sulfur recovery. An economic evaluation of the scheme was not indicated. Selection is assumed to be based on engineering judgment.

2. EPA 650/2-74-009-c, July 1974, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification; Section I: Lurgi Process," by Exxon Research and Engineering. Acid gas treatment was mainly based on the Stearns-Roger design for the El Paso Natural Gas Company. Rectisol with Stretford Process was selected. The selection was apparently the result of economic studies conducted by Stearns-Roger for El Paso.

3. EPA 650/2-74-009-b, December 1974, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification; Section I: CO_2 Acceptor Process," by Exxon Research and Engineering Company. The study states "consideration should be given to using an absorption/oxidation process such as Stretford, Takahax, IFP, etc., on the raw gas directly."

4. EPA 650/2-74-009-g, May 1975, "Evaluation of Pollution Control in Fossil Fuel Conversion Process; Gasification: Section 5. BI-GAS Process," by Exxon Research and Engineering. Benfield with Claus and tail gas recovery was selected for acid gas removal. This study did not include an economic evaluation. Selection was assumed to be based on engineering judgment.

5. EPA 650/2-74-009-j, September 1975, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification: Section 8. Winkler Process," by Exxon Research and Engineering Company. Benfield utilizing the selective mode of operation for acid gas removal was employed. A Claus Sulfur Plant with a Tail Gas Unit was selected for sulfur removal from acid gas. No economic evaluation was indicated.

6. EPA 650/2-74-072, July 1974, "Sasol-Type Process for Gasoline Methanol, SNG, and Low-Btu Gas from Coal," by M. W. Kellogg Co. Nonselective Rectisol plus Stretford Processes for removal of acid gas were utilized. No economic evaluation was indicated. Selection was assumed to be based on engineering judgment.

7. EPA 600/2-76-101, April 1976, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes: Final Report," by Exxon Research and Engineering Company. For acid gas removal units, the study states: "Each case must be examined individually, not only to choose the best type of acid gas removal process for the particular application, but also as to what modification to choose for the best type."

8. EPA-450/2-78-012, March 1978, "Guideline Series Control of Emissions from Lurgi Coal Gasification Plants," by the Environmental Protection Agency. The cost study compared: (1) Selective Rectisol, Stretford Unit on lean H_2S stream, Claus Plant followed by Tail Gas Incinerator on H_2S-rich stream, (2) Nonselective Rectisol, Stretford Unit and Tail Gas Incinerator, and (3) Selective Rectisol, Stretford Unit and Tail Gas Incinerator on lean gas stream, Claus Plant with Tail Gas Incinerator and tail gas scrubbing on H_2S-rich gas stream. A cost analysis indicated that the Nonselective Rectisol Process with a Stretford Unit was the most acceptable alternative from cost standpoint with comparable sulfur recovery efficiency.

9. DOE No. FE-2240-50, August 1978, "Sulfur Recovery in a Coal Gasification Plant," by C. F. Braun. Five different processing schemes were evaluated for both western and eastern coals. The study indicated that the Nonselective Selexol with Stretford Process and FMC Double-Alkali for boiler gas treating were the best selections for western (low-sulfur) coal. Selective Selexol with the Claus Plant and FMC Double-Alkali for the Boiler and tail gas treating were found most favorable for eastern coal. This study had one significant qualification: "Due to the large number of available alternatives and the limited number of cases that have been considered, the conclusions are only tentative."

10. DOE PNL 3140, September 1979, "Assessment of Environmental Control Technologies for Koppers-Totzek, Winkler and Texaco Coal Gasification Systems," by Pacific Northwest Laboratory. Acid gas removal discussions were general in nature.

11. ORNL-5722, August 1981, "The Impact of Environmental Control Costs on an Indirect Coal Liquefaction Process," by Oak Ridge National Laboratory/Fluor E & C, Inc., Houston, Texas. Six different cases were evaluated based on different stringency control and plant sizes. Case 4 contained the most stringent controls and an evaluation of methods of Boiler Flue Gas Emission Control. Nonselective Rectisol with a Flue Gas Desulfurization Unit was selected for the less stringent cases. Nonselective Rectisol with the Stretford Process was utilized for the most stringent control.

The various studies discussed indicate that selection of the most favorable process for acid gas removal and control of sulfur emissions is dependent upon the gasification process selected and the site location.

Coal gasification plants that utilize a coal-fired boiler for steam and power production may find it advantageous to integrate the boiler plant flue gas treating with the acid gas treating. This integration provides additional alternate schemes for consideration. Sulfur concentrations in boiler plant flue gases are low when compared to sulfur concentrations in the raw gas and acid gas streams. A sulfur removal efficiency of greater than 90 percent from boiler flue gases on a continuous basis places an excessive burden on the state of the art for some of the FGD processes. Table 3 illustrates the difference in sulfur concentrations of flue gas and Lurgi acid gas streams when processing Illinois No. 6 coal. Efficiency of removal is dependent on inlet flue gas concentration. This factor must be considered when integrating the acid gas treating system. In some instances, the acid gas stream routed to the FGD Unit may not have sufficient concentration to justify FGD treatment.

TABLE 3. ILLINOIS NO. 6 COAL - SULFUR CONTENT COMPARISON
(CALCULATED FROM ESTIMATED YIELD DATA)

	Lurgi Raw Gas	Acid Gas	Boiler Flue Gas
Gas Volume %	1% as H_2S	3.23% as H_2S	0.21% as SO_2

The cost of gas produced in a coal gasification plant is not competitive with the current cost of natural gas. Nonjustifiable expenditures resulting from delays in obtaining permits and from unnecessary environmental control systems create even more of a negative cost impact. Since synfuels plants are experiencing difficulty in meeting return on investment requirements essential for financing, every effort must be made to eliminate expenditures caused by unnecessary regulatory requirements.

BACT determinations and PSD regulations often create delays which outweigh their benefits. The regulations are burdening for both the regulator and those being regulated. Arriving at an agreement on a BACT determination, containing numerous options, creates never-ending arguments. On a case-by-case basis, these arguments become extremely burdensome for both the regulatory agency and the permittee. Allocation of PSD increments to satisfy all permittees is an assignment given to our regulators even though it is doubtful that Solomon, the wise man, could find a satisfactory solution to this problem.

Suggestions for better solutions to environmental regulations are as numerous as the process operations available for acid gas removal and treatment. Unfortunately, each solution is usually self-serving for those proposing the suggestion and does not consider the adverse effects on others. It is extremely difficult to arrive at a solution that is beneficial to the majority, since an active minority is often a controlling element in our political arena.

Industry, regulators and environmentalists must cease their role as adversaries and become partners in establishing regulations that provide maximum benefit to the majority. Since very few people can say their interests lie entirely in one direction, it should not be so difficult to work together for such a worthy goal.

Session IV: SOLID WASTE-RELATED ENVIRONMENTAL CONSIDERATIONS

Chairman: David A. Kirchgessner
U.S. Environmental Protection Agency
Research Triangle Park, NC

Cochairman: Kimm W. Crawford
TRW, Inc.
Redondo Beach, CA

PB83-128371

HEALTH EFFECTS BIOASSAY RESULTS FROM COAL CONVERSION SOLID WASTES*

M. P. Maskarinec, F. W. Larimer, J. L. Epler, C. W. Francis
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

To assist EPA and DOE in identifying solid wastes that may pose a potential hazard to human health and environment, the Oak Ridge National Laboratory has conducted studies on extracts from solid wastes obtained from various coal liquefaction and gasification processes. Analytical procedures to chemically characterize and separate the organic and inorganic constituents were developed. Various approaches to extraction were compared. Batteries of health effects and environmental assays were applied to the extracts or fractions thereof to serve as indicators of chronic hazards. The applicability and compatibility of the coupled chemical and biological procedures will be evaluated with particular emphasis on the Ames mutagenicity test.

INTRODUCTION

Recent examples of improper disposal at various hazardous chemical sites has dramatically increased the public awareness of the environmental and health effects associated with the disposal of solid and hazardous wastes (1). Therefore, increased emphasis has recently been placed on the regulatory aspects of the transport, treatment, storage and disposal of solid industrial waste (2).

At the same time, trends toward increased use of coal reserves in this country dictates that large volumes of solid wastes will result from various coal conversion technologies (3,4). These wastes include solids from coal-cleaning processes, flue-gas disulfurization sludges from ancillary boilers, spent catalysts, tar and oil sludges, and ash/slags. While the ashes and slags will constitute the largest volume of waste generated (> 90%), they are by and large devoid of organic material (5,6). Also, the sorptive capacity of these materials is usually large (6), and organic matter is not likely to migrate in the environment by dissolution. Thus, the environmeal and health consequences of these materials can largely be predicted from studies of inorganic content and leachability.

In the case of wastewater treatment plant sludges, which will be generated in considerably smaller but still signficant volumes, the organic content is likely to be much higher (7), and the leachability of organics from these solid wastes must be studied with respect to health and environmental effects.

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This is not to imply that inroganics should be ignored in such wastes, but only to indicate the presence of a new set of risks.

The steps involved in evaluating the health and environmental effects of wastewater treatment plant sludges from coal conversion solid wastes include: 1) physical/chemical characterization of the specific wastes; 2) determination of the environmental mobility of the various chemical constituents of the waste by evaluation of aqueous extracts intended to simulate specific disposal scenarios, and 3) preparation of the wastes and aqueous extracts for bioassay. This work represents a summary of data relevant to these three areas.

MATERIALS AND METHODS

Sample Collection

Samples were collected from operating pilot plants during a steady-state period Sample 1 was a filtered sludge from a pilot-scale coal liquefaction wastewater treatment plant, Sample 2 was collected from a coal cleaning plant and represented the final wastewater treatment plant solid waste. Sample 3 was collected as a centrifuged-residual from a liquefaction wastewater treatment plant.

Generation of Aqueous Extracts of Solid Wastes

Five techniques were used for the generation of aqueous extracts of the solid wastes. These included the EPA-EP, a distilled water extraction carried out in a manner identical to the EPA-EP (H_2O-EP), a sodium-resin displacement extraction, a citric acid extraction and an upward-flow column extraction with distilled water. The EPA-EP and the citric acid extractions are intended to mimic the co-disposal of municipal and industrial solid waste. The distilled water EP and sodium displacement techniques are more applicable to the disposal scenario of 100% industrial waste. The upward flow column extraction can be used to simulate either scenario depending on the extractant, but is primarily intended to avoid the artificial solid/solution separations inherent in the batch extractions, regardless of the extractant used. The variable and constant factors involved in the extractions are listed in Table 1.

Preparation of Solid Wastes and Extracts from Ames Bioassay

The solid wastes were prepared for the Ames test (8) in two ways. The solid wastes (50 g) were Soxhlet-extracted for 24 hours using methylene chloride (9). An aliquot of the Soxhlet extract was concentrated to dryness and redissolved in 2 ml dimethylsulfoxide. This solution was bioassayed.

In addition, the solid wastes were extracted using a three-step extraction procedure (10). Briefly, this procedure involves equilibration of the solid waste with acid, followed by base, followed finally by organic solvent. Thus, the procedure results in three fractions for bioassay: acids, bases

TABLE 1

EXTRACTION PROCEDURES: IDENTIFICATION OF VARIABLE AND CONSTANT LEACHING FACTORS

			Variable Factors		
	Extraction	Initial Leaching Medium	Mode of Extraction	pH Adjustment	Treatment of Leachate Solution for Extract Analysis
1.	EP	Distilled deionized	Batch: magnetically stirred	Adjust to pH 5 with 0.5 N acetic acid - maximum limit of 2 meq/g sample	Pressure filtered through 0.4 µm nuclepore filter
2.	Water	Distilled deionized water	Batch: magnetically stirred	None	Pressure filtered through 0.4 µm nuclepore filter
3.	Na-Resin	Distilled deionized water with 1 g calculated dry wt chelex 100/10 g sample	Batch: magnetically stirred	Adjust to pH 7 with 0.1 N HCl	Pressure filtered through 0.4 µm nuclepore filter
4.	Citrate Buffer	0.5 M citrate buffer	Batch: rotary extractor	None	Pressure filtered through 0.4 µm nuclepore filter
5.	Column	Distilled deionized water	Column: upward flow	None	Leachate from column directly passed through XAD-2 resin

Constant Factors

	Factor	Condition Used
1.	Sample particle size	< 9.5 mm
2.	Extraction temperature	room temperature
3.	Extraction time:	
	Batch mode	24-hour
	Column	until effective solid:solution ratio is reached
4.	Number of leachings on same sample	1
5.	Effective solid:solution ratio	1:20

and neutrals. An aliquot of easch fraction was concentrated to dryness and redissolved in dimethylsulfoxide for the Ames test.

The aqueous extracts were prepared as follows: a 500 ml aliquot was adjusted to pH 6.8 using phosphate buffer and to conductivity 20 mS using sodium chloride. The adjusted extract was passed through a column containing 4 ml XAD-2 resin. The resin was eluted with 20 ml acetone. The acetone was concentrated to dryness and the residue taken up in 2 ml dimethylsulfoxide. In the case of the column extraction, the XAD-2 was located directly above the column. This XAD-2 was extracted in a manner identical to that used in the batch extractions. An aliquot of the acetone was evaporated to dryness and taken up in 2 ml dimethylsulfoxide.

Analysis of Wastes and Extracts

All extract and fractions described above were characterized using gas chromatography and combined gas chromatography/mass spectrometry. GC was done on a Hewlett-Packard Model 5736-A gas chromatograph equipped with a flame ionization detector and a H-P Model 3390 integrator. A twenty-five meter fused silica capillary column (J&W Scientific) was used. GC/MS was done on a H-P Model 5985-A GC/MS/DS equipped with a similar column.

When possible, the solid waste extracts were applied to a preweighed filter pad; the solvent was evaporated and the pad reweighed. The difference was used as a crude indication of the mass of material present.

Ames Mutagenicity Test

The general methodology for the Salmonella/microsome assay has been described (11). In screening mode, the assay is restricted to two strains: TA 100, the hisG base-pair substitution in the uvrB rfa pKM101 background and TA 98, the hisD frameshift, also carrying uvrB rfa and pKM101. The full range of metabolic activation was examined, however, using microsomal preparations from both phenobarbital and Arochlor-treated rats.

RESULTS AND DISCUSSION

Analysis of Solid Wastes and Extracts

The results of the characterization work on the solid wastes and extracts are reported elsewhere (7), however, some general comments are appropriate here. In terms of the wastes themselves, considerably more organic material was extracted using the three-step procedure than was extracted by the Soxhlet extraction. This is true in terms of total mass as well as in terms of the levels of individual compounds. Qualitatively, the three wastes were similar. All contained a variety of compounds, although the neutral fraction was responsible for much of the organic content. All contained aromatic hydrocarbons and aromatic heterocycles (including nitrogen, oxygen, and sulfur containing species). In addition, all contained significant quantities of volatile organic compounds. Therefore, any assessment of the health and environmental effects of these materials must consider potential inhalation and air-quality problems. The levels of organics were highest from Sample 3 followed by Sample 1, and finally Sample 2.

The characterization of the aqueous extracts revealed the following general trends. The levels of organic materials in the extracts were more closely related to the technique used for extraction than to the extraction medium. For example, the extraction of volatile organics appeared to be superior in the citrate buffer extraction. However, this extraction is carried out in a closed system. Use of distilled water in the closed extractor produced comparable levels of volatile organics. Conversely, the extraction of phenol and the cresols did not appear to be relatd to the pH of the extractant. While no one batch extraction procedure was consistently superior in terms of extracting organics, when the organic content of the solid waste was high (e.g., Sample 3) all procedures were comparable. When the organic content of the solid wastes was low, the distilled water-EP appeared to be the most effective batch extraction technique.

The column extraction consistently extracted higher levels of organic compounds than did any of the batch extractions. This is due partly to the fact that no filtration is required, but also partly due to more aggressive displacement of organic compounds. This is particularly true when considering nonpolar compounds.

Ames Bioassay Results

The Ames Salmonella mutagenesis bioassay is widely recognized as an indicator of bacterial mutagenesis. It may also be an indicator of potential mammalian carcinogenesis. The test has the advantages of being relatively inexpensive, short-term, and simple to perform. The test is primarily sensitive to organic mutagens; thus, the characterization work described earlier is directly applicable to the Ames test.

The bioasay results from Samples 1 and 2 are shown in Tables 2 and 3. The extracts of Sample 1 were all extremely toxic. There was an indication of mutagenic activity in all but the most toxic extracts. The most active extract was the acid fraction, showing a non-linear dose-response in TA 98 (with phenobarbital activation) giving a peak mutation induction 15-fold over the untreated control (Figure 1). The extracts of Sample 2 were non-mutagenic, and only the Soxhlet extract and the acid fraction showed significant non-specific toxicity. The extracts of Sample 3 were extremely toxic; even at a 10-fold dilution these samples were too toxic for assay.

The results of the Ames test on the aqueous extracts of Sample 1 are shown in Table 4. Again, all exhibited some degree of toxicity. Those extracts which were not too toxic to test displayed mutagenic activity. The aqueous extracts of Sample 2 were not active in either strain. Extracts from Sample 3 were diluted 10-fold and the results are shown in Table 5. All were mutagenic including the EP extract, which displayed a linear dose-response (Figure 2), even after dilution.

TABLE 2
MUTAGENICITY OF SOLID WASTE SAMPLE 1

Revertants/plate

	TA 98				TA 100			
Conc (µl/plate)	Soxhlet	Acid	Base	Neutral	Soxhlet	Acid	Base	Neutral
PHENOBARBITAL ACTIVATION								
75	T*	T	T	T	T	T	T	T
50	93	609	T	60	T	670	T	T
25	94	556	T	61	T	645	T	T
10	97	391	T	52	T	536	T	T
0	22	39	22	42	199	167	91	106
AROCHLOR ACTIVATION								
75	T	T	T	T	T	T	T	T
50	T	T	T	T	T	T	T	T
25	70	156	T	T	T	T	T	T
10	70	202	T	54	T	229	T	T
0	22	48	42	35	192	126	153	123
NO ACTIVATION								
50	T	T	T	T	150	T	T	T
0	21	40	27	44	105	159	153	99

TABLE 3
MUTAGENICITY OF SOLID WASTE SAMPLE 2

Revertants/plate

	TA 98				TA 100				
Conc (µl/plate)	Soxhlet	Acid	Base	Neutral	Soxhlet		Acid	Base	Neutral
				PHENOBARBITAL ACTIVATION					
75	41	65	T	57	T	T		187	162
50	33	58	53	43	T	T		187	165
25	41	60	41	35	117	227		150	163
10	47	52	71	32	112	220		216	135
0	17	47	47	19	104	173		173	174
				AROCHLOR ACTIVATION					
75	T	T	46	54	T		T	207	173
50	T	T	52	40	T		T	160	160
25	T	T	46	30	T		T	138	151
10	47	39	59	32	107		231	205	163
0	27	28	28	20	98		182	182	98
				NO ACTIVATION					
50	T	T	26	33	T		T	204	92
0	29	35	35	28	118		192	192	103

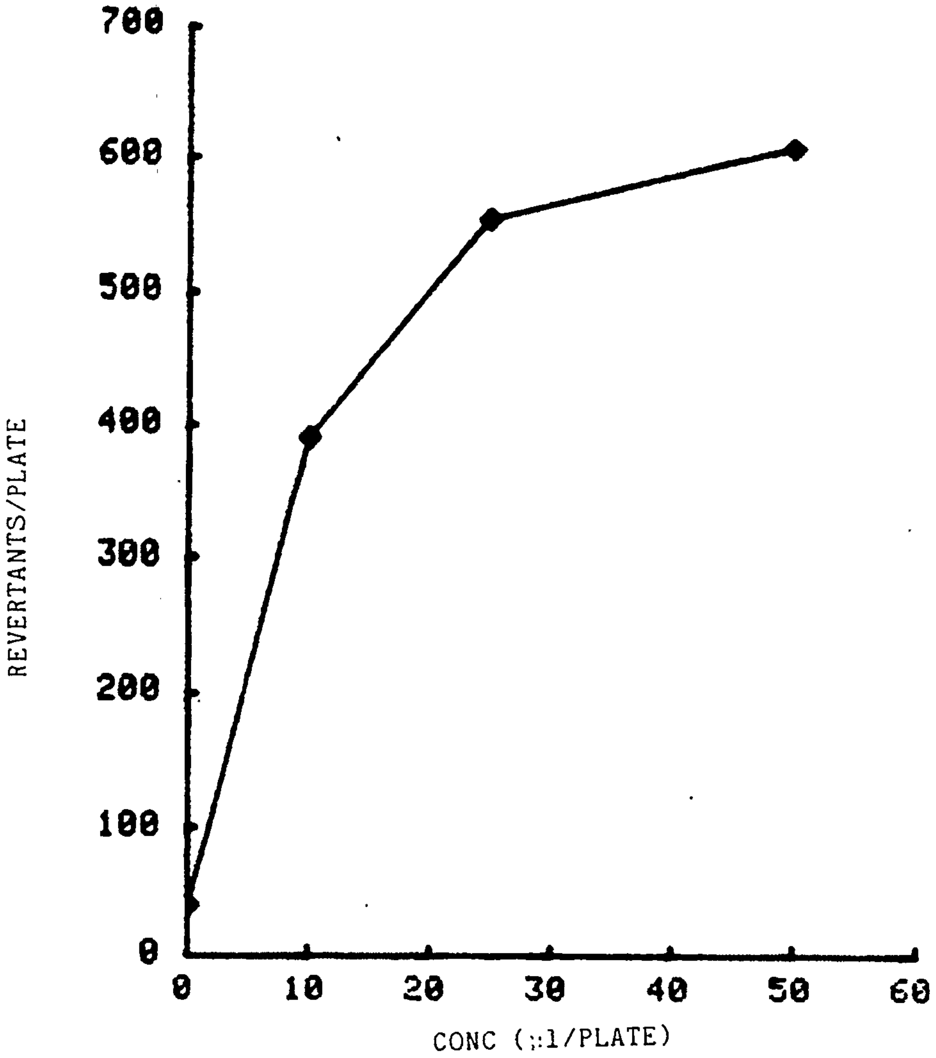

Figure 1. Mutagenicity of Acid Fraction of Sample 1 (TA 98, Phenobarbital Activation)

TABLE 4

MUTAGENICITY OF SOLID WASTE EXTRACTS FROM SAMPLE 1

Revertants/plate

	TA 98					TA 100				
Conc (µl/plate)	EP	H_2O-EP	Citrate	Na-Resin	Column	EP	H_2O-EP	Citrate	Na-Resin	Column
PHENOBARBITAL ACTIVATION										
75	T	T	T	T	T	T	T	T	T	T
50	T	T	T	T	T	T	T	T	T	T
25	T	58	T	35	94	T	T	T	T	T
10	44	41	45	33	78	156	T	T	117	149
0	17	52	22	16	42	109	110	154	111	112
AROCHLOR ACTIVATION										
75	T	T	T	T	T	T	T	T	T	T
50	T	T	T	T	T	T	T	T	T	T
25	T	T	T	T	119	T	T	T	T	T
10	31	42	T	19	48	T	T	T	108	117
0	13	43	28	8	31	96	91	167	94	108
NO ACTIVATION										
50	T	T	T	T	T	T	109	T	T	T
0	7	42	58	17	42	94	76	110	71	111

TABLE 5

MUTAGENICITY OF BATCH EXTRACTS FROM SAMPLE 3

Revertants/plate

	TA 98				TA 100			
Conc (µl/plate)	EP	H_2O-EP	Citrate	Na-Resin	EP	H_2O-EP	Citrate	Na-Resin
PHENOBARBITAL ACTIVATION								
7.5	110	34	71	T	T	T	163	119
5.0	92	52	57	45	T	71	213	165
2.5	46	45	54	46	117	136	169	125
1.0	30	27	49	70	93	119	152	123
0	19	16	42	22	85	80	150	106
AROCHLOR ACTIVATION								
7.5	98	74	80	T	T	T	156	151
5.0	59	52	86	T	T	T	165	109
2.5	53	27	48	110	T	78	214	182
1.0	29	29	39	97	78	70	176	143
0	20	18	40	29	65	74	135	110
NO ACTIVATION								
5.0	7	9	42	27	T	T	95	120
0	4	7	30	22	40	30	95	85

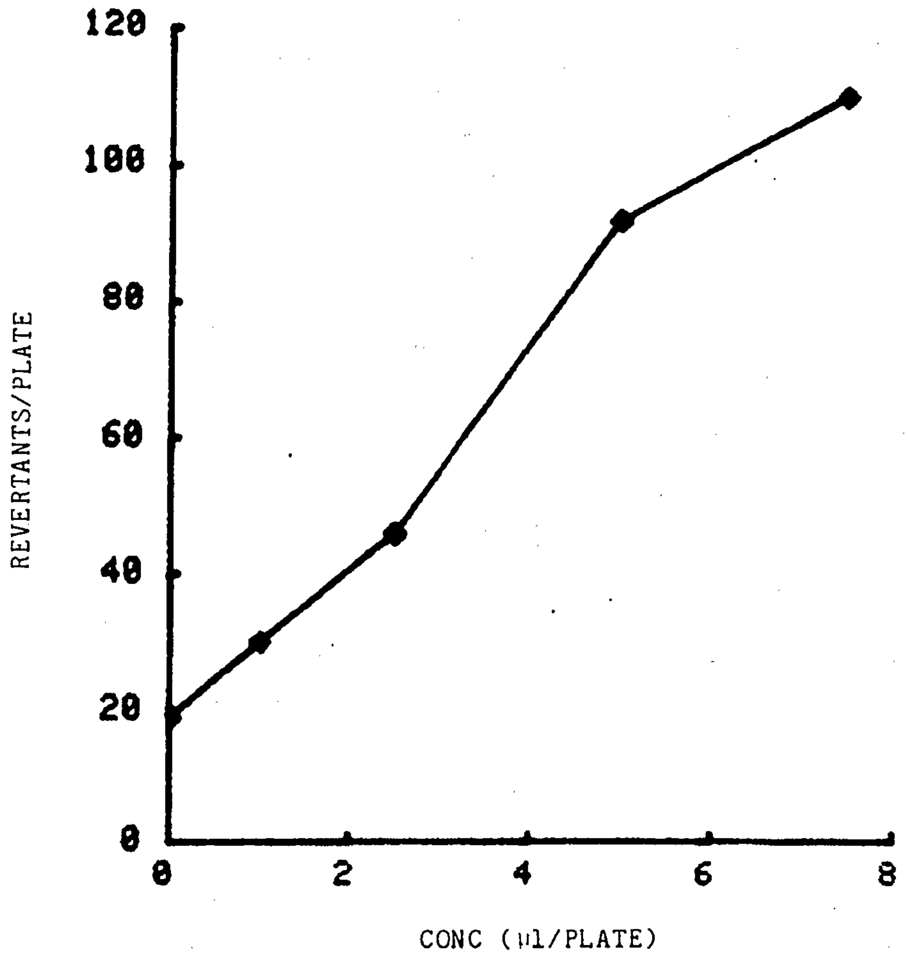

Figure 2. Mutagenicity of EP Extract of Sample 3
(TA 98, Phenobarbital Activation)

SUMMARY

The organic content of three solid wastes, representing coal conversion wastewater treatment plant sludges, were compared. State-of-the-art analytical techniques coupled with the Ames mutagenesis bioassay were used. A three-step fractionation/isolation scheme improved the bioassay results by isolating toxicity in the "acid" fraction. In addition, the wastes were extracted using five different environmental mobility tests. The extracts were analyzed and assayed (Ames test). In general, the results of the Ames Bioassay parallelled the results of the analytical characterization.

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A COMPARISON OF RCRA LEACHATES OF SOLID WASTES FROM COAL-FIRED UTILITIES † AND LOW- AND MEDIUM-BTU GASIFICATION PROCESSES

by: Michael R. Fuchs, Donnie L. Heinrich, Larry J. Holcombe, Kishore T. Ajmera
Radian Corporation
8501 Mopac Boulevard
Austin, Texas 78766

ABSTRACT

EPA has promulgated regulations which temporarily exclude utility wastes, including fly ash and bottom ash from coal-fired generating stations, from Subtitle C of Resource Conservation and Recovery Act (RCRA) regulations. EPA, using broad interpretation of amendments to the act, has also excluded coal gasification solid wastes from Subtitle C regulations and these wastes are listed as non-hazardous pending further data evaluation. This paper presents comparative results of RCRA leachates of the solid wastes from two low-BTU gasification processes and coal-fired utility solid wastes. The three facilities from which solid wastes were obtained used the same lignite feedstock. Also presented are comparable RCRA leachate results of solid wastes from a medium-BTU gasification process and a coal-fired power plant, both fueled with identical lignite feedstocks. The results indicate that solid wastes from coal-fired utilities and the solid wastes generated directly by low- and medium-BTU gasification processes are non-hazardous according to RCRA protocol and limits.

INTRODUCTION

On May 19, 1980, EPA promulgated regulations implementing Subtitle C of the Resource Conservation and Recovery Act (RCRA). The regulations define solid and hazardous wastes and establish criteria for handling and disposal of hazardous wastes. Excluded from Subtitle C regulations were fossil fuel combustion wastes which were then the subject of pending Congressional legislation. The Solid Waste Disposal Act of October 21, 1980 mandated the exclusion of fossil fuel combustion wastes from Subtitle C regulations and includes specifically fly ash waste and bottom ash waste of coal combustion processes (Reference 1).

The exclusion of coal combustion solid wastes from Subtitle C regulations is temporary. A revision of the exclusion of these wastes may be enacted pending the assessment of the environmental effect of these wastes by EPA.

Excluded from Subtitle C regulations by amendments to RCRA in November, 1980 were "solid waste from the extraction, beneficiation, and processing of ores and minerals". Under the interpretation that coal is a "mineral or ore", EPA has excluded solid wastes generated directly by coal gasification processes from Subtitle C regulations by considering gasification to be "extraction, beneficiation, and processing" of the "mineral or ore" i.e., coal. The exclusion from Subtitle C regulations of gasification solid wastes applies only to solid wastes produced directly by the gasification process. Wastes generated refining or upgrading the product are not excluded. This broad interpretation of the ruling will remain in effect until EPA has had an opportunity to evaluate the scope of specific exclusions (Reference 2).

Although the exclusion from Subtitle C regulations is temporary for both coal-fired power plants and coal gasification solid wastes, coal gasification is a fledgling industry in this nation, with limited data available to assess the environmental implications of the disposal of solid wastes generated by the various processes. On the other hand, utilities produce a substantial portion of the nation's electricity at coal-fired power plants. The characteristics of coal-fired power plant solid wastes are much more defined and recognized.

This paper presents data which provide an opportunity to evaluate comparative results of RCRA leachates of solid wastes from fossil fuel combustion and solid wastes from coal gasification processes. The data includes RCRA leachate results of the solid wastes from two low-BTU gasification processes and the solid wastes from a coal-fired power plant, the feedstocks of the three processes from the same mine. Other data presented are RCRA leachate results of a medium-BTU gasification solid waste and solid wastes from a coal-fired power plant, both facilities having the same lignite feedstock, but not the same as the low-BTU gasification feedstocks.

RCRA leachate results on the solid wastes from coal-fired power plants and gasification processes provide data developed from solid wastes produced under similar conditions. Coal-fired power plant bottom ash and coal gasification gasifier ash are subjected to the very hot temperatures associated with each process and are primarily fused ash having a coarse texture. One of the major differences of the two processes is that solid wastes from coal-fired power plants are generated in an oxidizing atmosphere while solid wastes from gasification processes are generated in a reducing atmosphere. Gasifier ash passes through both reducing and oxidizing zones within the gasifier. Wet samples of bottom and gasifier ashes are generally collected, either after sluicing to disposal ponds (bottom ash) or through the water pressure seal of the gasifier (gasifier ash). Precipitator ash and cyclone dust are finer particulate matter entrained in the combustion effluents or product gas. Precipitator ash is collected dry, but may be sluiced to disposal ponds. Cyclone dust samples are most often retrieved dry, but may be collected wet from water quench systems. The solid wastes from gasification processes (gasifier ash and cyclone dust) have considerable concentrations (approximately 20-50%) of carbon, while coal-fired power plant solid wastes have quite low concentrations ($< 1\%$) of carbon.

TECHNICAL APPROACH

As required by RCRA, EPA has established five categories to define the characteristics of hazardous waste. The five characteristics are:

- General - a solid waste is a hazardous waste if it exhibits any of the characteristics of hazardous waste.
- Ignitability - ignitable wastes have a low flash point, or are liable to cause fires or are oxidizers.
- Corrosivity - corrosive wastes have a pH of less than or equal to 2 or greater than or equal to 12 or corrode steel at a specified rate.
- Reactivity - reactive wastes react violently, generate toxic fumes or are explosive.
- Extraction Procedure (EP) Toxicity - an extraction procedure is specified and maximum concentrations of contaminants listed; the waste is hazardous if the concentration of any contaminant in the leachate is equal to or greater than the listed contaminant level.

The extraction procedure has been designed to identify wastes which would leach hazardous concentrations of toxic constituents into groundwaters under conditions of improper management. The characteristic of EP toxicity contaminants are presented in Tables 1, 5, and 7 along with the maximum allowable concentrations of each. The list of contaminants includes eight elements, four pesticides, and two herbicides.

The conclusions presented in this paper are based upon the characteristic of EP toxicity and primarily upon the inorganic element contaminants. The contaminants listed in the EP toxicity characteristic are the toxic contaminants listed in the National Interim Primary Drinking Water Standards (NIPDWS). The maximum concentration levels of the EP toxicity contaminants are ten times the concentrations specified in the NIPDWS.

Radian Corporation is presently under contract to the EPA to conduct an "Environmental Assessment of Low/Medium-BTU Gasification Technology". As part of this program, Radian has conducted source test and evaluations at commercial and pilot scale low- and medium-BTU gasification facilities. Included in the source test and evaluations, solid wastes of the gasification processes (gasifier ash and cyclone dust) have been subjected to the RCRA extraction procedure with subsequent analyses of the leachates for the eight RCRA elemental contaminants.

Two low-BTU gasification facilities tested were a Wellman-Galusha gasifier located at the U.S. Bureau of Mines, Twin Cities Metallurgy Research Center, Ft. Snelling site, in Minneapolis, Minnesota, and the Riley Gas Producer located at the Riley Research Center in Worcestor, Massachusetts. During testing, both units were operating with North Dakota Indianhead lignite. Both gasifiers are air-blown, atmospheric pressure units. The major difference between the two gasifiers is that the Wellman-Galusha is a thick fixed-bed (app. 4 feet) design while the Riley Gas Producer is a thin fixed-bed (app. 2 feet) design. At the Ft. Snelling site (Wellman-Galusha), the cyclone dust is water quenched after removal from the product gas.

To evaluate RCRA results of coal gasification and coal-fired power plant solid wastes generated from facilities operating with the same feedstock, Radian, with the aid of American Natural Service Company, identified a coal-fired power plant using the Indianhead lignite as the feedstock. United Power association, headquartered in Elk River, Minnesota, operates a mine-mouth power plant firing Indianhead lignite in Stanton, North Dakota. Radian received samples of lignite, bottom ash, and electrostatic precipitator ash from the Stanton Plant. As with the solid wastes of the gasification processes, the coal-fired power plant solid wastes (bottom ash and precipitator ash) were subjected to the RCRA extraction procedure and the leachates analyzed for the eight RCRA elemental contaminants.

Also as part of the EPA program, Radian has conducted source test and evaluations at a commercial Lurgi-based coal gasification facility located in the Kosovo region of Yugoslavia. A coal-fired power plant also operates at the plant site and utilizes the same coal feedstock as the gasification facility. During the site testing, samples of the gasifier ash from the Lurgi gasifiers and bottom ash and precipitator ash from the power plant were collected. The three samples were subjected to the RCRA extraction procedure and the leachates analyzed for the eight RCRA elemental contaminants.

To allow an evaluation of the similarities or dissimilarities of the feedstocks of the two low-BTU gasification processes, the lignite collected at each facility was analyzed for proximate and ultimate parameters and the eight RCRA element contaminants. The solid wastes from these processes were analyzed for the eight RCRA element contaminants to assess the relationship between RCRA leachate concentrations of the RCRA element contaminants to the concentrations of these elements in the solid. Proximate and ultimate analyses were performed on the solid wastes from the two low-BTU gasification processes and the Stanton Plant to review the similarities of the solid wastes with respect to major components.

RESULTS

LOW-BTU GASIFICATION

As discussed earlier, Radian has performed source test and evaluations at several low-BTU coal gasification facilities. The results of two facilities presented in this paper have been taken from source test and evaluation programs performed at the two facilities (Reference 3 and 4). The Riley Gas Producer STER will be finalized in November of this year. The United Power Association power plant data and the medium-BTU gasification data have been generated independently of the above two projects, but have been funded by EPA.

Table 1 presents the RCRA leachate results for the eight RCRA elemental contaminants of the solid wastes from the two low-BTU gasification processes and the Indianhead lignite-fired power plant. Also presented are maximum levels of the eight contaminant elements, any of which exceeded in the RCRA leachate of the solid wastes characterize the solid waste as hazardous and regulated under Subtitle C.

The concentrations of the eight RCRA elemental contaminants of the solid wastes from the two low-BTU gasification facilities and from the coal-fired power plant are presented in Table 2.

Concentrations of the eight RCRA elemental contaminants and proximate and ultimate analytical results of the lignite feedstocks from the two low-BTU gasification facilities and the coal-fired power plant are presented in Table 3.

Presented in Table 4 are proximate and ultimate analytical results of the solid wastes from the three processes with Indianhead lignite as the feedstock to allow a comparison of wastes generated by the two low-BTU gasification processes and the coal-fired power plant.

Table 5 presents the analyses of RCRA leachates of the Riley Gas Producer gasifier ash and cyclone dust for the contaminant pesticides and herbicides. These are the only RCRA leachates which were analyzed for these contaminants.

The percent of the total element of each solid waste leached by the RCRA extraction procedure from the solid wastes from the two low-BTU gasification processes and from the coal-fired power plant operating on Indianhead lignite is presented in Table 6.

MEDIUM-BTU GASIFICATION

Table 7 presents the analytical results for the eight RCRA protocol elements of the RCRA leachates of the Lurgi gasifier ash and the bottom ash and precipitator ash from a coal-fired power plant located at the plant site and using the same coal as feedstock. The RCRA elemental contaminant maximum levels are also presented.

The elemental concentrations of the eight RCRA protocol elements in the solid wastes from the gasification facility and coal-fired power plant at the Kosovo site are presented in Table 8.

Table 9 presents the percent of the total element of each solid waste leached by the RCRA extraction procedure from the solid wastes from the medium-BTU gasification process and from the coal-fired power plant at the Kosovo plant.

TABLE 1. RCRA LEACHATE RESULTS OF LOW-BTU GASIFICATION SOLID WASTES AND COAL-FIRED POWER PLANT SOLID WASTES HAVING SAME LIGNITE FEEDSTOCK

	Wellman-Galusha (Ft. Snelling)		Riley Gas Producer		United Power Assn. Stanton Plant		RCRA Contaminant Maximum Concentration* ug/L
Contaminant	Gasifier Ash ug/L	Cyclone Dust ug/L	Gasifier Ash ug/L	Cyclone Dust ug/L	Bottom Ash ug/L	Precipitator Ash ug/L	
Arsenic	19	33	33	4	8	58	5,000
Barium	1,000**	1,000**	680	390	300	920	100,000
Cadmium	<7**	NA	<0.5	<0.5	40	50	1,000
Chromium	1**	1**	<1	<1	<200	<200	5,000
Lead	7**	8**	<2	<2	300	400	5,000
Mercury	<0.6	<0.3	<0.5	<0.5	0.3	0.4	200
Selenium	14	6	6	2	<4	87	1,000
Silver	NA	NA	<0.5	<0.5	25	30	5,000

*Reference 1

**Analysis by spark source mass spectroscopy - all other analyses by atomic absorption spectroscopy

NA - not analyzed.

TABLE 2. ELEMENTAL CONCENTRATIONS OF LOW-BTU GASIFICATION SOLID WASTES AND COAL-FIRED POWER PLANT SOLID WASTES*

	Wellman-Galusha† (Ft. Snelling)		Riley Gas Producer††		United Power Assn. Stanton Plant	
Element	Gasifier Ash ug/g	Cyclone Dust ug/g	Gasifier Ash ug/g	Cyclone Dust ug/g	Bottom Ash ug/g	Precipitator Ash ug/g
Arsenic	30**	63**	58**	0.6**	19	53
Barium	1900***	630	3300***	1700***	>1000	>1000
Cadmium	0.8	2	<3	<0.1	2	2
Chromium	21***	<6.2***	<0.2***	43***	26	12
Lead	5	8	7	37	17	18
Mercury	1.7**	<3.2**	0.0005**	0.02**	NA	NA
Selenium	15**	14**	<1**	1.2**	4	10
Silver	0.6	2	<3	<0.1	<0.8	<0.4

*Analysis by spark source mass spectroscopy
**Analysis by atomic absorption spectroscopy
***Analysis by inductively coupled plasma emission spectrooscopy
NA-Not analyzed
†Reference 3
††Reference 4

TABLE 3. RCRA ELEMENTAL CONTAMINANTS AND PROXIMATE AND ULTIMATE ANALYTICAL RESULTS, INDIANHEAD LIGNITE FEEDSTOCKS*

	Wellman-Galusha† (Ft. Snelling) Lignite	Riley Gas Producer†† Lignite	United Power Assn. Stanton Plant Lignite
Proximate Analysis			
% Ash	10.91	12.09	9.15
% Volatile	41.93	42.40	39.69
% Fixed Carbon	47.16	45.51	51.16
BTU/lb	10475	10630	10923
% Sulfur	0.61	1.10	1.04
Ultimate Analysis			
% Carbon	62.69	63.32	66.27
% Hydrogen	4.60	4.31	4.41
% Nitrogen	0.91	1.02	0.75
% Chlorine	0.03	0.002	0.00
% Sulfur	0.61	1.10	1.04
% Ash	10.91	12.09	9.15
% Oxygen (diff.)	20.25	17.94	18.38
% H_2O		32.8	32.9
Arsenic	6.5***	23***	11**
Barium	630**	430****	>1000**
Cadmium	0.4**	3**	0.2**
Chromium	10**	3.2****	0.2**
Lead	2**	2**	1**
Mercury	0.4***	0.15***	NA
Selenium	1***	<0.5***	<0.1**
Silver	1**	<4**	0.1**

*dry basis
**analysis by spark source mass spectroscopy
***analysis by atomic absorption spectroscopy
****analysis by inductively coupled plasma emission spectroscopy
NA-not analyzed
†Reference 3
††Reference 4

TABLE 4. PROXIMATE AND ULTIMATE ANALYTICAL RESULTS OF LOW-BTU GASIFICATION SOLID WASTES AND COAL-FIRED POWER PLANT SOLID WASTES OPERATING ON INDIANHEAD LIGNITE*

	Wellman-Galusha** (Ft. Snelling)		Riley Gas Producer***		United Power Assn. Stanton Plant	
	Gasifier Ash	Cyclone Dust	Gasifier Ash	Cyclone Dust	Bottom Ash	Precipitator Ash
Proximate Analysis						
% Ash	74.41	18.97	62.54	39.93	98.68	99.57
% Volatile	6.56	24.41	10.59	15.00	3.92	3.98
% Fixed Carbon	19.03	56.62	26.87	45.08	-2.60	-3.65
BTU/1b	3747	10717	4993	8478	0	0
% Sulfur	1.09	1.51	1.64	1.67	0.01	0
Ultimate Analysis						
% Carbon	24.64	67.18	35.36	53.69	0.96	0.55
% Hydrogen	0.41	2.32	0.61	1.52	0.04	0.07
% Nitrogen	0.17	0.93	0.46	0.82	0.07	0.04
% Chlorine	0.02	0.03	0.003	0	0	0
% Sulfur	1.09	1.51	1.64	1.67	0.01	0
% Ash	74.41	18.97	62.54	39.93	98.68	99.67
% Oxygen (diff.)	0.60	9.06	0	2.39	0.24	-0.33

*dry basis
**Reference 3
***Reference 4

TABLE 5. RCRA PESTICIDE/HERBICIDE CONTAMINANTS RESULTS OF LOW-BTU GASIFICATION SOLID WASTES LEACHATES

	Riley Gas Producer*		RCRA
Contaminant	Gasifier Ash (ug/L)	Cyclone Dust (ug/L)	Contaminant Maximum Concentration** (ug/L)
Endrin	BDL	BDL	20
Lindane	BDL	BDL	400
Methoxychlor	BDL	BDL	10,000
Toxaphene	BDL	BDL	500
2,4-D	BDL	BDL	10,000
2,4,5-TP Silvex	BDL	BDL	1,000

BDL - Below detection limit

Detection Limits:

Endrin	<2 ug/L
Lindane	<0.2 ug/L
Methoxychlor	<2 ug/L
Toxaphene	<100 ug/L
2,4-D	<0.8 ug/L
2,4,5-TP Silvex	<0.3 ug/L

*Reference 4
**Reference 1

TABLE 6. LOW-BTU GASIFICATION AND COAL-FIRED POWER PLANT RCRA LEACHATES OF SOLID WASTES PERCENT OF TOTAL ELEMENT LEACHED

	Wellman-Galusha (Ft. Snelling)		Riley Gas Producer		United Power Assn. Stanton Plant	
Contaminant	Gasifier Ash	Cyclone Dust	Gasifier Ash	Cyclone Dust	Bottom Ash	Precipitator Ash
Arsenic	1.3	1.0	1.1	13.3	0.84	2.6
Barium	1.1	0.9	0.4	0.5	>0.6****	<1.8****
Cadmium	<17.5*	NA	***	***	40	50
Chromium	0.1	>0.3**	***	<0.05*	<33.3*	<33.3*
Lead	2.8	2.0	<0.6*	<0.1*	35.3	44.4
Mercury	<0.7*	***	<2000*	<50	NA	NA
Selenium	1.9	0.9	>12**	3.3	<2*	17.4
Silver	NA	NA	***	***	>62.5**	>150**

NA-not analyzed
*Leachate concentration below lower detection limit.
**Solid concentration below lower detection limit.
***All results below lower detection limit.
****Solid concentration above upper detection limit.

TABLE 7. RCRA LEACHATE RESULTS OF MEDIUM-BTU GASIFICATION SOLID WASTE AND COAL-FIRED POWER PLANT SOLID WASTES HAVING SAME LIGNITE FEEDSTOCK*

Contaminant	Lurgi Gasifier Ash ug/L	Power Plant Bottom Ash ug/L	Power Plant Precipitator Ash ug/L	RCRA Contaminant Maximum Concentration** ug/L
Arsenic	21	9	<3	5,000
Barium	1200	510	410	100,000
Cadmium	<0.5	<0.5	<0.5	1,000
Chromium	330	130	140	5,000
Lead	140	47	250	5,000
Mercury	<0.2	<0.2	<0.2	200
Selenium	<4	<4	<4	1,000
Silver	<1	<1	<1	5,000

*Analysis by atomic absorption spectroscopy
**Reference 1

TABLE 8. ELEMENTAL CONCENTRATIONS OF MEDIUM-BTU GASIFICATION SOLID WASTE AND COAL-FIRED POWER PLANT SOLID WASTES*

Element	Lurgi Gasifier Ash ug/g	Power Plant Bottom Ash ug/g	Power Plant Precipitator Ash ug/g
Arsenic	<5.7	<5.7	<5.7
Barium	970	280	560
Cadmum	<0.8	<0.8	<0.8
Chromium	100	69	86
Lead	<8	<8	<8
Mercury	NA	NA	NA
Selenium	<6	<6	<6
Silver	<0.1	<0.1	<0.1

*Analysis by inductively coupled plasma emissions spectroscopy.
NA-not analyzed

TABLE 9. MEDIUM-BTU GASIFICATION AND COAL-FIRED POWER PLANT RCRA LEACHATES OF SOLID WASTES PERCENT OF TOTAL ELEMENT LEACHED

Contaminant	Lurgi Gasifier Ash	Power Plant Bottom Ash	Power Plant Precipitator Ash
Arsenic	>7.4*	>3.2*	**
Barium	2.5	3.6	1.5
Cadmium	**	**	**
Chromium	6.6	3.8	3.2
Lead	>35*	>12*	>62*
Mercury	NA	NA	NA
Selenium	**	**	**
Silver	**	**	**

NA-not analyzed
*Solid concentration below detection limit.
**All results below detection limit.

CONCLUSIONS

Tables 10 and 11 present the percent of the RCRA elemental contaminants maximum concentration represented by the elemental concentrations in the RCRA leachates of the solid wastes from the coal-fired power plants and gasification processes. There are no values over ten percent, and only five values greater than or equal to five percent. The values above five of the percent of the RCRA contaminants maximum level represented by RCRA leachate concentrations are:

Stanton Plant - Precipitator Ash - Lead	8%
Stanton Plant - Precipitator Ash - Selenium	8.7%
Stanton Plant - Bottom Ash - Lead	6%
Kosovo Power Plant - Precipitator Ash - Lead	5%
Lurgi Gasifier - Gasifier Ash - Chromium	6.6%

The data indicates that the solid wastes tested from the

Wellman-Galusha Gasifier,
Riley Gas Producer,
Stanton Plant (power plant),
Lurgi Gasifier, and
Kosovo Power Plant

processes should be listed as non-hazardous according to the EP toxicity characteristic. Lead in coal-fired power plant precipitator ashes appears to be the single elemental contaminant which contributes most significantly to the toxicity of the RCRA leachates. This may be explained by the theory that lead, being a volatile element, is most probably vaporized during combustion of the coal and condenses upon the precipitator ash as the flue gases cool, thereby enriching the lead concentration in the precipitator ash.

The concentrations of the pesticide and herbicide contaminants in the RCRA leachates of the gasifier ash and cyclone dust from the Riley Gas Producer were not detected by the instrumental analytical method. This data indicates that no pesticides or herbicides, either generated by the process or present in the lignite feedstock, are emitted in gasification solid wastes.

One of the goals of this paper is to present RCRA leachate results developed on solid wastes of coal gasification processes and coal-fired power plants that were using the same feedstock. Table 3 presented proximate and ultimate results and elemental concentrations of the Indianhead lignite collected at the two low-BTU gasifiers and the coal-fired power plant. The proximate and ultimate data indicate that the feedstocks at the three facilities were quite similar. However, the elemental concentrations indicate considerable variability in the three feedstocks with respect to the eight RCRA elemental contaminants.

TABLE 10. LOW-BTU GASIFICATION AND COAL-FIRED POWER PLANT
RCRA LEACHATES OF SOLID WASTES
PERCENT OF RCRA CONTAMINANT MAXIMUM CONCENTRATION

	Wellman-Galusha (Ft. Snelling)		Riley Gas Producer		United Power Assn. Stanton Plant	
Contaminant	Gasifier Ash	Cyclone Dust	Gasifier Ash	Cyclone Dust	Bottom Ash	Precipitator Ash
Arsenic	0.38	0.66	0.66	0.08	0.16	1.4
Barium	1.0	1.0	0.68	0.39	0.30	0.92
Cadmium	<0.7	NA	<0.05	<0.05	0.4	0.5
Chromium	0.02	0.02	<0.02	<0.02	<4	<4
Lead	0.14	0.16	<0.04	<0.04	6	8
Mercury	<0.3	<0.15	<0.25	<0.25	0.15	0.2
Selenium	1.4	0.6	0.6	0.2	<0.4	8.7
Silver	NA	NA	<0.01	<0.01	0.5	0.6

NA - not analyzed

TABLE 11. MEDIUM-BTU GASIFICATION AND COAL-FIRED POWER PLANT RCRA LEACHATES OF SOLID WASTES PERCENT OF RCRA CONTAMINANT MAXIMUM CONCENTRATION

Contaminant	Lurgi Gasifier Ash	Bottom Ash	Precipitator Ash
Arsenic	0.42	0.18	<0.06
Barium	1.2	0.51	0.41
Cadmium	<0.05	<0.05	<0.05
Chromium	6.6	2.6	2.8
Lead	2.8	0.94	5
Mercury	<0.1	<0.01	<0.1
Selenium	<0.4	<0.04	<0.4
Silver	<0.02	<0.02	<0.02

The coal feedstocks of the gasification facility and the coal-fired power plant at the Kosovo site were retrieved from the same stocks, and parameter variabilities of the coal are applicable to both processes.

The data presented in Tables 6 and 9, percent of total element leached by the RCRA extraction procedure, is significantly affected by analytical sensitivities. Of the values not affected by analytical sensitivities, the highest percentages (17-50%) of elements from the solids leached were for cadmium, lead, and selenium in the bottom ash and precipitator ash of the power plant firing Indianhead lignite. The concentrations of these elements were also the highest values measured in the solid wastes; however, no concentration of any of these elements in the RCRA leachates represented as much as ten percent of the RCRA contaminant maximum level. Only one "percent of total element leached" value (Riley Gas Producer cyclone dust - 13.3%) of the RCRA contaminants for the gasification solid wastes exceeded ten percent. These results indicate that the majority of elemental contaminants present in coal gasification solid wastes and coal-fired power plant solid wastes are bound in the solids such that the leachability of the elements is relatively low.

The results of this paper indicate that the solid wastes of specific coal-fired power plants and coal gasification processes tested warrant listing as non-hazardous. However, the non-hazardous listing of these wastes is based upon the characteristic of EP toxicity and primarily upon the elemental contaminants and does not include a severe evaluation of the wastes using other pertinent criteria, such as organic constituents or radioactive components, that may need to be evaluated to determine if there may be a contribution to groundwater contamination. Additional data must be generated to apply the findings of this paper to the solid wastes generated by other coal combustion and coal gasification processes and feedstocks to fully evaluate the status of solid wastes from these industries with regard to Subtitle C regulations.

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CHARACTERIZATION OF SOLID WASTES FROM † INDIRECT LIQUEFACTION FACILITIES

by
Cora A. Hunter, Kar Y. Yu and Kimm W. Crawford
TRW Environmental Division

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ABSTRACT

Gasification ash and slag are the major solid wastes generated in indirect coal liquefaction facilities. Smaller amounts of spent catalysts and pollution control sludges may also be generated. There is a limited amount of data on the hazardous and nonhazardous characteristics of these solid wastes. Leachate data for gasifier ash and slag from Lurgi, Wellman-Galusha, and Texaco gasification have been presented elsewhere. The RCRA leaching characteristics of quenched gasifier slag and dust from commercial scale Koppers-Totzek gasification tests in Greece are presented in this paper. The potential accumulation of trace elements in the sludges from biological oxidation of Lurgi gasification condensates are estimated. Koppers-Totzek and Texaco gasification condensates will contain negligible amounts of organics as compared to the Lurgi gasification condensates and will not require biological oxidation. The potential accumulation of trace elements on high temperature shift catalyst are examined as a function of degree of gasification and feed coal characteristics.

1.0 INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) of 1976 directs the Environmental Protection Agency to promulgate regulations to insure the proper disposal of solid wastes for the protection of both human health and the environment. With the recent emphasis on America's coal resources, indirect coal liquefaction may soon be providing a portion of America's energy needs. The The proper disposal of solid wastes generated in the production of liquid fuels and chemicals from coal will be part of the environmental protection required under RCRA. EPA has set forth procedures to determine the potential hazards of solid wastes. Characterization of solid waste streams from indirect liquefaction facilities is the first step toward assuring proper disposal of these wastes.

There is a limited amount of data on the hazardous and nonhazardous characteristics of solid wastes from indirect coal liquefaction facilities. The data are dependent upon the coal used. Leachate data for gasifier ash and slag from Lurgi, Wellman-Galusha, and Texaco gasification have been presented elsewhere.(1,2) The RCRA leaching characteristics of quenched gasifier slag and dust from commercial scale Koppers-Totzek gasification tests in Greece are presented in this paper. The potential accumulation of trace elements in the sludges from biological oxidation of Lurgi gasification condensates is estimated. The potential accumulation of trace elements on high temperature shift catalyst is examined as a function of degree of gasification and feed coal characteristics.

2.0 INDIRECT LIQUEFACTION PROCESSES AND SOLID WASTES

Indirect liquefaction combines coal gasification technologies with catalytic synthesis technologies to produce a range of liquid fuels and chemicals. Figure 1 indicates the basic sequence of process steps necessary for indirect liquefaction. The raw coal is prepared to gasifier feed specifications and gasified (gasification technologies currently in use or under development include the Lurgi, Koppers-Totzek, and Texaco processes). The raw product gas is quenched and upgraded for synthesis by dust removal, shift conversion, and acid gas (e.g., CO_2 and H_2S) removal. The purified synthesis gas is catalytically converted into crude liquid products which can either be used directly as fuels or further refined (synthesis processes currently in use or under development include Fischer-Tropsch, Methanol, and Mobil M gasoline synthesis). Not shown in Figure 1 are the units necessary for on-site steam and power generation, boiler flue gas desulfurization (FGD), oxygen production, raw water treatment, and process cooling.

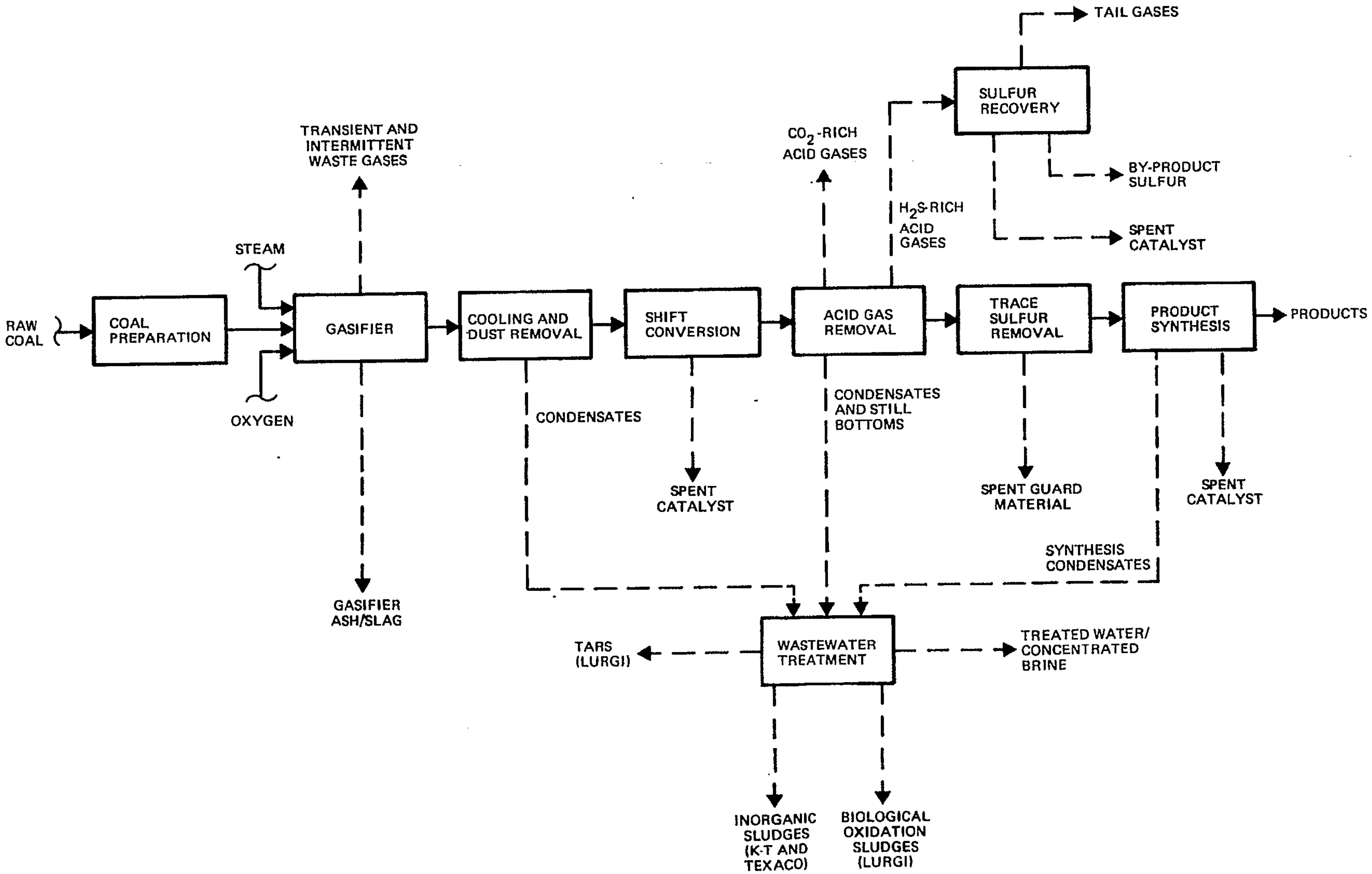

Figure 1. Types of Wastes Generated in Indirect Coal Liquefaction Facilities

The major solid waste streams from indirect liquefaction facilities include quenched gasifier ash and slag, gasifier dust, heavy tars and oils, boiler bottom and fly ash, flue gas desulfurization sludge, biological treatment sludges, and sulfur (if not sold as a by-product). Other solid waste streams include spent catalysts, spent sulfur guard, raw water treatment sludges, and chemical precipitation sludges. Leachable trace elements are pollutants of potential concern in all of the solid waste streams. With the exception of the biological oxidation sludges, all of the solid waste streams are inorganic based. The key solid waste streams addressed in this paper are gasifier slag, gasifier dust, biological oxidation sludges, and spent catalysts.

The dry ash Lurgi gasifier operates at temperatures below coal ash fusion temperatures (1815 to 1930°C), while Koppers-Totzek and Texaco gasifiers operate at higher temperatures (2100 to 2600°C). A portion of the coal ash will leave the K-T and Texaco gasifiers as dust entrained in the raw gas stream while the remaining coal ash exits as molten slag from the bottom. Gasifier ash, slag, and dust will consist mainly of nonvolatile and unreacted portions (primarily mineral matter) of the feed coal. Toxic trace elements and substances derived from the parert coal are potential pollutants of concern. Gasifier ash and slag are ordinarily quenched with process water for cooling and/or transportation purposes, and thus will contain substances found in the quench water. Gasifier dust may contain substances found in the wash water.

Biological oxidation sludges result from biological wastewater treatment processes used to treat gasification and synthesis condensates. Nonbiodegradable toxic organic compounds and trace elements derived from gasification and synthesis condensates are the potential pollutants of concern. Koppers-Totzek and Texaco gasification condensates will contain negligible amount of organics as compared to the Lurgi gasification condensates due to the higher combustion temperatures in the Koppers-Totzek and Texaco gasifiers. Lurgi gasification condensates will contain large amounts of dissolved and suspended organics ranging from simple phenols to complex organic acids. Condensates from the Fischer-Tropsch, Methanol, or Mobil M gasoline synthesis section of integrated indirect liquefaction facilities will also contain high loadings of soluble organic pollutants (e.g., alcohols, ketones, organic acids).

There are several types of catalysts which may be used in indirect liquefaction facilities. Shift catalysts include cobalt-molybdate, copper/zinc, and iron chrome based catalysts. Copper/zinc based catalysts are used for Methanol synthesis. Fischer-Tropsch synthesis catalysts are iron based with transition elements as promoters. Zeolites are used for Mobil M gasoline synthesis. Methanation catalysts are nickel based. Certain catalysts are known to contain toxic consituents (e.g., methanation catalysts are nickel-based). High temperature shift catalysts may accumulate toxic constituents through prolonged contact with raw coal gases.

3.0 RCRA HAZARDOUS WASTE CLASSIFICATION CRITERIA

The current Federal hazardous waste regulations define the testing procedures and thresholds which cause a solid waste to be classified as hazardous. A solid waste is considered hazardous if it meets test criteria for ignitability, corrosivity, reactivity, or toxicity. EPA can also list wastes as hazardous if the waste has been found to be fatal to humans in low doses or toxic as indicated by the LD_{50} or LC_{50} levels. Solid wastes containing any of the EPA-specified hazardous constituents* may also be listed as hazardous after taking into consideration some intrinsic factors such as concentration of the constituents in the waste, persistence of the constituent, quantity of wastes, the nature of the toxicity presented by the constituent, and other appropriate factors.

The toxic characteristics of solid wastes are measured by the RCRA Extraction Procedure (EP) Toxicity Test, which is designed to roughly approximate the extraction of soluble material with rain water. The solid is extracted with a sixteen-fold excess of leaching solution at a pH of 5.0 for a 24-hour time period at room temperature. Following the extraction period, the sample is diluted to an aqueous volume of 20 times the sample weight and then filtered to separate the liquid and solid phases. The extract is then analyzed for eight trace elements (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) and other identified hazardous constituents which are listed in the Extraction Procedure.(3) The RCRA standards for these eight trace elements are 100 times the Primary Drinking Water Standards.

4.0 CHARACTERISTICS OF INDIRECT LIQUEFACTION WASTES

No indirect coal liquefaction solid wastes are listed as hazardous wastes at the present time. There is insufficient information available at present to

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*There are more than 350 specified hazardous constituents including cyanides, nickel, vanadium pentoxide, phenols, naphthylamines, etc. (see 40 CFR 261, May 19, 1980).

determine the hazardous or nonhazardous characteristics of many of the wastes according to RCRA criteria. Some of these wastes are known to contain certain identified constituents of concern (e.g., methanation catalysts are known to contain nickel).

4.1 GASIFIER SLAG AND DUST

The RCRA leachate characteristics of quenched gasifier slag from commercial-scale Koppers-Totzek gasification of Greek Lignite and Illinois #6 coals in Ptolemais, Greece are shown in Table 1.(4) Although the quenched gasifier slag samples were collected under various gasifier operating conditions, the RCRA leachate trace element concentrations are quite uniform. When compared to the RCRA Standard (100 times the primary drinking water standards), none of the samples analyzed would be classified as hazardous. In fact, most of the RCRA leachate trace element concentrations are less than 10 times the primary drinking water standards (selenium concentrations may actually be less than 10 times the primary drinking water standard, but analytical sensitivity is limited in these data). Neutral pH leachate tests on these samples resulted in uniform leachate trace element concentrations similar to those found for the RCRA leachates.(4) The leachate characteristics of the Koppers-Totzek gasifier slag are similar to those presented by other investigators for other coal gasification ashes.(1,2,5)

As with K-T slag, dust from Koppers-Totzek gasification of Greek lignite coal would not be classified as hazardous from a trace element standpoint based on data in Table 2.(4) Most of the RCRA leachate trace element concentrations are less than 10 times the primary drinking water standards (selenium concentrations may actually be less than 10 times the primary drinking water standard, but were not detected as such in these tests). Neutral pH leachate tests on these samples resulted in fairly uniform leachate trace element concentrations with minor differences between the RCRA leachate and neutral pH leachate.(4) There is little difference in the leachate characteristics of gasifier slag and dust disposed of in settling ponds.

The commercial-scale Koppers-Totzek gasification tests with Illinois #6 coal employed a cyclone for dry collection of gasifier dust samples, since the wet sludge from clarification of wash water associated with Illinois #6 coal could not be isolated from that of Greek lignite. In conventional plant designs, the dust is removed from the raw gas in a washer cooler system and this dust would exit the system as solids suspended in the wash water. Some of the toxic

TABLE 1. RCRA LEACHATE CHARACTERISTICS OF QUENCHED KOPPERS-TOTZEK GASIFIER SLAG (GREEK LIGNITE AND ILLINOIS #6 COAL)(4)

Trace Element	Leachate Trace Element Concentration (mg/l) Greek Lignite Coal*	 Illinois #6 Coal†	 RCRA Standard‡
Ag	<0.01	<0.01	5
As	<0.4	<0.4	5
Ba	0.1	<0.03	100
Cd	<0.007	<0.007	1
Cr	<0.04	<0.04	5
Hg	<0.0002	<0.0002	0.2
Pb	<0.05	<0.09	5
Se	<0.4	<0.4	1

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[*] Average value obtained from two samples

[†] Average value obtained from nine samples

[‡] 100 times the Primary Drinking Water Standards

TABLE 2. RCRA LEACHATE CHARACTERISTICS OF KOPPERS-TOTZEK GASIFIER DUST DISPOSED IN SETTLING PONDS (GREEK LIGNITE COAL)(4)

Trace Element	Leachate Trace Element Concentration (mg/l) Greek Lignite Coal*	RCRA Standard†
Ag	<0.01	5
As	<0.2	5
Ba	0.38	100
Cd	< 0.007	1
Cr	<0.04	5
Hg	<0.0002	0.2
Pb	<0.05	5
Se	<0.4	1

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[*] Average value obtained from four samples

[†] 100 times the Primary Drinking Water Standards

components in the gasifier dust would become solubilized in the wash water. Also, toxic components in the wash water could be introduced into the wet dust. The leachate characteristics of dry dust samples from Koppers-Totzek gasification of Illinois #6 coal shown in Table 3(4) are thus a conservative estimate of the leachate characteristics of dust that would be collected in washer cooler systems neglecting the addition of any toxic components that might come from the wash water since some leaching will occur as a result of contact with wash water. The levels of silver, barium, chromium, mercury, and lead are well below the RCRA Standard for classification as a hazardous waste. The arsenic, cadmium, and selenium concentrations are also below the RCRA Standard, but the margin of safety is lower. The neutral pH leachate characteristics are fairly similar to the RCRA leachate characteristics, except for barium and cadmium, which are more readily leached under neutral pH conditions. Although there is no RCRA Standard for boron, its RCRA leachate concentration of 2.2 mg per liter(4) exceeds the irrigation water quality standard of 0.75 mg per liter. Thus, leachability of boron may be an important water quality concern at specific disposal sites even though this element is not considered to be toxic to man or higher animals. It should also be mentioned that the leaching characteristics of the K-T dust do not differ significantly from that of the parent Illinois #6 coal itself.

All available data indicate that gasification ash/slag and dust would be classified as nonhazardous based on the RCRA Extraction Procedure requirements.(1,2) However, it is possible that some of these wastes could be hazardous RCRA if process wastewaters containing leachable toxic substances are used to quench the raw gas or ash.

Leachable trace elements are not the only basis upon which gasifier slag and dust may be listed or classified as hazardous. In the case of both K-T and Texaco gasification dust, leachates may contain substances such as cyanides, sulfides, thiocyanates and ammonia derived from the aqueous condensates or wash waters which have been in contact with dust. Only limited data are currently available regarding the presence and leachability of any such constituents in the "wet" dust from the subject processes.

4.2 BIOLOGICAL OXIDATION SLUDGES

Biological treatment of gasification and synthesis wastewaters is envisioned for many proposed synthetic fuel facilities in the U.S. especially those based upon Lurgi gasification. In these facilities, biological sludges would be generated as a waste from the treatment process. Although there are very limited

TABLE 3. RCRA LEACHATE CHARACTERISTICS OF DRY DUST SAMPLES FROM KOPPERS-TOTZEK GASIFICATION (ILLINOIS #6 COAL)(4)

Trace Element	Leachate Trace Element Concentration (mg/l)	
	Cyclone Dust*	RCRA Standard†
Ag	<0.01	5
As	0.35	5
Ba	<0.02	100
Cd	<0.007	1
Cr	<0.02	5
Hg	<0.0002	0.2
Pb	<0.15	5
Se	0.6	1

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*One sample

†100 times the Primary Drinking Water Standards

leachate and bioassay data available at present on the characteristics of such sludges, the presence of potentially toxic organics (e.g., aromatic amines) and/or trace elements (e.g., Hg, Cd) in the raw wastewaters would suggest that the sludges could be hazardous.

It is possible to estimate the amounts of various trace elements which may accumulate in Lurgi gasification condensate biological oxidation sludges since a limited amount of data are available on the trace element composition of Lurgi gasification condensates.(6,7,8) The accumulation of trace elements in the biological oxidation sludges can be estimated from removal efficiencies achieved for biological treatment of industrial and municipal wastewaters.(9,10,11) The maximum trace element concentrations leachable from Lurgi gasification condensate biological oxidation sludges are estimated in Table 4, assuming that all of the accumulated material is leachable. As indicated in the table, the maxium leachate trace element concentrations may exceed 100 times the Primary Drinking Water Standards. Although barium is not listed in Table 4, it should not be a problem due to its low concentration in the Lurgi raw gas liquor and relatively high RCRA standard concentration. The Lurgi gasification condensate concentrations and biological oxidation removal efficiencies are summarized in the Appendix.

Incineration of biological oxidation sludge has also been proposed for Lurgi facilities to destroy the toxic organics in the waste. However, the incineration residue may also be hazardous due to leachable trace elements, as indicated by calculations in Table 4. The trace element concentrations could be increased by a factor of three or more due to incineration. For these calculations, incineration is assumed to result in a 70 percent reduction in waste quantity (on a dry basis). All of the trace elements present in the biological oxidation sludge are also assumed to accumulate in the incineration residue and to be leachable.

4.3 SPENT CATALYSTS

There is insufficient information available at present to determine the hazardous or nonhazardous characteristics of spent catalysts from indirect liquefaction processes. Due to the proprietary nature of most catalysts, there is little data publicly available on their specific compositions. Some catalysts are known to contain certain identified hazardous constituents (e.g., methanation catalysts are nickel-based). However, many catalysts are presumed to not contain any hazardous constituents (e.g., Mobil M gasoline synthesis and Claus

TABLE 4. PREDICTED RCRA LEACHATE CHARACTERISTICS OF SLUDGE FROM BIOLOGICAL OXIDATION OF LURGI GASIFICATION CONDENSATES, WORST CASE

	Predicted Maximum Leachate Trace Element Concentration (mg/l)		
Trace Element	Biological Oxidation Sludge	Incineration Residue	RCRA Standard*
Rosebud Coal			
Ag	5.5	18.2	5
As	0.5	1.8	5
Cd	4.1	13.8	1
Cr	54.5	181.8	5
Hg	2.4	7.9	0.2
Pb	5.5	18.2	5
Se	2.9	9.7	1
Illinois #6 Coal			
Ag	5.8	19.2	5
As	0.9	2.9	5
Cd	4.4	14.6	1
Cr	172.8	576.1	5
Hg	30.0	99.9	0.2
Pb	172.8	576.1	5
Se	23.0	76.8	1
Dunn Lignite Coal			
Ag	7.2	24.0	5
As	53.9	179.8	5
Cd	0.8	2.7	1
Cr	1.1	3.6	5
Hg	1.4	4.7	0.2
Pb	7.2	24.0	5
Se	115.1	383.6	1

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*100 times the Primary Drinking Water Standards catalysts which are zeolite- and alumina-based catalysts, respectively).

Although fresh catalysts may not contain any toxic constituents, they may accumulate such constituents through prolonged contact with the coal gases. In particular, potentially volatile trace elements originally present in the feed coal (e.g., As, Cd, Cr, Hg, Pb, and Se) may accumulate in the sulfur tolerant shift catalyst over time, since this type of catalyst is directly exposed to hot raw gas and is known to have an affinity for various trace elements.(12,13) There is essentially no leachate data available in the public domain on any of the catalysts used in indirect liquefaction processes. .

The potential accumulation of various trace elements on the shift catalyst could be estimated based on the trace element composition of the raw coal gas, however, sufficient data are not available. Some data are available to allow indirect calculation of the degree of gasification of several trace elements in various gasifiers, although a wide range of values can be derived depending on which set of data are used.(14,15) For purposes of this paper, therefore, the accumulation of trace elements on shift catalyst have been estimated as a function of degree of gasification and feed coal characteristics. Table 5 summarizes the trace element contents of American coals.

Assuming all of the gaseous trace elements are deposited on by the shift catalyst and are subsequently leachable, the time required for shift catalyst to become hazardous due to trace element deposition can be estimated. Figures 2 to 4 show the results as a function of trace element concentration in the coal and percent of the trace element gasified. Shift catalysts is estimated to become hazardous within twelve hours under the worst case (i.e., 100 percent gasification) for coals with the mean concentrations of the trace elements shown in Table 5. The nonhazardous lifetime would be increased to about 3 months when only one percent gasification of the trace elements occurs. Minimum trace element levels found in American coals would still result in a hazardous catalyst within a week if 100 percent of the trace elements are gasified. The nonhazardous lifetime of the shift catalyst would be increased to about 3 years when only one percent gasification of the trace elements occurs.

Although there are large uncertainties in the exact levels of various elements which would accumulate on the shift catalyst, the calculations presented indicate a reasonable potential for the spent catalyst to become hazardous. Als shift catalyst may be affected by trace elements in terms of activity. Elements

TABLE 5. TRACE ELEMENT CONTENTS OF AMERICAN COALS(14,15)

Trace Element	Concentration in Coal (ppm)		
	Mean	Minimum	Maximum
As	16.4	0.5	357
Cd	1.8	0.02	100
Cr	15.3	<0.5	70
Hg	0.17	0.01	3.3
Pb	21.2	<0.7	283
Se	3.6	<0.10	150

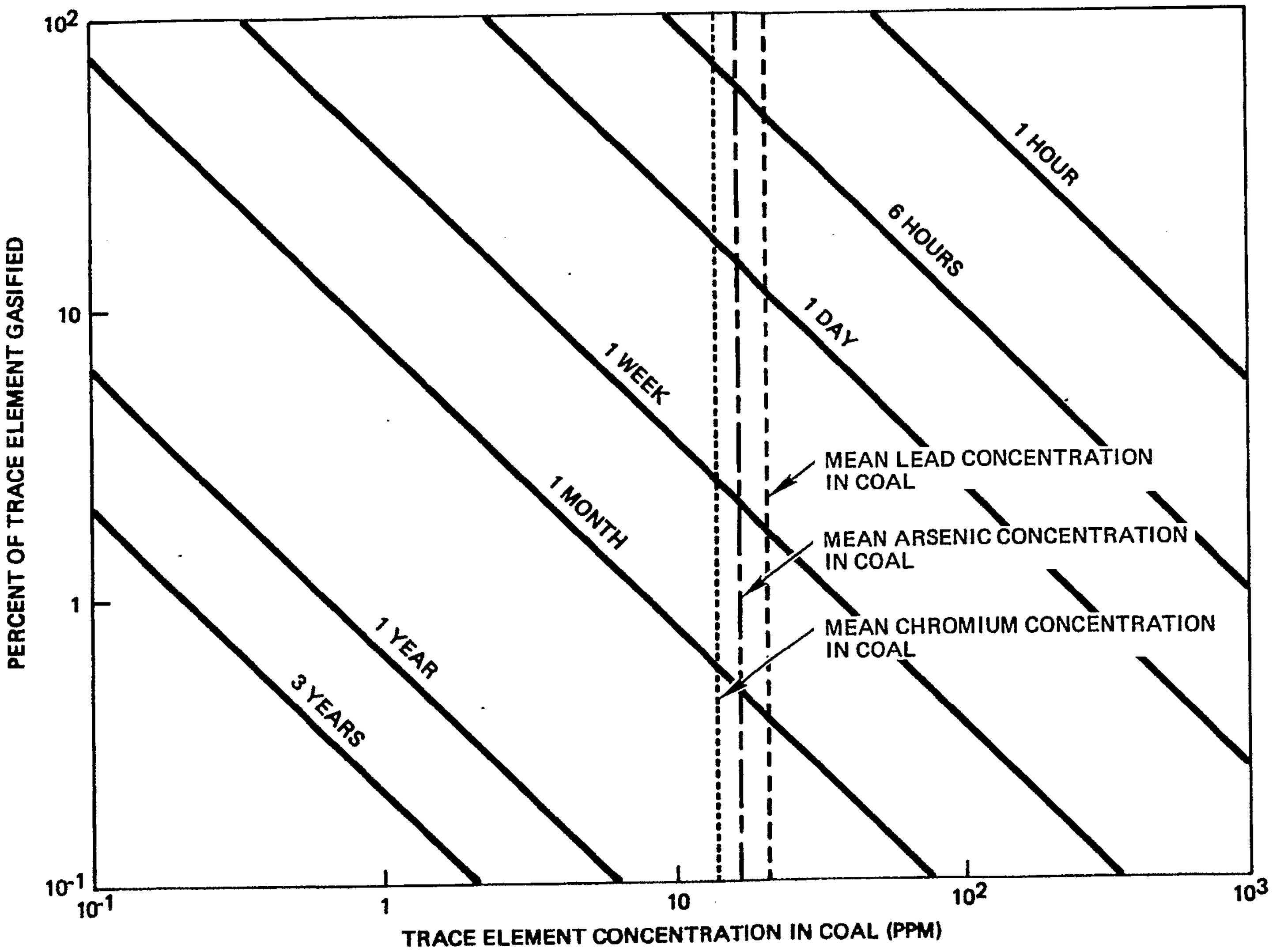

Figure 2. Predicted Shift Catalyst Lifetime Required to Reach RCRA Leachate Standards for As, Cr, and Pb (5 mg/l) *

* (BASED ON 2 KG RAW COAL GAS PER HOUR PER KG CATALYST)

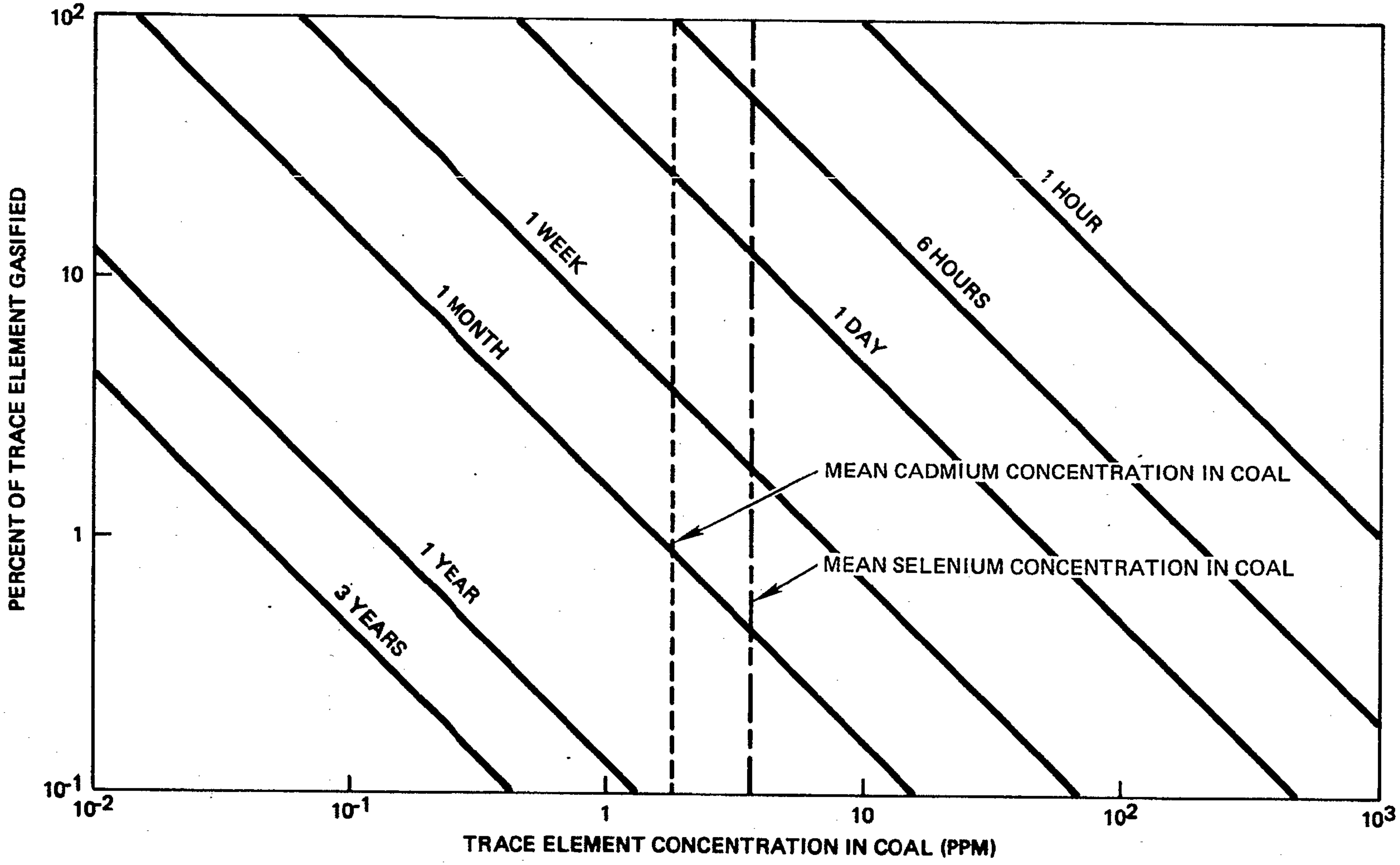

Figure 3. Predicted Shift Catalyst Lifetime Required to Reach RCRA Leachate Standards for Cd and Se (1 mg/l) *

* (BASED ON 2 KG RAW COAL GAS PER HOUR PER KG CATALYST)

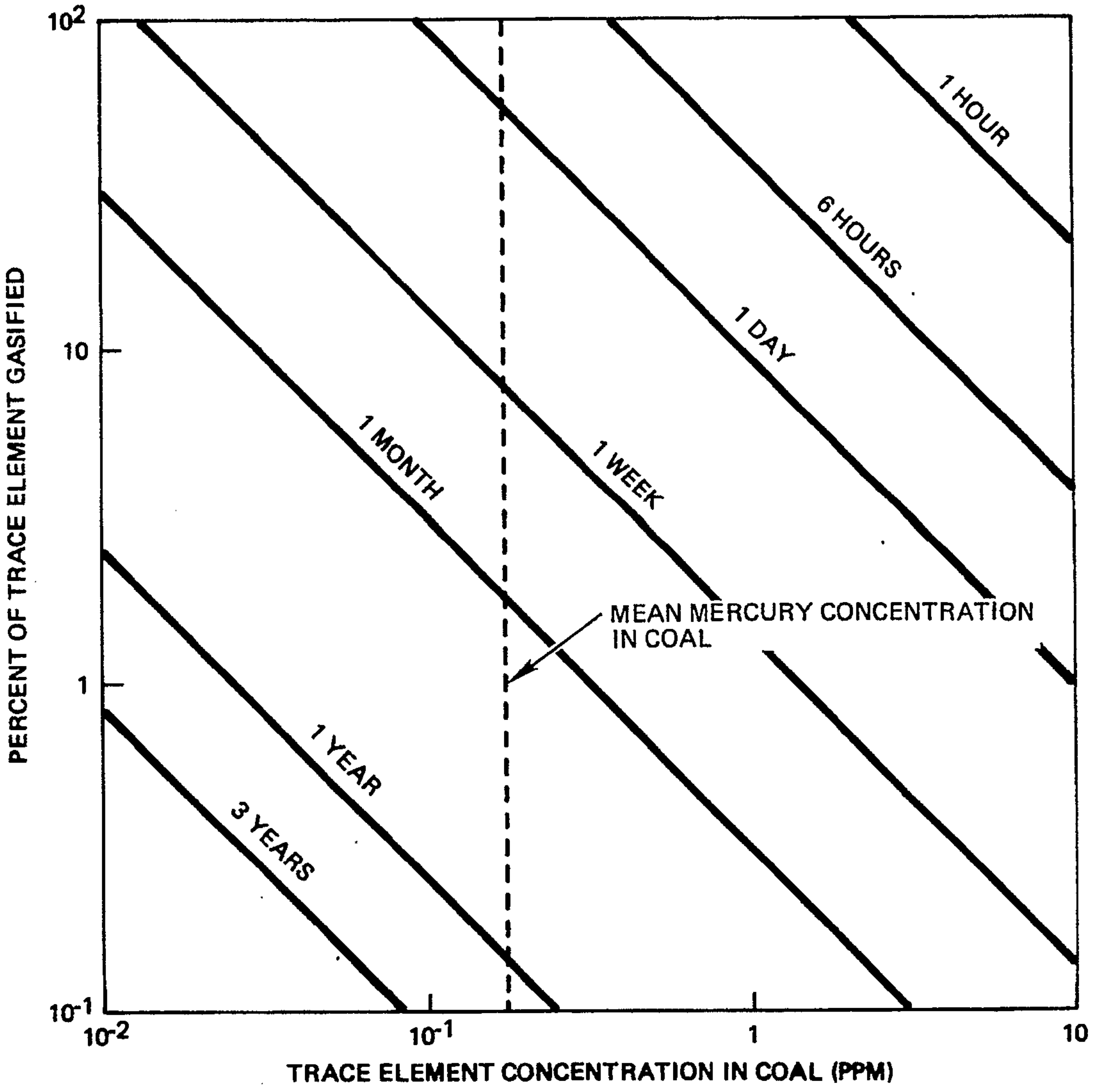

Figure 4. Predicted Shift Catalyst Lifetime Required to Reach RCRA Leachate Standard for Hg (0.2 mg/l) *

* (BASED ON 2 KG RAW COAL GAS PER HOUR PER KG CATALYST)

such as As, Pb, Cr, Hg, and Cd are likely to be catalyst poisons at some levels, and hence catalyst life could actually be shorter than that found in non-coal applications due to deactivation by trace element accumulation. Process designers should be aware of the potential for catalyst deactivation by coal derived trace elements. Finally, it should be mentioned that many catalysts contain metals of commercial value and hence may not have to be viewed as wastes if these metals are reclaimed.

5.0 CONCLUSIONS

(1) Commercial-scale Koppers-Totzek gasification tests with Greek lignite and Illinois #6 coals in Ptolemais, Greece indicate that quenched gasifier slag and dry or wet dust would not be classified as hazardous based upon RCRA leachate criteria for trace elements. However process or wastewaters used to cool or quench solids may introduce toxic constituents.

(2) Calculations indicate that maximum trace element concentrations leachable from Lurgi gasification condensate biological oxidation sludges may exceed 100 times the Primary Drinking Water Standards. Although incineration of the biological oxidation sludge is expected to destroy the toxic organics in the sludge, the incineration residue may still be hazardous.

(3) Certain spent catalysts (e.g., nickel based methanol or methanation catalysts) are expected to be inherently hazardous. High temperature shift catalysts may become hazardous due to accumulation of leachable trace elements through prolonged contact with coal gases.

6.0 RECOMMENDATIONS

(1) Additional RCRA leachate data for gasifier ash and slag produced by various gasification technologies using several coals would be helpful to verify the nonhazardous characteristics of the ash and slag. The presence of toxic organic or inorganic compounds in ash quenched with process wastewater could be indicated by both chemical analyses and bioassay testing of solids and/or leachates.

(2) RCRA leachate data should be collected to determine the hazardous or nonhazardous characteristics of biological oxidation sludges from wastewater treatment. Performance of bioassay tests would

provide information on the trace elements and the nonbiodegradable but toxic organics that might be present in these sludges.

(3) Obtaining RCRA leachate and bioassay data on fresh catalysts would allow determination of the hazardous and nonhazardous characteristics of the basic catalyst materials. RCRA leachate and bioassay data on spent catalysts would provide insight into the potential accumulation of trace elements or toxic organics through contact with coal derived gases.

APPENDIX

EXPECTED CHARACTERISTICS OF LURGI GASIFICATION CONDENSATES

	Rosebud Coal(6)	Illinois #6 Coal(6)	Dunn Lignite Coal(7,8)
Trace Elements (mg/ℓ)			
Ag	0.3	0.1	<0.2
As	0.06	0.03	3
Ba	<0.01	<0.1	--
Cd	0.3	<0.1	0.03
Cr	3	8	<0.03
Hg	0.1	0.4	<0.03
Pb	0.3	3	0.2
Se	0.1	0.25	2
Raw Gas Liquor Production Rate (1000 kg/hr)	304	507	441
Biological Oxidation Sludge Production Rate (kg/hr)	1900	1000	1400

Design Basis - 2.5 x 10^{10} kcal/day energy output from Methanol Synthesis

BIOLOGICAL OXIDATION REMOVAL EFFICIENCIES

Trace Element	Percentage Removal	Reference
Ag	50	(9)
As	25	(10)
Cd	38	(10)
Cr	50	(11)
Hg	65	(11)
Pb	50	(11)
Se	80	(11)

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ASH/SLAG RESIDUALS AND WASTEWATER TREATMENT PLANT SLUDGES FROM SYNFUELS FACILITIES: CHARACTERIZATIONS AND IMPLICATIONS FOR DISPOSAL

by: Ronald D. Neufeld, Associate Professor of Civil Engineering
Georg Keleti, Associate Professor Graduate School of Public Health
J. Bern, C. Moretti, S. Wallach, H. Erdogen, Graduate Students
University of Pittsburgh
Pittsburgh, PA 15261

ABSTRACT

The purpose of this paper is to present an overview of research conducted at the University of Pittsburgh in the area of coal conversion ash and slag. Residuals were obtained from the GFETC "slagging Lurgi type" gasifier (two different runs), METC (Wellman-Galusha type) pressurized gasifier, DOE-Chapman gasifier fly ash, and two H-Coal vacuum bottoms residuals. A first screen bioassay of SRC-II Fort Lewis coal liquefaction residuals and sludges is also presented. In addition, research has been conducted at the University of Pittsburgh for the past few years in the area of developing a stable pretreatment and biological treatment facility for the processing of phenolic type coal gasification wastewaters. During the processing of wastewaters, sludges are produced which are assessed for toxicity, mutagenicity and overall disposability characteristics.

OVERVIEW OF RESULTS

It may be expected that a commercial sized coal conversion facility will produce a variety of solid waste residuals. The wastes generated that may exert the greatest influence on residuals management are: (1,2)

1. COAL PREPARATION PLANT RESIDUALS-to include coal refuse, coal dust and wastewater from the tailing pond

2. COAL GASIFICATION PLANT AREA WASTES-to include residual ash, slag and quench waters

3. STEAM AND POWER PLANT GENERATION WASTES-to include residual ash flue gas desulfurization sludge

4. RAW WATER TREATMENT AREA-to include sludge from solids in the raw water source

5. WASTEWATER TREATMENT PLANT AREA SLUDGES-to include lime sludge, organic sludge, waste biological sludges and oil and tar residuals

6. TAR SEPARATION AREA

7. PHENOL REMOVAL AREA-to include filter backwash and sludges containing phenolics when solid extraction processes are used

8. SULFUR REMOVAL AREA SLUDGES-to include elemental or product sulfur if nonsaleable or stored on site

9. TAILGAS TREATMENT AREA SLUDGES-to include residual sludge materials.

Land disposal of solid residuals is an economically logical choice for an overall management scheme of commercial scale synthetic fuel facility solid wastes. Such land disposal, however, must be done in an environmentally and "RCRA" acceptable manner. Bern et al.(1) have outlined management alternatives that are available to owners of commercial sized synthetic fuels facilities.

Neufeld et al.(2) have reported on chemical and biological properties of coal conversion ash residuals derived from U.S. DOE sponsored large scale coal gasification and direct liquefaction facilities. Characterizations of such solid wastes include proximate analysis, development of natural particle sized distributions, and heavy metal analysis of leachates from each sized fraction. This work showed that the smaller sized fractions yield much greater quantities of heavy metals in derived leachates. In no case did resulting leachates using the EPA "EP" procedures and ASTM-A distilled de-ionized water leaching procedures yield concentrations in excess of one hundred times the concentration of primary drinking water heavy metals; a value above which wastes are determined to be "hazardous". In addition, no coal conversion waste ash or slag residual gave positive result in Ames testing. On the other hand, evidence of Daphnia toxicity was observed in some coal conversion derived leachates.

Wastewater treatment sludges were generated as part of our study of METC gasifier effluent control technology development. Wastewater treatment plant sludges that were studied include lime sludges developed from pH adjustment prior to ammonia stripping, organic sludges developed by filtration and precipitation prior to biological oxidation, and biological sludges from the treatment of fixed bed coal gasification wastewater. Leachates from such sludges are shown to be toxic to <u>Daphnia magna</u> while negative results were observed in Ames testing.

DESCRIPTION OF COAL CONVERSION SOLID RESIDUALS

CHAPMAN (WILPUTTE) GASIFIER

The Chapman fixed bed dry bottom gasification facility at Kings Port, Tennessee produces a low BTU product gas used for combustion fuel. Gas cleaning and purification operations involve cyclone removal of dry particulates and aqueous gas quenching. Solid wastes coming from this facility are gasifier and cyclone ash with cyclone ash being used in our experimental procedures. It should be noted that cyclone ash differs inherently from the more familiar coal combustion facility fly ash in that gasifier particulates have gone through a reducing zone as compared to coal combustion fly ash particulates which go through an oxidizing zone.

GRAND FORKS ENERGY TECHNOLOGY CENTER

The Grand Forks Energy Technology Center has a "Lurgi type" oxygen blown slagging gasifier. Two samples were obtained from this facility, the first being a brown colored slag from run #R-52 using Indian-Head lignite coal, the second being a black colored slag obtained from run #RA-93.

MORGANTOWN COAL CONVERSION FACILITY

The Morgantown Energy Technology Center gasifier is a pressurized "Wellman-Galusha" type of system. The solid waste material obtained was bottom ash/slag from the gasifier when operated using a bituminous coal and was composed of principally large (2") particle sizes.

H-COAL LIQUEFACTION WASTES

The H-Coal process is a direct liquefaction facility developed by Hydrocarbon Research Incorporated. The two H-Coal solid waste samples obtained were both vacuum still bottoms from the direct liquefaction step. One sample was generated from Illinois coal when the system was operated in the "syncrude" mode, while the second sample was generated from Illinois coal when operated in the "fuel oil" mode. These samples will be referred to as "H-Coal #3" and "H-Coal #4". Both H-Coal samples were irregularly shaped black "chunks" of materials with a majority of chunks larger than three inches by three inches.

WASTEWATER SLUDGE SAMPLES

Figure 1 is a flow diagram of the research pretreatment and biological treatment steps associated with the processing of METC coal gasification wastewaters as conducted at the University of Pittsburgh. Wastewater was provided to the University from the hot gas quench of the stirred fixed bed gas producer located and operated by METC. The goal of the treatment processes at the University of Pittsburgh were to develop a linkage of operations that could effectively treat coal conversion wastewaters in a stable fashion. Stability for the bioreactor was defined as occurring when at least three sludge ages had passed.

Table 1 is a characterization of three different shipments of METC wastewaters. The first shipment represents a "nontypical sample" produced at least one year earlier to our testing while the second sample was "more typical" being produced within several months of our evaluations. Sludges for this study are generated from the "typical" wastewater sample.

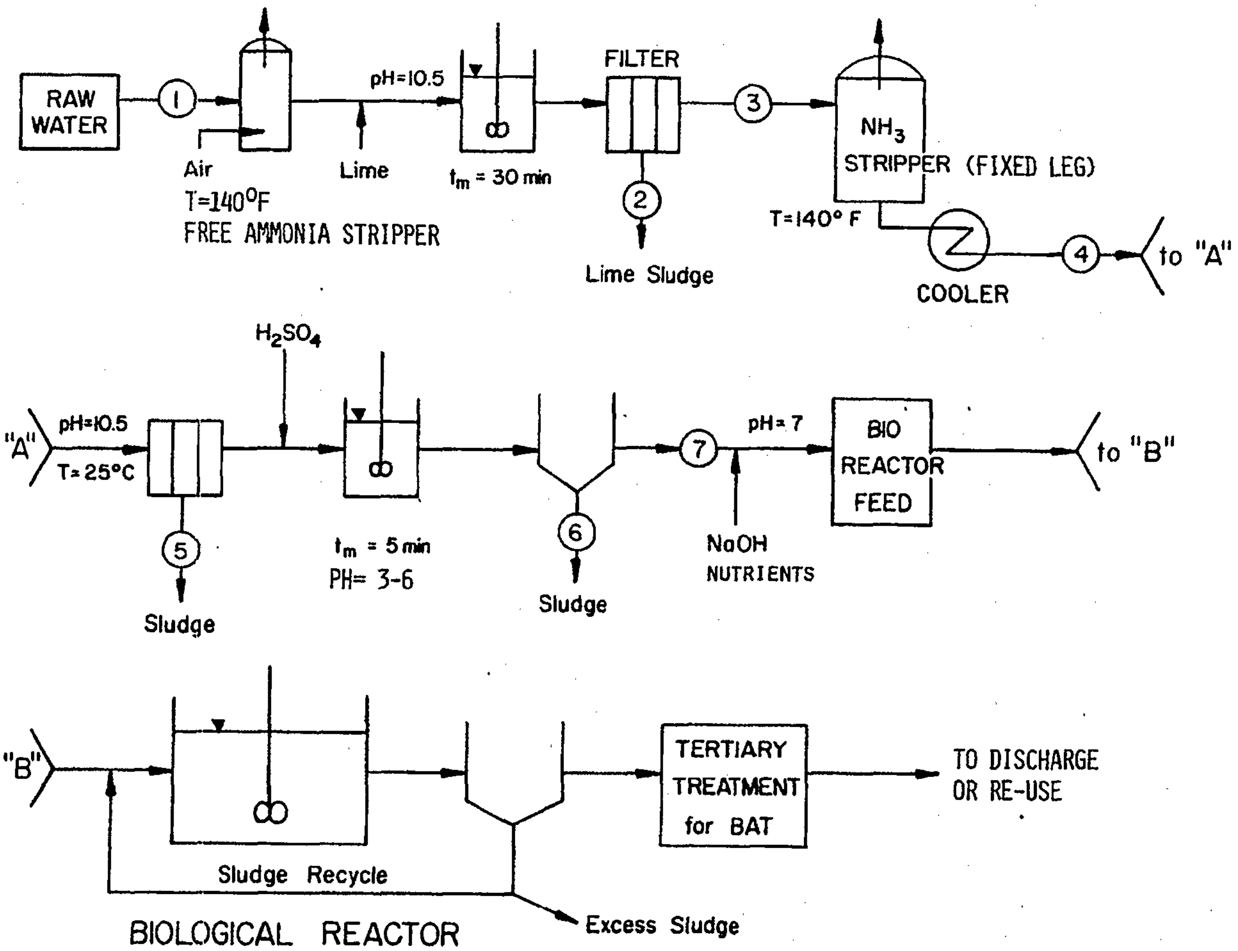

Figure 1. METC Gasifier Wastewater Process Flow Diagram

TABLE 1. METC WASTEWATER CHARACTERIZATION

ITEM	SHIPMENT #1 (AGED SAMPLE) CONCENTRATION	SHIPMENT #2 RUN 94 CONCENTRATION	SHIPMENT #3 RUN 95 CONCENTRATION
PHENOL	970 MG/L	2,375 MG/L	3,750 MG/L
COD	53,024 MG/L	13,350 MG/L	12,750 MG/L
TOC	14,102 MG/L	5,374 MG/L	5,390 MG/L
TIC	30 MG/L	242 MG/L	4,350 MG/L
TOTAL RESIDUE	72,334 MG/L	1,349 MG/L	4,420 MG/L
FIXED RESIDUE	1,334 MG/L	143.2 MG/L	630 MG/L
VOLATILE RESIDUE	71,000 MG/L	1,205.8 MG/L	3,790 MG/L
FREON SOL. OIL & GREASE	356 MG/L	1,495.0 MG/L	----
ACETONE SOL. OIL & GREASE	1,633 MG/L	106.3 MG/L	----
pH	7.5	8.0	8.8
ALKALINITY (pH 4.5)	2,100 MG/L	23,750 MG/L	21,855 MG/L
SCN	----	372 MG/L	----
NH_3	11,000 MG/L	3,200 MG/L	7,000 MG/L
PHENOL/TOC RATIO	.069	.44	.70

The pretreatment train used to treat coal conversion waters, and to develop sludges within our laboratory represent a linkage of steps as follows:

Step 1-Free Ammonia Leg

This is accomplished in a laboratory via aerating a 15 to 20 gallon batch of wastewater at a temperature of 60°C. Such aeration liberates noticeable quantities of H_2S, volatile organics, free ammonia, and results in a reduction in the overall alkalinity of solution, thus minimizing lime requirements for the fixed leg.

Step 2-Lime Addition

Lime (as CaOH) is added to the wastewater in sufficient quantities to bring the pH to a range of 10 to 11.

Step 3-Filtration to Remove Lime Sludge

A large Buchner funnel with coarse grade filter paper is utilized to remove precipitated lime. The resultant sludge is brown in color, and contains organic materials. This sludge, referred to as "lime sludge", was subsequently dried and leached in accordance with the EPA "EP" and ASTM-A extraction procedures and tested for heavy metal content and toxicity to *Daphnia magna*.

Step 4-Fixed Leg Ammonia Stripping

Ammonia is stripped at 140°F and pH 10½ batchwise in a 15 gallon stripper to simulate commercial scale fixed leg ammonia stripping. The wastewater is kept in the ammonia stripper until the total ammonia in solution reaches about 100 mg/l. The wastewater is then removed from the ammonia stripper and placed into a large glass jar where it is subsequently air cooled.

Step 5-Filtration

After ammonia stripping, the wastewater is pH adjusted using sulfuric acid. Polymerization of trace organics appears to take place in the stripper thus resulting in an organic sludge formation which is filtered out prior to subsequent biological oxidation. Our approach is to remove the maximum quantity of organics possible prior to biological oxidation via judicious pH adjustment, flocculation and filtration. This sludge, called an "alum sludge" (due to the addition of alum to promote coagulation/floculation) was also tested in this study for leachate evaluations using *Daphnia magna* and atomic adsorption spectrosocopy.

Step 6-Biological Reaction Phase

Pretreated wastewater is diluted as desired and fed on a continuous basis to completely mixed activated sludge type bio-reactors with hydraulic detention times of 1.0 days and sludge ages in the range of 20 days. During one of our studies, a maximum of 60% wastewater diluted with tap water was utilized. Phase II of our present study is an attempt to minimize dilution water requirement in the biological reaction phase. Biological sludges harvested from the activated sludge reactors are being subjected to Ames testing, Daphnia toxicity testing and extensive chemical evaluations during the current phase of study.

PHYSICAL/CHEMICAL ANALYSIS OF ASH/SLAG SOLID WASTE RESIDUALS

All samples, with the exception of the lime and alum sludges from the wastewater treatment train, were subjected to particle size distribution analysis without altering the nature of samples. The philosophy of this approach was to more properly reflect that which would be placed in landfill systems; thus, crushing and grinding were not done. H-Coal samples were subjected to crushing and grinding because of the rather large chunks of materials received.

All sieving was conducted with U.S. standard sieves #'s 10, 20, 40, 60, 100 and 200 for sufficient duration to collect enough sample of each size fraction as required for leaching tests.

Samples of each of the mesh sizes were subjected to leaching via the ASTM-A leaching procedure and current EPA-EP leaching test and a self designed "University of Pittsburgh" procedure using pH=2 HNO_3. A portion of the leachates were segregated for heavy metal AA analysis, and Daphnia magna evaluations.

DAPHNIA TOXICITY EVALUATIONS

Acute toxicity testing was conducted on generated sludge using Daphnia magna standarized procedures outlined in Standard Methods, and in draft ASTM procedures. It should be noted, however, that all samples of leachates were adjusted to a pH between 7.4 and 7.6 before being subjected to the Daphnia magna testing. The philosophy of our approach is not to evaluate the toxicity of H^+ and OH^-, but rather than to evaluate the toxicity of constituents contained in the leachates. Figure 2 is a typical plot of data showing conductivity of GFETC lignite slag leachates as a function of particle size of solid waste. As may be seen from this figure, smaller particle sizes tend to leach greater quantities of dissolved materials than larger particles. The differences in conductivity value from one test to another is a function of water to solid ratio and additives specific to each leaching procedure.

Table 2 is a summary of GFETC solid waste heavy metal constituents in leachates as a function of the leaching test procedures also showing smaller particle sizes leaching greater quantities of specific key metals. For comparison purposes, table 3 list results of leaching tests using "H-Coal #3" solid waste samples. Similar data was developed for the H-Coal #4, METC and Chapman leachates, as was done to the GFETC leachates. Table 4 is a summary of the compositional results of leaching of lime and alum sludges produced from the treatment of METC gasification wastewaters.

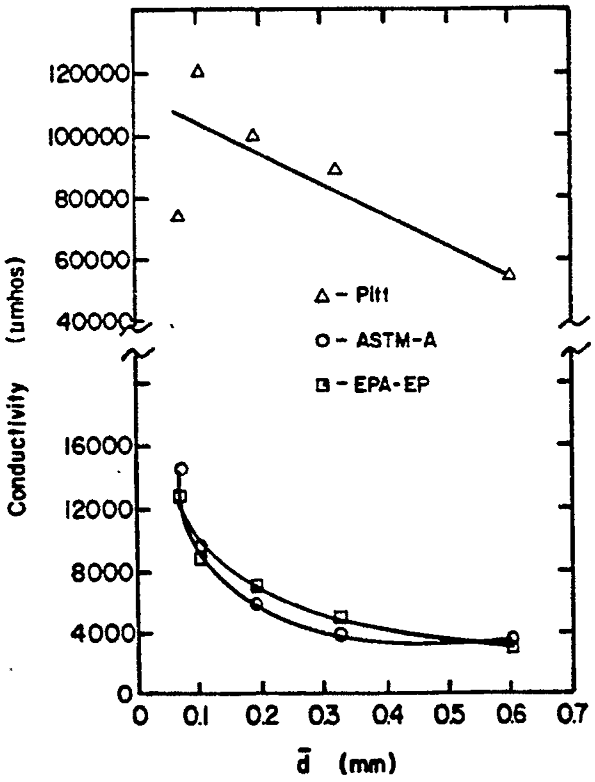

Figure 2. Conductivity Data - GFETC NO. 1
(Gasifier Bottom Slag from RA-52 Using Lignite Coal)

TABLE 2. RESULTS OF LEACHING TESTS - GFETC
(GASIFIER BOTTOM SLAG FROM RA-52 UAING LIGNITE COAL

Metal Concentrations (all units mg/l)

Test Procedure	Mesh Size	pH	Ag	Be	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Pb	Zn
ASTM-A	20-40	9.62	0	0	196	0	0	0	0	1.7	0	0	0.1
ASTM-A	40-60	9.25	0	0	220	0	0	0	0	1.8	0	0	0.1
ASTM-A	60-100	9.01	0	0	300	0	0	0	0	1.8	0	0	0.3
ASTM-A	100-200	8.80	0	0	380	0	0	0	0	2.1	0	0	0.4
ASTM-A	<200	8.58	0	0	580	0	0	0	0	2.2	0	0	0.7
EPA-EP	20-40	4.97	0	0	344	0	0	0	84	75	0.8	0	0.3
EPA-EP	40-60	4.98	0	0	540	0	0	0	96	90	1.6	0	0.3
EPA-EP	60-100	5.44	0	0	800	0	0	0	165	100	1.8	0	0.4
EPA-EP	100-200	5.66	0	0	1140	0	0	0	78	105	2.9	0	0.4
EPA-EP	<200	5.76	0	0	1440	0	0	0	93	105	5.3	0	0.9
PITT	20-40	2.03	0	0	2870	0	0	0	420	1200	2.9	0	0.7
PITT	40-60	1.70	0	0.5	4800	0	0	0	540	1980	4.4	0	1.3
PITT	60-100	1.64	0	0.5	5400	0	2.5	0	680	2200	5.0	1.5	1.4
PITT	100-200	1.69	0	0.8	6400	0	3.7	0	1040	2940	8.0	1.5	2.3
PITT	<200	1.74	0	0.5	3920	0	3.7	52.8	2150	1700	10.5	1.5	39.0

TABLE 3. RESULTS OF LEACHING TESTS - H-COAL #3
(LIQUEFACTION VACUUM STILL BOTTOMS FROM SYNCRUDE MODE USING ILLINOIS COAL)

Metal Concentrations (all units mg/l except Hg - ug/l)

Test Procedure	Mesh Size	pH	Ag	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Zn
ASTM-A	20-40	11.03	0	0	130	0	0	0	0	0.6	0.2	0	0	0
ASTM-A	40-60	11.22	0	0	160	0	0	0	0	0.3	0.3	0	0	0.1
ASTM-A	60-100	11.33	0	0	190	0	0	0	0	0.6	0.4	0	0	0.1
ASTM-A	100-200	11.48	0	0	300	0	0	0	0	0.3	0.4	0	0	0.3
ASTM-A	<200	11.49	0	0	370	0	0	0	0	0.3	0.3	0.2	0	0.6
EPA-EP	20-40	4.96	0	0	150	0	0	0	1.1	0	1.0	1.0	0	0
EPA-EP	40-60	4.90	0	0	220	0	0	0	2.0	0	1.2	1.4	0	0
EPA-EP	60-100	4.88	0	0	320	0	0	0	3.4	0	1.7	2.3	0	0.1
EPA-EP	100-200	4.87	0	0	400	0	0	0	4.8	0.3	2.0	2.9	0	0.3
EPA-EP	<200	4.91	0	0	420	0	0	0	4.8	0	2.0	2.9	0	0.4
PITT	20-40	1.72	0	0	184	0	0	0.9	7.0	0.3	1.4	1.2	0	0.3
PITT	40-60	1.74	0	0	270	0	0	1.3	10.0	0	1.7	1.6	0	0.3
PITT	60-100	1.76	0	0	340	0	0	1.3	15.0	0.3	1.9	2.3	0	0.4
PITT	100-200	1.77	0	0	430	0	0	1.3	33.0	0.3	4.8	3.1	0	0.4
PITT	<200	1.71	0	0	410	0	0	1.3	32.0	0.3	5.5	2.9	0	0.4

TABLE 4. RESULTS OF LEACHING TESTS - LIME AND ALUM SLUDGES
(FROM TREATMENT OF METC WASTEWATER

Concentrations (all units mg/l)*

Material	Test Procedure	pH	Ca	Cd	Cu	Fe	Mg	Zn	Conductivity (umhos)	TOC (mg/l)	Phenol (mg/l)
LIME	ASTM-A	11.84	640	0	0	1.4	0.1	0	4800	1590	720
LIME	EPA-EP	7.29	1620	0.1	0	0.8	26	0.2	6400	2630	155
ALUM	ASTM-A	7.75	340	0	0	7.0	176	0	5300	1960	1550
ALUM	EPA-EP	6.92	1800	0	0.3	0.8	26	0.4	7100	2800	455

*Ag, Be, Cr, Mn, Pb below detectable limits

Figure 3 is a plot of Daphnia toxicity information for leachates derived from the EPA-"EP" extraction procedures utilizing the smallest and largest particle sizes of GFETC solid waste residuals. The 48 hour LC-50 values for the largest particle size is 8.9% dilution, while for the smallest particle size, is 7.0% dilution. In a summary of LC-50 data on table 5, ASTM-A distilled water leaching protocol always showed LC-50 values on the order of 100% dilution with lower values for the EPA-EP test. It may thus be concluded that the inherent nature of the EPA-"EP" procedure using acetic acid causes Daphnia toxicity, thus raising questions as to the validity of the application of Daphnia toxicity testing to leachates produced in accord with the EPA approach. Evaluation, however, of Daphnia toxicity to acetic acid reagents as used in the EPA extraction procedure test where no solid wastes are leached (after neutralization) show the LC-50 value to be 85% in concentration and thus do not explain the total toxicity of EPA leachates of solid wastes to Daphnia. It was noted from this and a series of similar tests, that results using EPA extraction procedure protocols appear far more toxic to Daphnia in all cases than results using the ASTM-A "distilled water" approach.

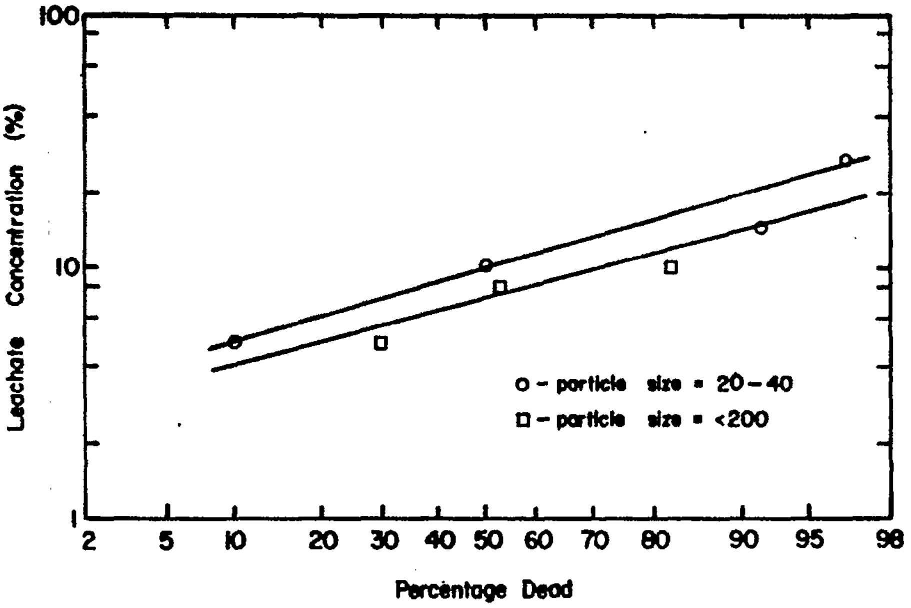

Figure 3. _Daphnia_ Toxicity Data From GFETC NO. 1 EPA-EP LEACHATES

TABLE 5. RESULTS OF _DAPHNIA MAGNA_ TOXICITY TESTING

Material	Test Procedure	Mesh Size	48hr LC50 %	95% Confidence Limits	
				UCL	LCL
CFA	ASTM-A	20-40	>100	--	--
CFA	ASTM-A	<200	>100	--	--
CFA	EPA-EP	20-40	2.9	3.4	2.4
CFA	EPA-EP	<200	4.8	5.8	3.9
H-COAL #4	ASTM-A	20-40	>100	--	--
H-COAL #4	ASTM-A	<200	>100	--	--
H-COAL #4	EPA-EP	20-40	2.0	2.5	1.6
H-COAL #4	EPA-EP	<200	1.8	2.3	1.4
H-COAL #3	ASTM-A	20-40	>100	--	--
H-COAL #3	ASTM-A	<200	>100	--	--
H-COAL #3	EPA-EP	20-40	22	27	18
H-COAL #3	EPA-EP	<200	23	29	18
GFETC #1	ASTM-A	20-40	>100	--	--
GFETC #1	ASTM-A	<200	>100	--	--
GFETC #1	EPA-EP	20-40	8.9	11.1	7.1
GFETC #1	EPA-EP	<200	7.0	8.0	6.1
GFETC #2	ASTM-A	< 60	>100	--	--
GFETC #2	EPA-EP	< 60	11.2	12.6	9.9
METC	ASTM-A	> 10	>100	--	--
METC	ASTM-A	< 60	>100	--	--
METC	EPA-EP	> 10	0.28	0.37	0.20
METC	EPA-EP	< 60	0.12	0.17	0.09
LIME SLUDGE	ASTM-A	--	1.4	1.6	1.2
LIME SLUDGE	EPA-EP	--	4.3	5.2	3.6
ALUM SLUDGE	ASTM-A	--	0.74	0.82	0.67
ALUM SLUDGE	EPA-EP	--	1.6	1.7	1.4
ACID CONTROL	---	--	85	95	76

Table 5 also indicates that Daphnia, toxicity to wastewater treatment sludge leachates are far more toxic than leachates produced from gasification bottom ash or slag residuals. As one illustration, figure 4 is a plot of Daphnia toxicity from leachates produced from lime sludges generated from the waste treatment scheme when processing METC fixed bed coal conversion wastewaters. As can be seen, despite the numerical difference of results when leaching via the EPA or the ASTM-A approach, toxicities of waste treatment plant sludges are considerably greater than toxicities of ash/slag leachates. It should be noted, however, that in no case did primary drinking water heavy metals exceed 100 times drinking water standards; thus implying that such sludges are not to be considered as hazardous in a "RCRA" context.

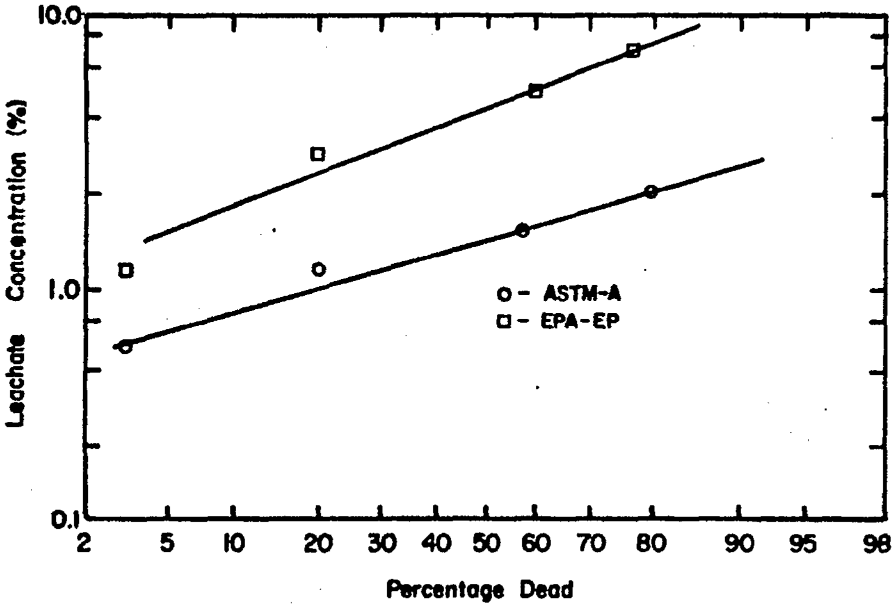

Figure 4. Daphnia Toxicity Data From Lime Sludge Leachates

CORRELATION OF DAPHNIA TOXICITY DATA WITH CHEMICAL COMPOSITION DATA

Biesinger (3) published Daphnia magna 48 hour LC-50 data for various primary and secondary EPA drinking water metals. Figure 5 is our plot of Biesinger's data illustrating that an empirical relationship exists for most heavy metals with EPA drinking water standards. It should be noted that drinking water standards are not based upon Daphnia magna toxicity data, and the correlation illustrated on figure 5 is quite emperical. The outlier points for copper and zinc represent the extreme toxicity of these metals to Daphnia magna, and lack of such toxicities to mammals and humans in specific.

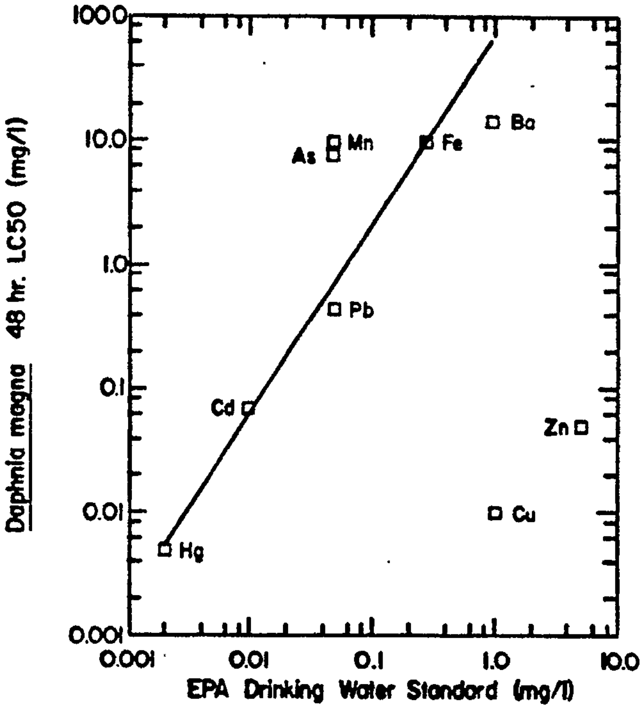

Figure 5. Correlation Between Daphnia Toxicity and Drinking Water Standards

In an attempt to correlate LC-50 data with metal characterization data of leachates, measured metal concentrations were weighted to account for the fact that some substances are more toxic to Daphnia magna than are other metals. The weighting procedure used was based upon the following equation:

$$\Sigma M = (Ca/Ca_o)+(Cd/Cd_o)+(Cu/Cu_o)+(Fe/Fe_o)+(Mg/Mg_o) +(Mn/Mn_o)+(Pb/Pb_o)+(Zn/Zn_o)$$

The numerator for each metal is the metal concentration for leachates as measured, and the denominator represents data published by Biesinger (3). The resultant equation, for application to data developed in this research is:

$$\Sigma M = (Ca/52)+(Cu/0.01)+(Fe/9.6)+(Mg/140) +(Mn/9.8)+(Zn/0.1)$$

Figure 6 is a correlation of Daphnia toxicity LC-50 values as measured in the course of this research with the measured weighted metal concentrations (ΣM) for leachates generated from coal conversion ash and slag residuals. The correlation with trace metals did not hold for wastewater treatment plant sludges, however, as shown on figure 7, LC-50 values for Daphnia toxicity are correlated with phenol concentrations measured in the ASTM-A and EPA "EP" leaching protocols of generated lime and alum wastewater treatment sludges.

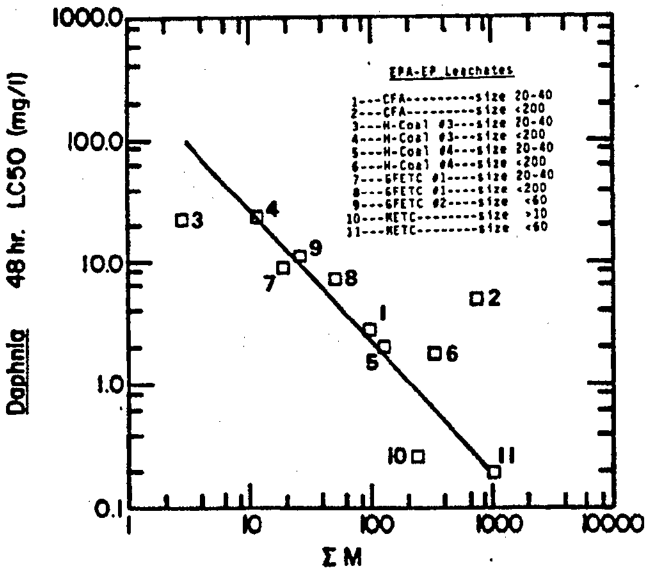

Figure 6. Relationship Between Daphnia Toxicity and Weighted Metal Concentrations of Ash and Bottom Leachates

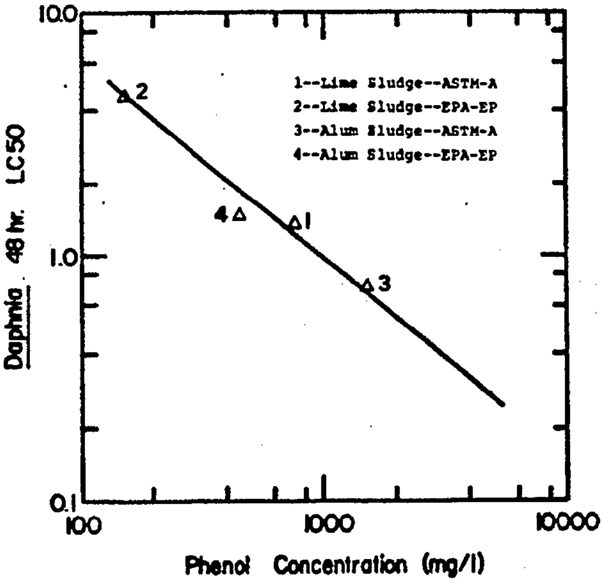

Figure 7. Relationship Between Daphnia LC50 Data and Phenol Concentration of Sludge Leachates

AMES TESTING FOR MUTAGENICITY POTENTIALS

SRC-II solid wastes generated at the Ft. Lewis pilot plant were provided by the Pittsburgh and Midway Coal Company under the guidance of the U.S. Department of Energy, Pittsburgh Energy Technology Center. The samples received were two shipments of vacuum bottoms from the vacuum flash drum of the direct liquefaction step, and wastewater sludges consisting of alum sludge from the pre-biological (flotation) step, waste activated biological sludge, and digested activated biological sludge. These samples were subjected to simple chemical screening analysis and Ames testing for potential mutagenicity. Both whole materials and liquid phases filtered from whole materials (for clarifier and digester biosludges) were evaluated for mutagenicity. In addition, a serial organic extraction protocol was developed using hexane, toluene, methylene chloride, and acetonitrile to gain a qualitative assessment of the polarity and chemical nature of leached substance causing mutagenicity. For clarifier and digester biosludges, both liquid and solid phases of filtered sludges were analyzed for Ames mutagenicity. It is interesting to note that in all cases, the filtrate of sludge samples showed negative Ames results while the whole sample and retained filtered solid samples showed positive results. Samples of the dried sludge were processed by sequential organic extraction as outlined above to generate four additional extracts and residue for testing. Five tester strains, TA98, TA100, TA1535, TA1537 and TA1538 were employed in the tests with and without microsomal activation. Routine sterility and toxicity checks were made during the course of the run. It was found that none of the mutagenicity tests which used TA1535 without S9 and TA1537 with S9 resulted in positive plates in early phases of the investigation, therefore, TA1535 was eliminated from all tests and TA1537 were not used when microsomal activation was applied.

The standard criteria used to define a positive result in the Ames bioassay for mutagenic activity include (a), a two-fold or greater increase in the number of revertants exposed to the test material compared to respontaneous revertant rates; (b), repeatability i.e...a confirmation of the positive result by running the test again after a two week period; (c), for compounds of low mutagenicity, a reproducible dose response rate.

Ames test results were uniformly negative where microsomal activation was not included in the test procedures. The most sensitive tester strain showing the greatest number of revertants compared to the spontaneous revertant rate is shown to be strain TA98 with S9, a result which agrees with other investigations. All other tester strains showed marginal positive results.

Toxicity to the tester organisms by test materials was encountered in all of the individual bioassays with alum sludges showing perhaps the highest toxicity. It is hypothesized that this may be due to either organics, or to the fine alum "slime" particles which interfered with growth of revertants.

The highest mutagenicity activity observed (revertants per mg) were exhibited by the vacuum bottoms solid wastes. Vacuum bottoms solid wastes contain organics that are not highly water soluble and thus the probability of release in a landfill is small. Clearly, mutagenic substances exist on these solid waste residuals as evidenced by conducting Ames testing of whole materials dissolved in organic solvents, but aqueous leachates show no mutagenic activity. Philosophical questions are raised leading to a need for policy delineation by EPA as to the acceptability of disposing of such materials in hazardous or conventional waste landfills.

Table 6 is a summary of Ames test results using tester strains TA98 with S9 activation. It should be noted that the average number of revertants for the control is 46 with standard deviation of 16. This table shows the whole vacuum bottoms residual gave rise to 13.2 times the number of revertants on a negative control plate (spontaneous revertants) for sample number 1936, while for vacuum bottoms sample number 2277 (sample numbers provided by the Pittsburgh and Midway Coal Mining Company), a ratio of 21.4 times spontaneous revertants were observed. As can be seen from this table, from a column of data using whole substances, the vacuum bottoms from the SRC-II Ft. Lewis facility show far more mutagenicity than do the other solid residuals measured. All solid residuals, as observed from the Ft. Lewis facility, give rise to positive mutagenicity potentials as determined by criteria of values being greater than 2 times the spontaneous revertants indicating positive Ames tests.

TABLE 6. AMES TESTING OF SRC-II FORT LEWIS SOLID WASTE RESIDUALS AND EXTRACT FRACTIONS

				ORGANIC SOLVENT EXTRACT FRACTIONS									
TEST SAMPLE	SAMPLE NUMBER	WHOLE*		HEXANE		TOLUENE		METHYLENE CHLORIDE		ACETONITRILE		RESIDUE	
		rev/mg	(R)	rev/mg	(R)	rev/mg	(R)	rev/mg	(R)	rev/mg	(R)	rev/mg	(R)
VACUUM BOTTOMS	1936	2875	13.2	11600	16.6	3695	39.4	2365	13.6	20330	25.5	560	2.5
	2277	11095	21.4	2567	15.6	12200	44.0	5552	13.8	9578	19.9	NM	2.0
ALUM SLUDGE	2280	7705	3.0	NM	NM	NM	NM	1987	5.1	1295	4.5	NM	NM
CLARIFIER SLUDGE	1937	4050	5.8	1268	3.9	1290	3.9	1349	5.0	14720	31.0	NM	NM
	2278	932	3.8	NM	NM	NM	NM	960	2.4	NM	NM	NM	NM
DIGESTER SLUDGE	1938	530	6.2	236	2.6	984	2.8	NM	NM	NM	NM	NM	NM
	2279	1273	2.8	NM	NM	2803	2.4	868	2.5	NM	NM	247	2.5

NOTE:
* "Specific Mutagenic Activity" for Vacuum Bottoms in revertants/mg for all other whole materials (sludges) in revertants/ml.
NM Not Mutagenic
R Ratio of revertants on test plate (spontaneous + induced)/spontaneous revertants on control plate

Work is continuing at the University of Pittsburgh in the area of evaluating mutagenicity potentials of wastewater sludges and their leachates when treating GFETC wastewaters, and the evaluations of methodologies of changing the pretreatment and biological treatment step to minimize such mutagenicity and toxicity potentials.

RESEARCH IN COMPUTER MODELING OF LEACHATE CONCENTRATIONS AT LANDFILL BOUNDARIES

A series of five simultaneous differential equations utilizing concepts of diffusivity, film diffusion, intraparticle diffusion and liquid-solid equilibria has been developed for the prediction of leachate compositions at the boundary line from a landfill containing coal gasification solid waste residuals. The model is based upon deterministic concepts and simple equilibrium and diffusion data and was calibrated in the lab using GFETC #1 slag residuals. The system of simultaneous differential equation has been solved using numerical computational methods.

This model has been extrapolated from lab scale to predict concentration profiles of a commercial scale landfill (600 meters x 600 meters x 6 meters deep) filled with coal conversion solid wastes. Under the assumption of unidirectional flows and small fluid velocity, profiles of concentration with duration at the landfill boundary were computed. As an example of the results of computer modeling, figure 8 is a plot of predicted concentration in leachates versus time for a coal conversion solid waste landfill where particle sizes are in range of 20 to 40 mesh at flooded conditions with indicated groundwater velocities through the landfill site.

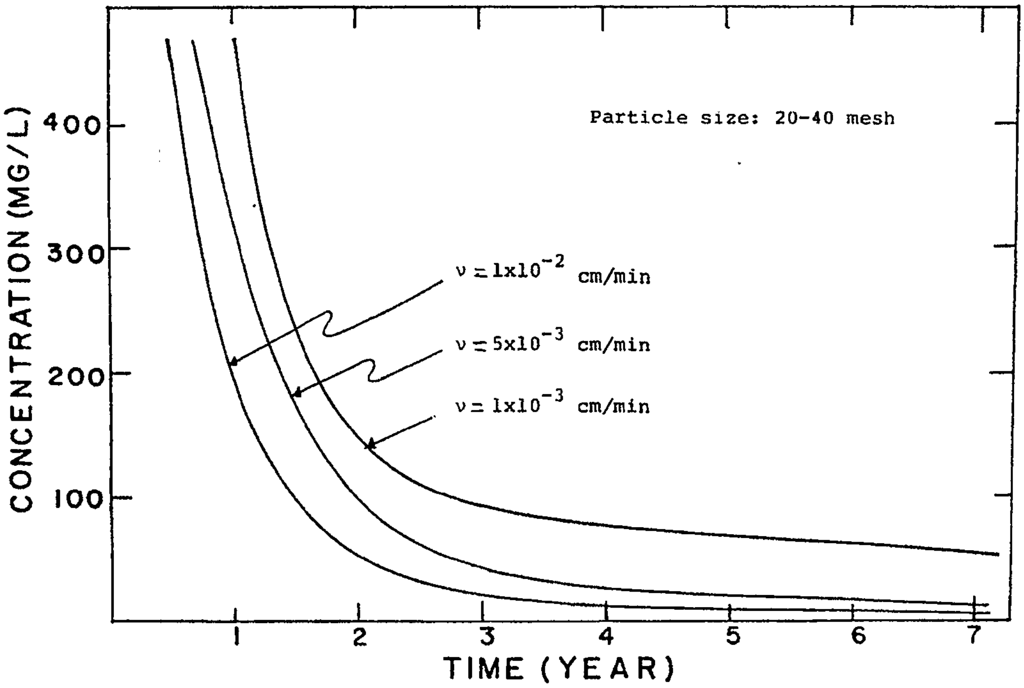

Figure 8. Calculated Calcium Concentration Profiles for a Landfill

By understanding the concepts and implications of intraparticle diffusion, figure 9 was developed for conditions of discontinuous flow. The breaks in the curve indicate periods of "no rain" or dry conditions. This figure illustrates the concept of "a first flush phenomena" by showing that under flooded conditions, steady state mass transfer from the solid phase to the liquid phase occurs, and is predictable. Under dry conditions, however, concentration of leachable pollutants at the particle surface increases with time to become uniform throughout due to intraparticle diffusion. The first flush phenomena, as shown on figure 9, predicts an increase in aqueous concentration over that which would be ordinarily expected under the flooding conditions shown in figure 8. The overall area under all the curves of figure 9 is proportional to the total quantity of leachable substances produced. As can be seen, commensing of flooding causes high excursions in aqueous concentration; this concept we call a "first flush phenomena". This model may predict difficulties in compliance with concentration restrictions as outlined by RCRA regulations for ash/slag landfills under conditions of "first flush" or discontinuous flows. Additional details are available in a dissertation by Erdogan (4).

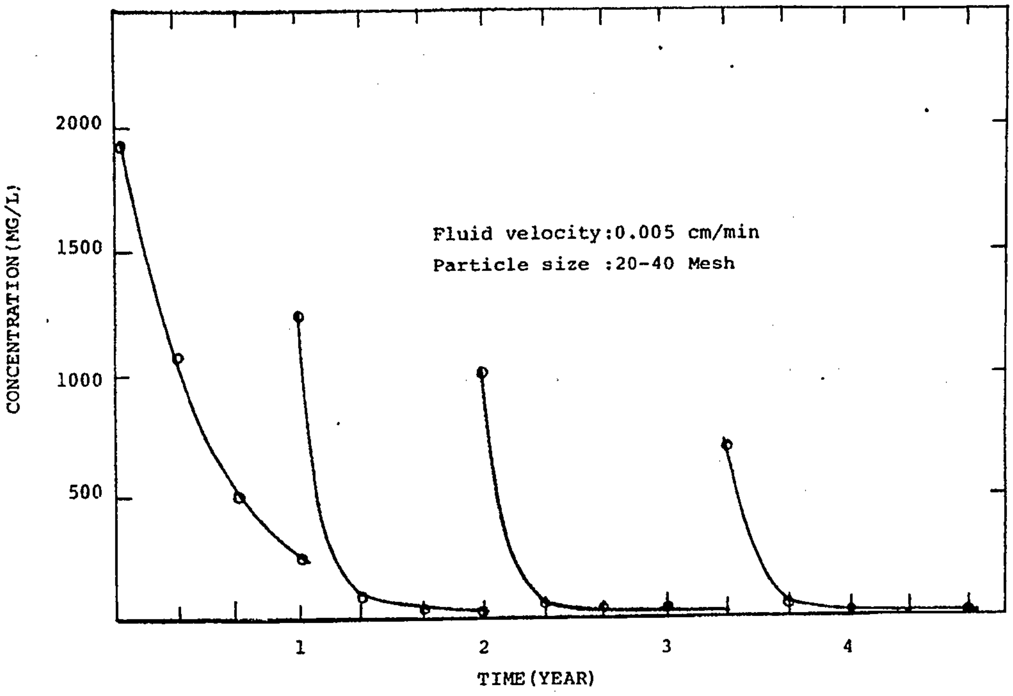

Figure 9. Predicted Concentration Profile for a Landfill with Discontinuous Flow

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The Senior Author would like to thank the Grand Forks Energy Technology Center for solid waste samples and for support of Mr. S. Wallach who conducted Daphnia toxicity evaluations, Mr. H. Erdogan who conducted mathematical modeling of solid waste residuals, Mr. J. Bern who conducted Ames toxicity testing and developed concepts for disposal of solid waste residuals. The Morgantown Energy Technology Center provided wastewater and supported Mr. C. Moretti, Graduate Student, who conducted treatability evaluations of METC gasifier wastewater and developed the wastewater sludges used in this research. The Pittsburgh Energy Technology Center provided supported testing and provided samples of SRC-II solid waste residuals for Ames test evaluation as conducted under the supervision of Dr. Keleti at the Graduate School of Public Health.

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UPDATE ON EPA'S REGULATORY VIEWS ON COAL CONVERSION SOLID WASTES†

by: Yvonne M. Garbe
Office of Solid Waste
U.S. Environmental Protection Agency
Washington, DC 20460

ABSTRACT

The Resource Conservation and Recovery Act of 1976 (RCRA) charges EPA with the responsibility for establishing a program for the management of hazardous solid wastes. This paper summarizes current and anticipated RCRA regulations affecting the synfuels industry. Included in the various RCRA issues pertaining to the synfuels industry is a discussion of the RCRA mining exemption. An overview is given of the Office of Solid Waste's planned research activities to support future synfuels solid waste regulations.

(Only the abstract is published herein.)

Session V: MULTIMEDIA ENVIRONMENTAL CONSIDERATIONS

Chairman: T. Kelly Janes
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Research Triangle Park, NC

Cochairman: John T. Dale
U.S. Environmental Protection Agency, Region VIII
Denver, CO

A PERMITTER'S VIEW OF SYNFUEL COMMERCIALIZATION†

by: George L. Harlow
Air and Hazardous Materials Division
U.S. Environmental Protection Agency
Region IV
Atlanta, GA 30365

ABSTRACT

The Environmental Protection Agency has responsibility for the issuance of permits to synfuel plants for the control of various liquid, gaseous, and solid waste streams. These permits comprise the Prevention of Significant Deterioration (PSD) under the Clean Air Act of 1977, the National Pollutant Discharge Elimination System (NPDES) and the Section 404 Dredge and Fill permits under the Clean Water Act of 1977 and the hazardous waste permits under the Resource Conservation and Recovery Act (RCRA) of 1976.

Since there will likely not be federal regulations established by EPA setting standards on requirements for the first generation synfuel plants, the environmental permits will have to be individually negotiated, case by case, with each applicant using best engineering practice. This places an unusual burden upon the permit writer who will be negotiating with the discharger from an uninformed and defenseless position. In order to overcome this burden and to avoid long, time-consuming delays in the permit process, the company should disclose in its application for permit exactly what steps will be taken to control air emissions, water discharges and hazardous wastes.

(Only the abstract is published herein.)

PB83-128413

COMPARISON OF ENVIRONMENTAL DESIGN ASPECTS † OF SOME LURGI-BASED SYNFUELS PLANTS

Milton R. Beychok, Consulting Engineer
William J. Rhodes, EPA/IERL-RTP

INTRODUCTION

A number of commercial-scale projects have been proposed in the United States for the production of gas and liquid synfuels from coal. Many of these proposed projects are planning to use Lurgi coal gasifiers and related Lurgi technology such as the Rectisol gas purification process and the Phenosolvan process for recovering phenols from coal gasification wastewaters. These projects represent several different architectural and engineering contractors and, therefore, probably different design philosophies and preferences. As a result, a comparison of how each contractor handled some of the environmental concerns would indicate a segment of industry's views on plant configurations and control alternatives.

Table 1 identifies 14 Lurgi-based synfuels projects which are currently being proposed, studied, or underway in the United States. In terms of their design progress, their environmental permitting status, and their investment financing arrangements, the most advanced project among those listed in Table 1 appears to be the Great Plains Gasification Associates' project in North Dakota. Some of the other projects have completed fairly detailed feasibility studies and have prepared environmental impact studies as well as environmental permitting applications. However, none of the other projects appear to be as well advanced as the Great Plains project in North Dakota.

Process design information has been obtained for five of the projects listed in Table 1[1 – 9], and this paper describes and compares the key environmental design aspects and features of these five projects:

- The Great Plains Gasification Associates' project in North Dakota (initiated by the American Natural Gas Service Company).
- The Hampshire Energy Company's project in Wyoming.
- The Nokota Company's project in North Dakota (initiated by the Natural Gas Pipeline Company of America).
- The Tenneco project in Montana (known as the Beach-Wibaux project).
- The WyCoalGas, Inc. project in Wyoming (a subsidiary of Panhandle Eastern Pipe Line Company).

TABLE 1. PROPOSED COAL GASIFICATION PROJECTS PLANNING TO USE LURGI GASIFIERS

PROJECT SPONSOR	LOCATION	TYPE OF GASIFIERS	TOTAL COAL, T/D (Mg/D)	A&E CONTRACTOR	PRIMARY PRODUCTS
Tri-State Synfuels	Kentucky	Lurgi	28,000 (25,400)	Fluor	High-Btu SNG, gasoline, and chemicals
Louisiana Gasification Associates	Louisiana	Lurgi	n.a.	n.a.	Synthesis gas
Crow Indians	Montana	Lurgi	12,000 (10,900)	Fluor	High-Btu SNG
Tenneco Coal Gasification	Montana	Lurgi	41,000 (37,200)	Fluor	High-Btu SNG
Texas Eastern Synfuels	New Mexico	Lurgi	30,000 (27,200)	Bechtel	High-Btu SNG and methanol
Great Plains Gasification Associates	N. Dakota	Lurgi	28,700 (26,000) [b]	Lummus	High-Btu SNG
Nokota Company	N. Dakota	Lurgi	42,000 (38,100)	Fluor	High-Btu SNG and methanol
North Dakota Synfuels Group	N. Dakota	Lurgi	20,000 (18,100)	Stone & Webster	High-Btu SNG and methanol
Exxon USA	Texas	Lurgi	42,000 (38,100)	n.a.	Synthesis gas
Transco Energy Company	Texas	Lurgi	n.a.	n.a.	Medium-Btu gas
Ohio Valley Synthetic Fuels	W. Virginia	BGC/Lurgi [c] and Texaco	50,000 (45,400) [d]	Foster Wheeler	High-Btu SNG and methanol
Hampshire Energy Company	Wyoming	Lurgi and KBW [a]	15,000 (13,600)	Fluor	Gasoline, propane, and butanes
Lake Desmet Synfuels	Wyoming	Lurgi	38,000 (34,500)	n.a.	High-Btu SNG and methanol
WyCoalGas, Inc	Wyoming	Lurgi	32,600 (29,600)	Bechtel	High-Btu SNG

[a] Koppers and Babcock-Wilcox entrained gasifiers.

[b] To be built in 2 phases, each for 14,350 T/D (13,000 Mg/D) of coal.

[c] British Gas Corporation and Lurgi slagging gasifiers.

[d] To be built in 3 phases: phase 1 = 5,000 T/D (4500 Mg/D) coal, phase 2 = 25,000 T/D (22,700 Mg/D) coal, phase 3 = 50,000 T/D (45,400 Mg/D).

n.a. Not available, or not yet selected

The gasifier feedstock coals for the five projects are summarized below, on a "run-of-mine" basis:

PROJECT	COAL RANK	AMOUNT T/D (Mg/D)	HEATING VALUE, Btu/lb (kJ/kg)	SULFUR % Wt
Great Plains	Lignite	28,670 (26,000)	7,185 (16,710)	1.01
Hampshire	Subbituminous	15,000 (13,600)	8,075 (18,780)	0.33
Nokota	Lignite	28,350 (25,700)	6,985 (16,250)	0.85
Tenneco	Lignite	33,000 (29,900)	7,020 (16,330)	0.82
WyCoalGas	Subbituminous	22,820 (20,700)	8,450 (19,650)	0.32

These coal amounts refer specifically to the gasifier feedstock coal, whereas the amounts given in Table 1 include any coal burned in boilers to generate plant steam as well as any coal fines returned to the mine or sent elsewhere.

OVERALL PROCESS DESIGNS

The five coal-to-synfuels plant designs described in this paper use a number of individual process steps, arranged in various configurations. The major process steps are briefly described below:

Lurgi gasification — Coal, steam, and oxygen are reacted and result in a crude gas containing hydrogen, carbon monoxide, carbon dioxide, methane, excess steam, hydrogen sulfide, ammonia, and various byproducts and impurities. The crude gas is washed and cooled, condensing out a "gas liquor" containing water, tars, oil, phenols, and ammonia.

Shift conversion — Part of the carbon monoxide in the crude gas is "shifted" (i.e., converted to carbon dioxide and hydrogen), so as to provide the ratio of hydrogen to carbon monoxide needed for the subsequent synthesis of methanol or methane. The shifted gas is then further cooled, condensing out additional gas liquor.

Gas purification – The acid gases hydrogen sulfide and carbon dioxide are removed from the shifted gas by absorption in a solvent, using the Rectisol process and, in one case, the Selexol process. The shifted and purified gas is then routed to the subsequent synthesis step to produce either methanol or methane. The absorbed gases are stripped from the absorption solvent and recovered as acid gas streams. Those which are rich in hydrogen sulfide are processed further for conversion into sulfur.

Methanol synthesis – The hydrogen and carbon monoxide in the purified gas are reacted in the presence of a specific synthesis catalyst to form methanol. The methanol synthesis step also generates a purge gas stream, which may be further processed for conversion into methane and/or to provide a source of hydrogen for hydrotreating of Lurgi byproduct naphtha. The methanol produced may be sold as a product or may be processed further for conversion into gasoline.

Methanation – The hydrogen and carbon monoxide in the purified gas (from shift conversion and gas purification), or in the methanol synthesis purge gas, are reacted in the presence of a specific methanation catalyst to form methane. Methane is the principal constituent of the product SNG (substitute natural gas).

Gas liquor cleanup – Tars and oils are separated from the gas liquor and recovered. Next, the bulk of the phenols in the gas liquor are removed by the Phenosolvan process[10], which uses extraction by a selective solvent. Ammonia is then stripped from the dephenolized gas liquor and recovered as a byproduct. The further treatment of the residual wastewater (stripped and dephenolized gas liquor) is described later in this paper.

Partial oxidation – Liquid hydrocarbon byproducts (such as the Lurgi tars, oils, naphtha, and phenols) may be reacted with steam and oxygen to result in a crude gas containing hydrogen, carbon monoxide, carbon dioxide, excess steam, hydrogen sulfide, ammonia, and a very small amount of methane and other impurities. The subsequent processing of the partial oxidation crude gas is very similar to that described herein for the Lurgi crude gas.

Gasoline production – The MTG (methanol to gasoline) process first catalytically converts methanol to a mixture of methanol, dimethyl ether, and water vapor. The methanol and dimethyl ether are then catalytically converted to form hydrocarbons in the gasoline boiling range (C_4 to C_{10}). The hydrocarbons are fractionated into stabilized gasoline, LPG, and butanes. Part of the butanes are alkylated to form additional high-octane gasoline. The Lurgi naphtha is desulfurized in a catalytic hydrotreater to provide an additional gasoline component. Thus, the product gasoline includes stabilized MTG gasoline, alkylate, and hydrotreated Lurgi naphtha.

KBW gasification — Lurgi gasifiers require a sized coal in the range of 0.25 – 1.50 in. (0.64 – 3.8 cm). Thus, the coal fines produced from crushing and sizing of run-of-mine coal could be used as boiler fuel, disposed of in the mine or elsewhere, or gasified in some other type of gasifier. Entrained bed gasifiers, such as the KBW gasifiers (see Table 1), may be used to react the coal fines with steam and oxygen to produce a crude gas containing hydrogen, carbon monoxide, carbon dioxide, excess steam, hydrogen sulfide, ammonia, and a very small amount of methane and other impurities. The subsequent processing of the crude gas is very similar to that described herein for the Lurgi crude gas.

Sulfur recovery — It is beyond the scope of this paper to describe the many different processes that could be used for converting hydrogen-sulfide-rich acid gases into recovered sulfur. However, since four of the five coal-to-synfuels plant designs discussed in this paper plan to use the Stretford process, that process is described briefly herein.

The Stretford process involves liquid-phase oxidation of hydrogen sulfide in an aqueous solution of sodium vanadate and anthraquinone disulfonic acid (ADA). The hydrogen sulfide is absorbed and oxidized to sulfur, which is subsequently removed as a froth by flotation and purified by centrifuging followed by melting. The Stretford process can be designed to remove essentially all of the hydrogen sulfide in the feedstock gas and convert it into byproduct sulfur. However, the Stretford process accomplishes little, if any, removal and conversion of organic sulfur compounds such as carbonyl sulfide (COS), carbon disulfide (CS_2), and mercaptans (RSH), all of which are present in varying amounts in the gasification crude gases.

The flow diagram in Figure 1 presents the overall process design for the Hampshire project. Some key points of this design are:

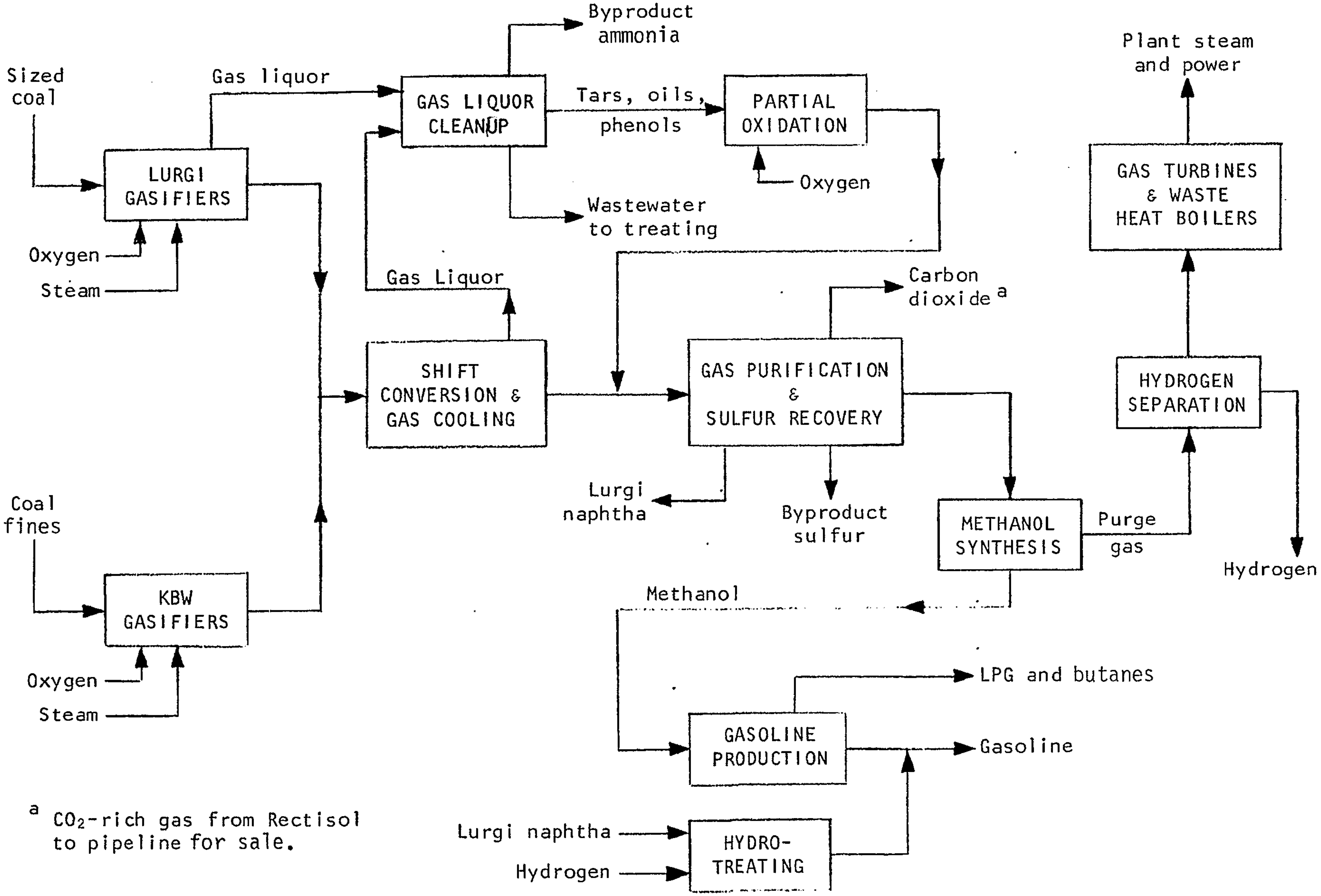
- The products and byproducts are gasoline, LPG, butanes, sulfur, ammonia, and carbon dioxide.
- Coal fines are gasified in KBW gasifiers, eliminating the need to burn any coal fines.
- Plant steam and power are supplied by burning methanol synthesis purge gas in gas turbines and generating steam by recovering heat from the turbine exhaust flue gases.
- Lurgi byproduct tars, oils, and phenols are gasified via partial oxidation.
- The combined Lurgi, KBW, and partial oxidation crude gases are purified in a selective Rectisol unit.
- Sulfur recovery utilizes the Adip, Claus, and Scot processes.

The flow diagram in Figure 2 presents the overall process design for the Tenneco project. Some key points of this design are:

- The products and byproducts are SNG, sulfur, and ammonia.
- Coal fines are burned in steam-generating boilers. Electrostatic precipitators (ESPs) followed by wet limestone scrubbers provide flue gas particulate removal and flue gas desulfurization.
- Lurgi tars, oils, naphtha, and phenols are gasified via partial oxidation.
- The Lurgi crude gas is purified in a non-selective Rectisol unit, and the partial oxidation crude gas is purified in a selective Selexol unit.
- Sulfur recovery utilizes the Stretford process.

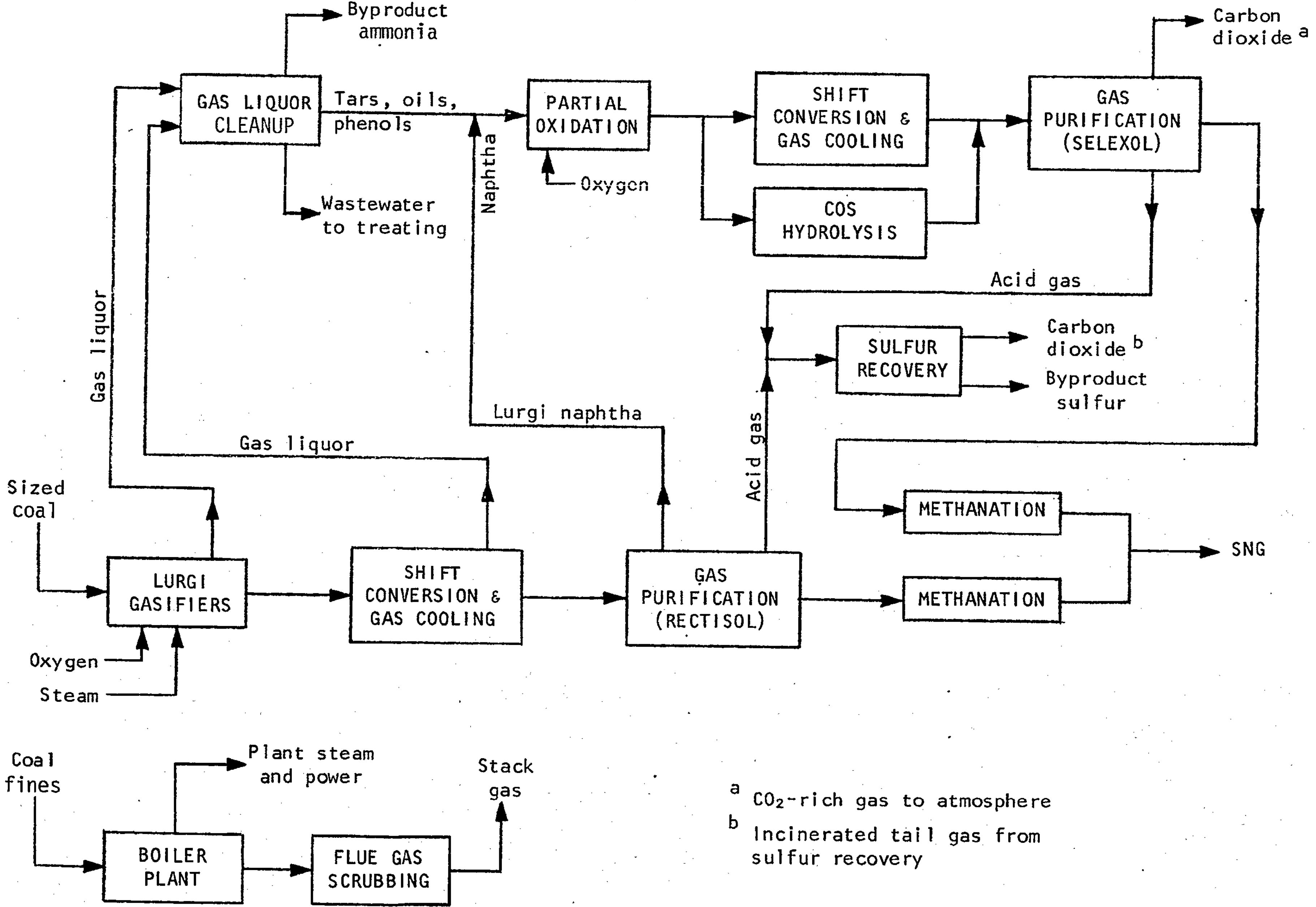
The flow diagram in Figure 3 presents the overall process design for the Nokota project. Some key points of this design are:

- The products and byproducts are methanol, SNG, phenols, oil, naphtha, sulfur, and ammonia. Excess coal fines will be either a byproduct or waste.
- Coal fines and Lurgi tars are burned in steam-generating boilers. Dry scrubbing followed by baghouses provide flue gas desulfurization and flue gas particulate removal.
- The Lurgi crude gas is purified in a selective Rectisol unit.
- Sulfur recovery utilizes the Stretford process.



[a] CO_2-rich gas from Rectisol to pipeline for sale.

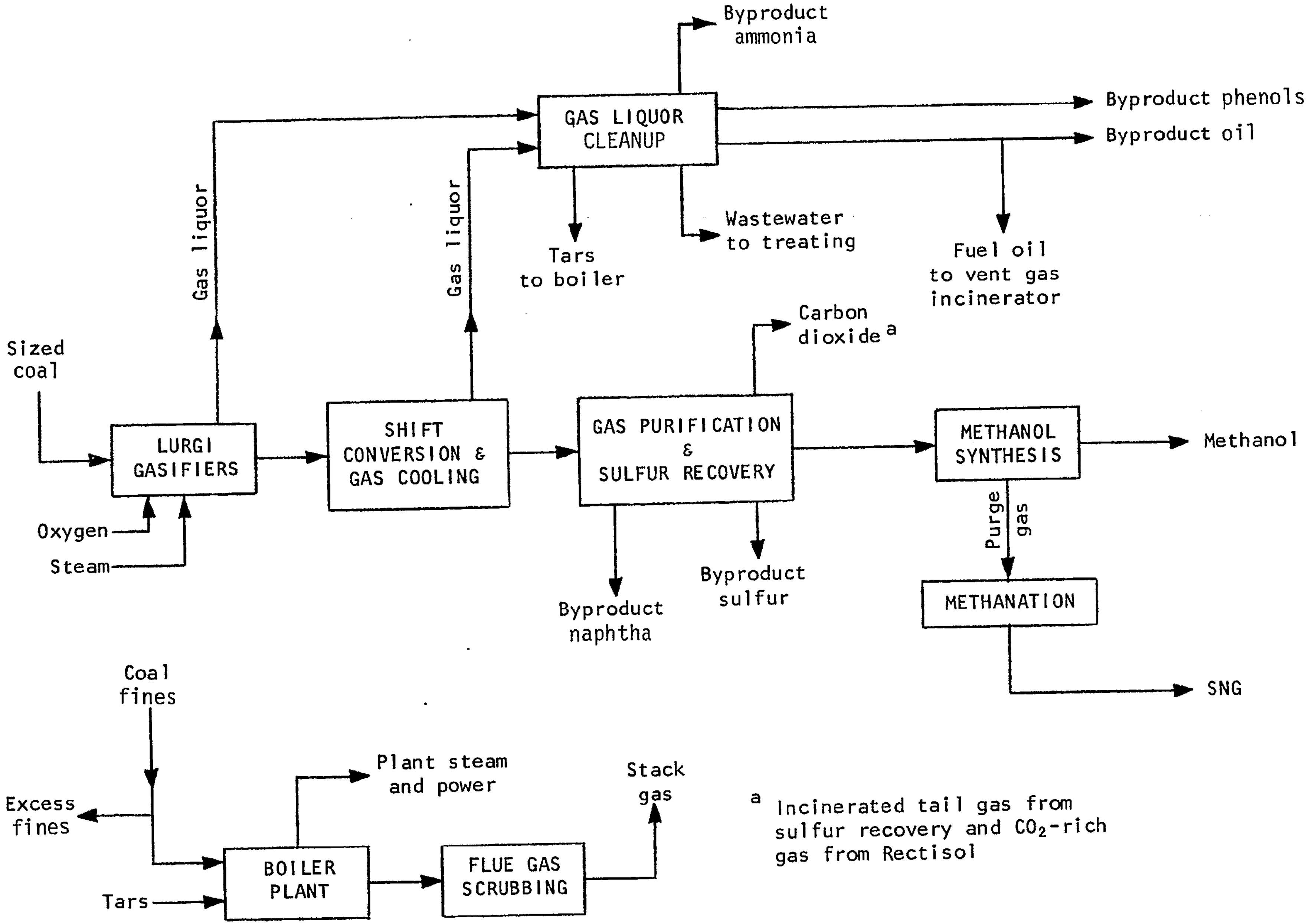
FIGURE 1. HAMPSHIRE ENERGY COMPANY (WYOMING) PROJECT



[a] CO_2-rich gas to atmosphere

[b] Incinerated tail gas from sulfur recovery

FIGURE 2. TENNECO COAL GASIFICATION (MONTANA) PROJECT



[a] Incinerated tail gas from sulfur recovery and CO_2-rich gas from Rectisol

FIGURE 3. NOKOTA COMPANY (NORTH DAKOTA) PROJECT

The flow diagram in Figure 4 presents the overall process design for the WyCoalGas project. Some key points of this design are:

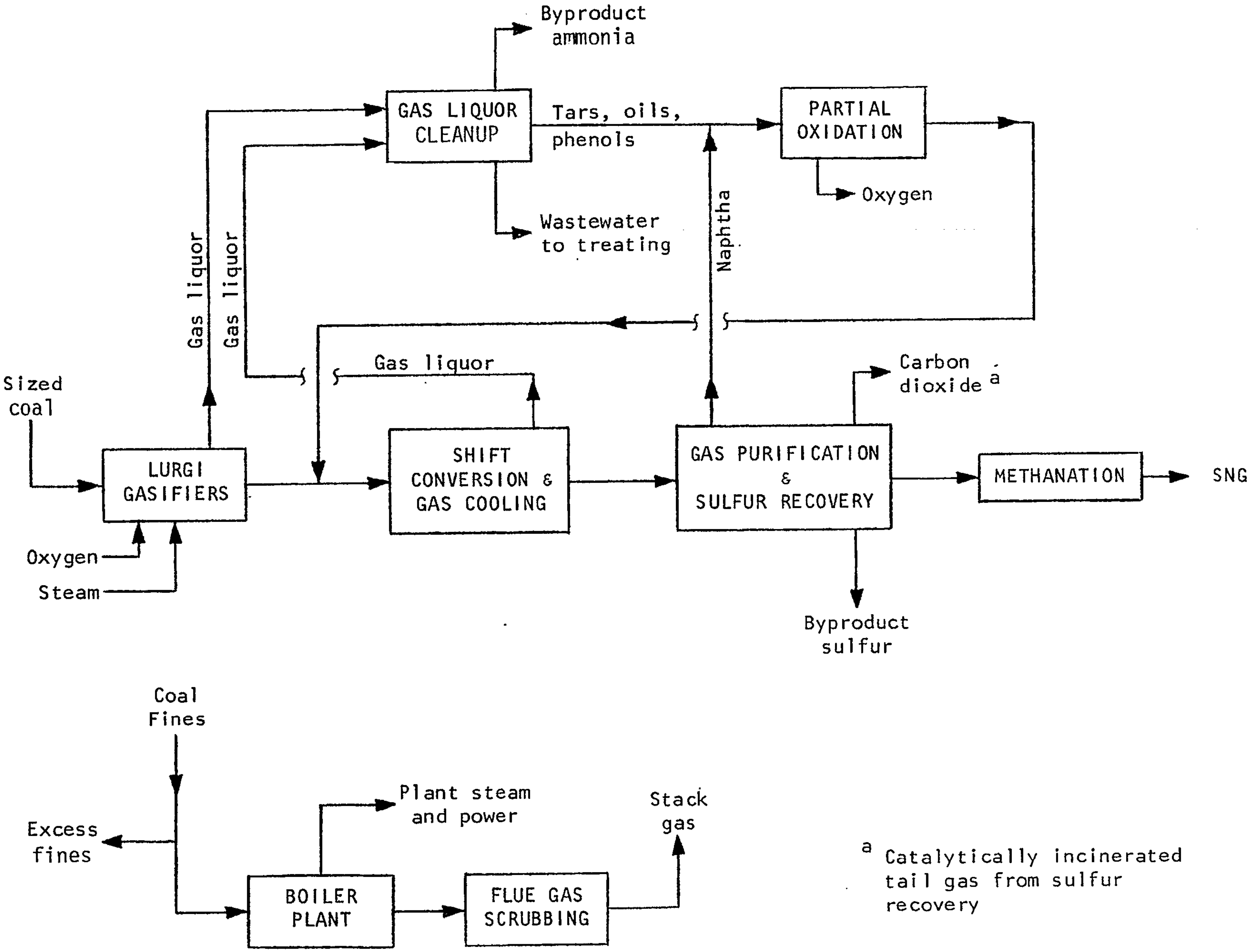
- The products and byproducts are SNG, sulfur, and ammonia. Excess coal fines will be either a byproduct or a waste.
- Coal fines are burned in steam-generating boilers. ESPs followed by wet limestone scrubbers provide flue gas particulate removal and desulfurization.
- Lurgi tars, oils, naphtha, and phenols are gasified via partial oxidation.
- The combined Lurgi and partial oxidation crude gases are purified in a non-selective Rectisol unit.
- Sulfur recovery utilizes the Stretford process.

The flow diagram in Figure 5 presents the overall process design for the Great Plains project. Some key points of this design are:

- The products and byproducts are SNG, sulfur, ammonia, and all of the coal fines.
- Lurgi tars, oils, naphtha, and phenols are burned as fuel in steam generating boilers. Particulates are removed from the tar-fired superheater's flue gas by an ESP.
- Lurgi naphtha and phenols are also burned as fuel in wastewater incinerator.
- The Lurgi crude gas is purified in a non-selective Rectisol unit.
- Sulfur recovery utilizes the Stretford process.
- A small amount of methanol is produced for Rectisol absorbent makeup.

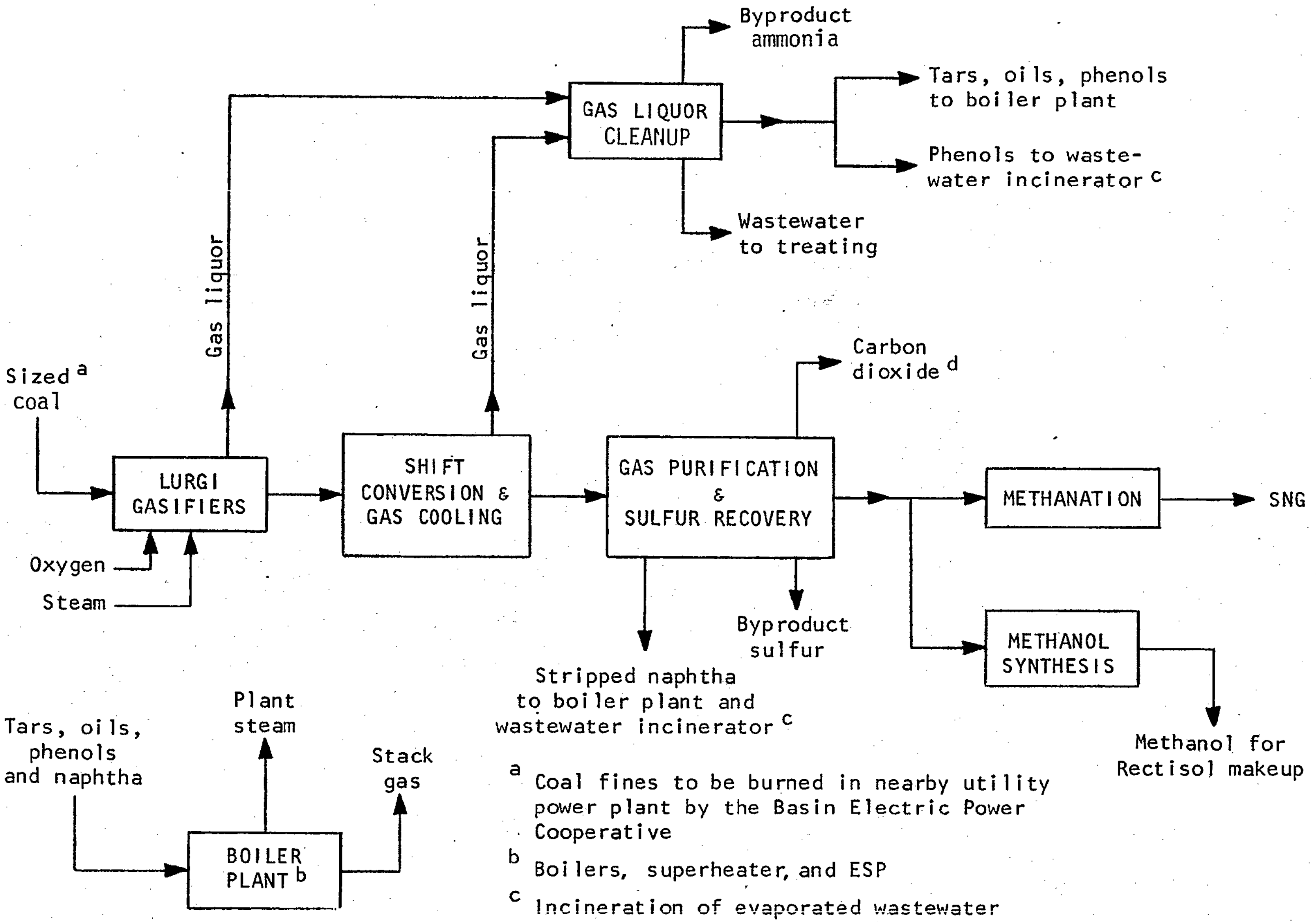
As an overall commentary on the five plant designs, it is of interest to note the following:

- Three of the five designs use partial oxidation to gasify the Lurgi liquids (tars, oils, naphtha, and phenols) for on-site use.
- Four of the five designs utilize the Stretford sulfur recovery process.
- Two of the designs use selective Rectisol for acid gas removal, two use non-selective Rectisol, and one uses both a selective Selexol unit and a non-selective Rectisol unit.



[a] Catalytically incinerated tail gas from sulfur recovery

FIGURE 4. WYCOALGAS, INC. (WYOMING) PROJECT



[a] Coal fines to be burned in nearby utility power plant by the Basin Electric Power Cooperative

[b] Boilers, superheater, and ESP

[c] Incineration of evaporated wastewater concentrate using naphtha and phenols as fuel

[d] Incinerated tail gas from sulfur recovery

FIGURE 5. GREAT PLAINS GASIFICATION ASSOCIATES (NORTH DAKOTA) PROJECT

- All three of the designs which burn coal to generate steam include flue gas desulfurization. The one design which burns liquids to generate steam does not include flue gas desulfurization.
- One design gasifies the coal fines and generates steam and power by burning purge gas in gas turbines.
- There is a broad diversity of products, byproducts, and process configurations among the five designs.

SULFUR EMISSIONS CONTROL

Figure 6 presents flow diagrams of the sulfur emissions control systems in each of the five coal-to-synfuels designs. In examining these systems, certain process characteristics should be kept in mind:

> Selective acid gas removal processes (either Rectisol or Selexol) are those which produce (a) carbon-dioxide-rich offgas from which most of the hydrogen sulfide has been removed and (b) an acid gas stream (often called the hydrogen-sulfide-rich stream) which is also carbon-dioxide-rich but contains most of the hydrogen sulfide removed from the shifted, gasifier product crude gas.
>
> Non-selective acid gas removal processes (either Rectisol or Selexol) are those which produce a single acid gas stream containing all of the carbon dioxide and all of the hydrogen sulfide removed from the shifted, gasifier product crude gas.
>
> The carbon-dioxide-rich offgas and the acid gas streams, produced by either selective or non-selective Rectisol or Selexol processes, contain hydrocarbon gases. Independent of any sulfur emissions control considerations, the carbon-dioxide-rich offgas and acid gas streams could be controlled (e.g. by incineration), to reduce the emissions of hydrocarbons[11].
>
> The designs indicate that essentially all of the hydrogen sulfide fed to the Stretford process is converted into byproduct sulfur, but little (if any) organic sulfur is converted into byproduct sulfur. Thus, the residual tail gas from a Stretford process might be incinerated for two reasons: (a) to control the emissions of hydrocarbons as discussed above and (b) to convert organic sulfur to sulfur dioxide.
>
> An Adip unit concentrates a hydrogen-sulfide-containing acid gas by removing hydrocarbons and some carbon dioxide from the acid gas. About 94 – 98 percent of the hydrogen sulfide in the acid gas can then be converted into byproduct sulfur in a Claus unit. A Scot unit converts the residual sulfur compounds in a Claus unit tail gas into hydrogen sulfide, which is then recovered and recycled to the Claus unit. The only sulfur species remaining in the Scot unit tail gas in any potentially significant amount (200 – 500 ppmv) is hydrogen sulfide, and the tail gas is usually incinerated to convert the hydrogen sulfide into sulfur dioxide.

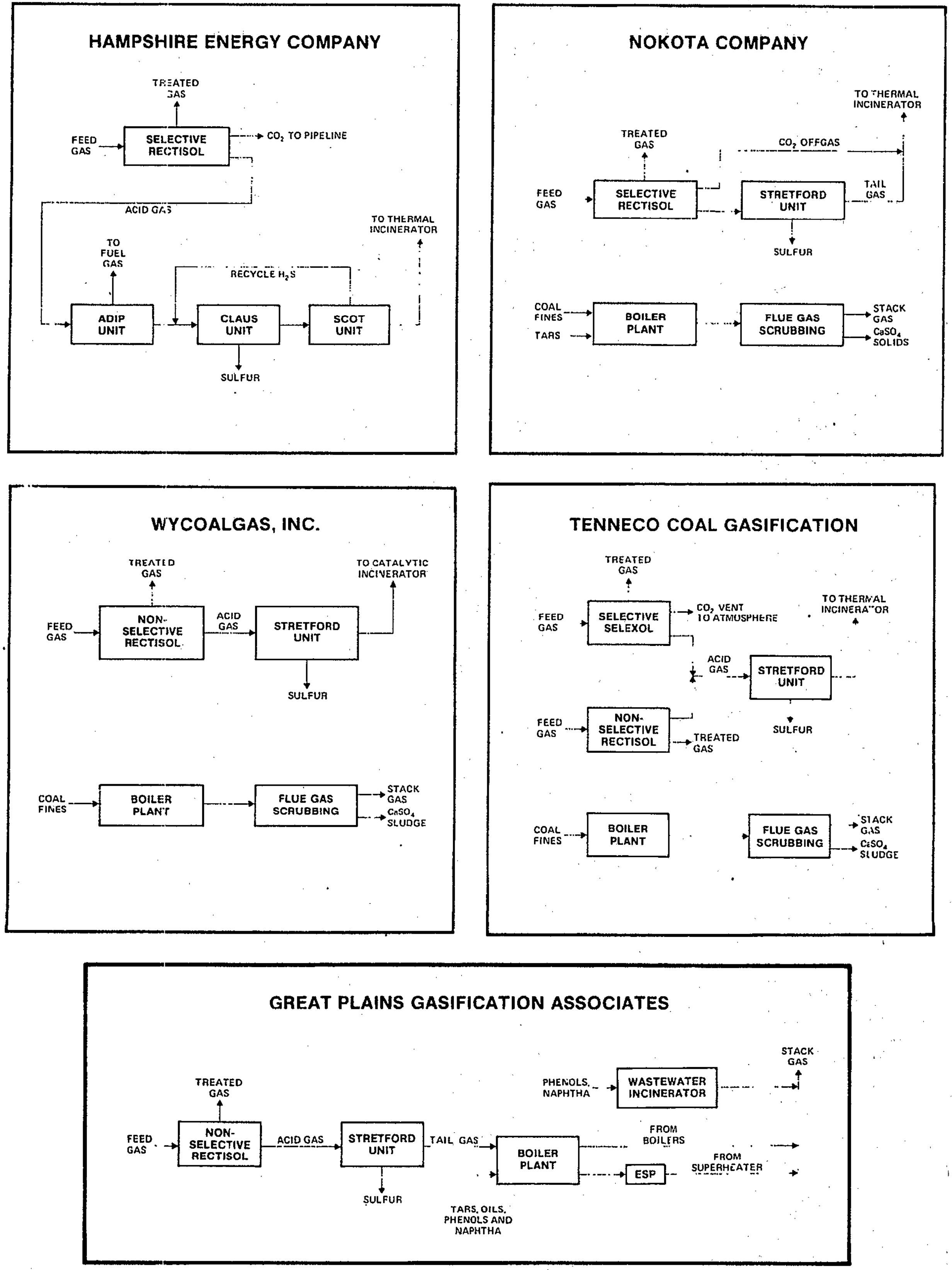


FIGURE 6. SULFUR EMISSIONS CONTROL IN FIVE OF THE PROPOSED COAL GASIFICATION PROJECTS

> Depressuring the coal lockhoppers on the Lurgi gasifiers, each time they are loaded with feedstock coal, requires the venting of gas from the lockhoppers. That gas contains hydrocarbons and acid gases, and it may be desirable to recover and/or incinerate the gas.

It should be noted that the Nokota and Tenneco designs incinerate Stretford tail gas in fuel-fired incinerators, the WyCoalGas design catalytically incinerates the Stretford tail gas, and the Great Plains design incinerates the Stretford tail gas in the boiler fireboxes. The Scot tail gas in the Hampshire design is incinerated in a gas-fired incinerator.

Table 2 summarizes the sulfur balances for the gasification process units for the five designs (excluding sulfur derived from any burning of coal fines). As a percentage of the sulfur in the gasified coal, the sulfur discharges for the five designs range from 2.8 to 5.3 percent. In terms of equivalent sulfur dioxide, the discharges for the five designs range from 0.02 to 0.15 lb per million Btu (8.6 to 65 ng/J) of gasified coal. Also note that the sulfur allocated to the gasifier ash in three of the designs ranges from about 3 to 7 percent of the sulfur in the gasified coal, which is within the usual range of assumption. However, one of the designs allocates 0.1 percent of the coal sulfur to the gasifier ash, and another of the designs allocates 13 percent of the coal sulfur to the gasifier ash. It is not known if special circumstances or data are available to support these assumptions.

WATER USAGE AND WASTEWATER TREATMENT

As shown in Table 3, the intake and usage of raw water ranges for the five coal-to-synfuels designs from 1.00 to 1.80 tons (1.00 to 1.80 Mg) of water per ton (Mg) of gasified coal, and the average is 1.26 tons (1.26 Mg) per ton (Mg) of gasified coal. Using that average, the gasification of 28,000 tons (25,400 Mg) of coal per day requires about 5,900 gpm (1340 m^3/hr) of water intake, which is equivalent to about 9,500 acre-ft (11.7 km^3) of water per year.

TABLE 2. GASIFICATION SULFUR BALANCES AND DISCHARGES IN FIVE OF THE PROPOSED PROJECTS
(Excluding sulfur derived from any coal fired in steam generators)

	HAMPSHIRE PROJECT	WYCOALGAS PROJECT	NOKOTA PROJECT	TENNECO PROJECT	GREAT PLAINS PROJECT
COAL GASIFIED, 10^9 Btu/D (TJ/D)	242 (255)	386 (407)	396 (418)	462 (487)	412 (435) [a]
SULFUR INPUT, T/D (Mg/D):					
In gasified coal	49.5 (44.9)	73.0 (66.2)	244.0 (221)	271.3 (246.1)	290.5 (263.5)
SULFUR OUTPUTS, T/D (Mg/D):					
As byproduct sulfur	44.0 (39.9)	66.1 (60.0)	223.7 (202.9)	249.1 (225.9)	231.4 (209.9)
In $CaSO_4$ [b]	na	nil	10.2 (9.2)	5.0 (4.5)	na
In Na_2SO_4 [c]	na	na	na	na	4.1 (3.7)
In gasifier ash	3.5 (3.2)	4.6 (4.2)	0.3 (0.27)	9.2 (8.3)	38.8 (35.2)
In product SNG	na	nil	nil	nil	nil
In product methanol	na	na	nil	na	na
In liquid products and byproducts	nil	na	3.0 (2.7)	na	0.9 (0.82)
	47.5 (43.1)	70.7 (64.2)	237.2 (215.1)	263.3 (238.7)	275.2 (249.6)
Sulfur discharges	2.0 (1.8)	2.3 (2.0)	6.8 (6.2)	8.0 (7.3)	15.3 (13.9)
	49.5 (44.9)	73.0 (66.2)	244.0 (221.3)	271.3 (246.0)	290.5 (263.5)
SULFUR DISCHARGES AS:					
Percent of sulfur input	4.0	3.2	2.8	2.9	5.3
lb of SO_2/(10^6 Btu of gasified coal) (ng/J)	0.03 (12.9)	0.02 (8.6)	0.07 (30.1)	0.07 (30.1)	0.15 (64.5)

[a] Total for ultimate full-size plant.

[b] Gasification sulfur outputs allocated to $CaSO_4$ occur only for those plants burning tars, oils, naphtha, phenols, lock gas, etc. in boiler plants equipped with flue gas desulfurizing scrubbers.

[c] Recovered from Stretford unit waste liquid.

na Not applicable

nil Essentially zero

TABLE 3. RAW WATER USAGE AND GAS LIQUOR TREATMENT IN FIVE OF THE PROPOSED PROJECTS

	HAMPSHIRE PROJECT	WYCOALGAS PROJECT	NOKOTA PROJECT	TENNECO PROJECT	GREAT PLAINS PROJECT
RAW WATER INTAKE:					
Gal./min(m^3/hr)	2,500 (570)	3,860 (880)	6,000 (1,360)	6,800 (1,540)	8,600 (1,950)
Tons/ton (Mg/Mg) of gasified coal	1.00 (1.00)	1.01 (1.01)	1.27 (1.27)	1.24 (1.24)	1.80 (1.80)
GAS LIQUOR TREATMENT AND FLOW SEQUENCE:					
Phenols extraction [a]	●	●	●	●	●
H_2S and NH_3 removal [b]	●	●	●	●	●
Biological oxidation	●	●	●	●	
Evaporation [c]		●			
To cooling tower as makeup water	●	●	●	●	●
Cooling tower blowdown:					
Evaporation [d]	f	●	●	f	●
Incineration	f			f	●
Disposal of residual:					
To gasifier ash quenching	●	e		●	e
To ash handling		e	●		e
To evaporation pond	●	e			e

---

[a] Via Phenosolvan process

[b] Via stripping process (such as Phosam process)

[c] Evaporation ahead of cooling tower, with condensate used as cooling tower makeup. Blowdown from cooling tower returns to the evaporation unit.

[d] Evaporation of cooling tower blowdown, with condensate reused inplant.

[e] The residual disposal is not made clear in the available references.

[f] Cooling tower blowdown sent directly to residual disposal.

The contaminated gas liquor generated by Lurgi coal gasification constitutes the major wastewater stream in a coal gasification plant. The quantity of dephenolized, stripped gas liquor for three of the five designs is:

Project	gpm (m^3/hr)	tons of gas liquor per ton of gasified coal (Mg/Mg)
Great Plains	4,700 (1,070)	1.0 (1.0)
Hampshire	1,700 (390)	0.7 (0.7)
WyCoalGas	3,130 (710)	0.8 (0.8)

The gas liquor treatment sequence for the five designs is also presented in Table 3. It is of interest to note that:

- All five designs use the Phenosolvan process for extracting the bulk of the phenols from the gas liquor.
- All five of the designs use a stripping process to remove hydrogen sulfide and to recover byproduct ammonia from the gas liquor. Three of the designs plan to use the Phosam stripping process and one of the designs plans to use the Chemi-Linz/Lurgi (CLL) stripping process.
- Four of the designs further treat the stripped liquor via biological oxidation prior to using the treated wastewater as cooling tower makeup. One of the designs uses the stripped liquor as cooling tower makeup without prior biological treatment.
- Three of the designs evaporate the cooling tower blowdown to recover water for inplant reuse. One of those three designs evaporates the stripped liquor and the cooling tower blowdown to obtain the cooling tower makeup.
- One of the designs incinerates the concentrate from evaporation of the cooling tower blowdown.

It is also of interest to note that a Lurgi author[12] recommends that the treatment sequence be: phenol extraction, stripping, biological oxidation, activated carbon adsorption, and ion exchange. The recommended treatment is stated to be needed prior to using the treated water as cooling tower makeup.

GAS VENTING FROM COAL LOCKHOPPERS

As discussed earlier herein, technologies such as incineration or recovery/reuse are available for gases vented from the Lurgi gasifier coal lockhoppers. Table 4 summarizes how that venting is handled in three of the designs. The venting of gasifiers during shutdown and start-up is also summarized in Table 4.

TABLE 4. HANDLING OF COAL LOCK VENTING AND OF GASIFIER START-UP/SHUTDOWN VENTING IN THREE OF THE PROPOSED PROJECTS

	GREAT PLAINS PROJECT	WYCOALGAS PROJECT	NOKOTA PROJECT
COAL LOCK VENTING:			
High pressure gas	Vented through venturi scrubber to Stretford unit for desulfurizing and then routed to the boilers for incineration.	Vented to a gas holder and recompressed back into the process gas.	The available reference documents are unclear on this point.
Low pressure gas	Vented through venturi scrubber and recompressed to join the high pressure vent gas routed to the Stretford unit and then to the boilers.	Displaced by slipstream of cooled process gas and vented to gas holder for recompression back into the process gas.	Displaced by slipstream of carbon dioxide offgas from the Rectisol unit and vented to the boiler fireboxes for incineration.
Exhaust gas	Evacuated by ejector, using motive air, and vented to atmosphere.	Evacuated by fans and incinerated in the boiler fireboxes.	Evacuated by ejector, using motive air, and vented to the atmosphere.
GASIFIER START-UP AND SHUTDOWN VENTING:			
Crude process gas	Vented to start-up incinerator.	Vented to plant flare for incineration.	It has been assumed that the plant's vent gas incinerator would also handle this service

REFERENCES:

(1) "Coal To Gasoline Plant," brochure describing Hampshire Energy Company's proposed project at Gillette, Wyoming, provided by Hampshire Energy Company by transmittal dated August 1981.

(2) Meeting and discussion with Hampshire Energy Company personnel in August 1981.

(3) Flow diagrams and fact sheet for Tenneco's proposed project in Montana, provided by Tenneco by transmittal dated August 1981.

(4) "Prevention Of Significant Air Quality Deterioration Permit Application," February 1980, submitted by Nokota Company to the North Dakota Department of Health. Provided by Dames and Moore by transmittal dated August 1981.

(5) "Air Quality Permit Application For A Proposed Coal Gasification Plant," June 1981, submitted by WyCoalGas, Inc. to the Wyoming Department of Environmental Quality.

(6) Flow diagram and process description for WyCoalGas's proposed project in Wyoming, provided by the Panhandle Eastern Pipe Line Company by transmittal dated August 1981.

(7) "Plant Sulfur Disposition, " WyCoalGas flow diagram provided to the EPA's NAPCTAC committee in 1977.

(8) "Request For Amendments To The Permit To Construct For The ANG Coal Gasification Plant (Great Plains Gasification Associates), Mercer County, North Dakota," submitted by ANG Coal Gasification Company to the North Dakota State Department Of Health, February 1979.

(9) "Final Environmental Impact Statement, Great Plains Gasification Project, Mercer County, North Dakota," U.S. Department of Energy, August 1980.

(10) Beychok, M.R., "Coal Gasification And The Phenosolvan Process," Division of Fuel Chemistry, 168th National ACS Meeting, Atlantic City, September 1974.

(11) Beychok, M.R., "Sulfur Emission Controls For A Coal Gasification Plant," EPA-600/2-76-149 (NTIS PB257-182), Symposium Proceedings: Environmental Aspects Of Fuel Conversion Technology, II, (December 1975, Hollywood, Florida), June 1976.

(12) Rolke, D., "Treatment Of Gas Liquor From Coal Gasification Plants," Lurgi Information No. 7, Vol. 6, July 1981.