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TREATMENT OF FOSSIL FUEL DERIVED WASTEWATERS WITH POWDERED ACTIVATED CARBON/ACTIVATED SLUDGE TECHNOLOGY

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ABSTRACT

The treatment of high strength fuel conversion wastewaters by conventional biological treatment processes may be operationally troublesome and only marginally effective from the standpoint of treatment system stability and performance. The addition of powdered activated carbon to the activated sludge process not only greatly improves product water quality but also provides cost savings compared to more conventional waste treatment and carbon regeneration processes.

This paper describes the powdered carbon/activated sludge wastewater treatment process, discusses the advantages of powdered carbon addition including performance obtained on fossil fuel derived wastewaters, and presents cost comparison data for wastewater treatment and spent carbon regeneration.

INTRODUCTION

Development of the synthetic fuels production industry is contingent in part on successful treatment of the production wastewaters since environmental regulations for treated wastewater discharges are likely to be very stringent and effluent reuse will be necessary in many facilities. Efficient, reliable waste treatment is of critical concern due to the constituents present in most synfuels wastes and the variability anticipated. These concerns have spurred investigation of powdered activated carbon addition to the activated sludge wastewater treatment process for improved treatment performance* and improved organics removals** among others.

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* Luthy, R.G., Stamoudis, V.C., and Campbell, J.R., "Removal of Organic Contaminants from Coal Conversion Condensates." Presented at the 54th Annual WPCF Conference, Detroit, Michigan (October, 1981).

** Wei, I.W., and Chen, J.C.Y., "Fate of Organics in the Treatment of Oil Shale Retort Water." Presented at the 54th Annual WPCF Conference, Detroit, Michigan (October, 1981).

The addition of powdered carbon to the activated sludge process, termed PACT*, provides enhanced treatment performance and reliability over that found in pure biological treatment systems. The addition of PAC provides improved COD removals and permits nitrification of the synfuels wastewater.

When Wet Air Carbon Regeneration is applied to the PACT process, the process is called the Wastewater Reclamation System (WRS) and is hereafter referred to as such.

Application of Wet Oxidation to synthetic fuels wastes, for spent carbon regeneration of solids wasted from the Wastewater Reclamation System and for oxidation of concentrated production wastes, enables economical disposal of concentrated, difficult to treat wastes and provides cost-effective spent carbon regeneration.

TREATMENT CONCEPTS

The addition of powdered activated carbon (PAC) to the activated sludge process combines simultaneously the advantages of physical adsorption and biological stabilization in the same "biophysical" treatment system. The presence of the active adsorbent (PAC) provides removal of non-biodegradable, adsorbable organics in the waste stream--organics which would otherwise escape untreated from a pure biological system. Furthermore, the high concentration of activated carbon in the treatment system ensures maintaining reasonable treatment even if biological upset should occur.

The benefits of adsorption and biodegradation are exploited by combining both methods of treatment in a single operation. The combined effects are illustrated in Figure 1 which shows carbon adsorption isotherms of two wastes, A and B. Waste A (solid line) is treatable by carbon adsorption as indicated by the shallow slope of the isotherm. Waste B is not readily treatable by activated carbon as indicated by the steep slope of the isotherm. Waste B apparently contains organic constituents which are not readily adsorbable.

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* PACT is a registered servicemark of DuPont.

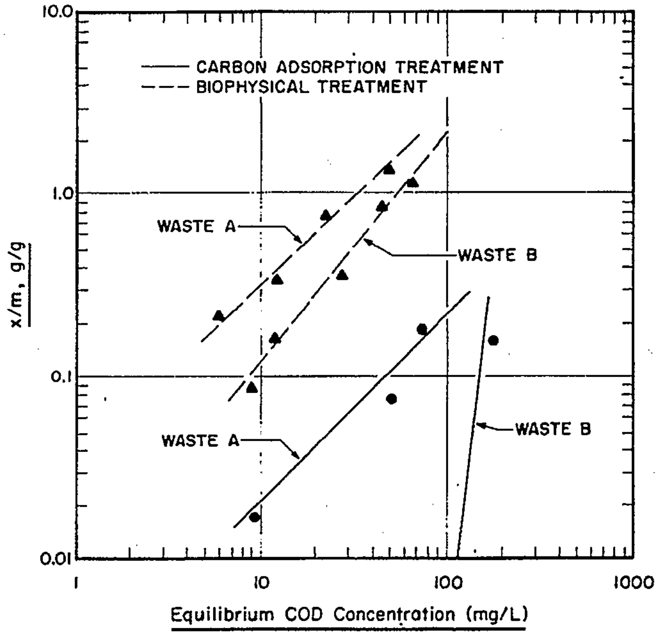


Figure I. PHYSICAL AND BIOPHYSICAL ISOTHERMS

The dashed lines show isotherms for the same two wastes when both biological treatment and adsorption are simultaneously imposed. Waste B is now treatable as indicated by the similarity of the two isotherms. In addition, considerably higher organic loading rates are obtained resulting in a smaller wastewater treatment system. The activated sludge has aided the activated carbon in removing organic constituents which are not readily adsorbable. For synfuels wastes, most of the particularly obnoxious fossil fuel related components such as multi-phenolics are adsorbable and are effectively removed in biophysical treatment. Performance of the Wastewater Reclamation System on synfuels wastewaters indicate that greater than 95 percent removal of COD can be obtained with only very low COD residuals remaining following treatment.

In addition to enhanced performance and increased organic loading rates, PAC addition to activated sludge adsorbs toxic or inhibitory components enabling the micro-organisms to function efficiently. This is important since synfuels wastewaters frequently contain toxic components in sufficient concentration to inhibit metabolic rates and nitrification. Further, carbon acts as a toxic sink to dampen organic fluctuations resulting from production process variations or upset.

The presence of PAC also provides a catalytic or perhaps best termed an alleo-catalytic effect on biological treatment. The active adsorbent concentrates on the PAC surfaces the extra-cellular enzymes needed for organics assimilation in addition to adsorption of waste organics and molecular oxygen. This concentration effect serves to catalyze the biological mechanisms.

Perhaps more important is that contaminants that are slow to degrade will be held by the activated carbon in the treatment system for the solids residence time, not the much shorter hydraulic residence time which would be the case where carbon is not present. Thus, additional organics are removed biologically which would otherwise have to be treated by granular carbon, ion exchange or ozonation.

The foregoing arguments explain the superior performance seen in powdered carbon/activated sludge systems on a micro-basis. However, there are some important design considerations that contribute to the success of the process. Of primary importance is the settleability of the sludge. The carbon nucleus of the floc particles serves as a weighting agent. The sludge can be readily settled and compacted and therefore carried at very high levels in the aeration basins. The Wastewater Reclamation System will typically operate at 15-25,000 mg/l mixed liquor suspended solids whereas a conventional activated sludge system is typically 2,000-4,000 mg/l. Though a major fraction of the WRS mixed liquor is PAC, volatile biological solids levels easily exceed conventional activated sludge systems and may approach 7,000 mg/l in normal operation.

THE WASTEWATER RECLAMATION SYSTEM

The Wastewater Reclamation System has been or will be used in numerous applications and will treat a wide variety of wastewaters including night soil, combined domestic and textile wastes, nitrification of domestic and industrial wastes, pharmaceutical wastes and organic chemicals wastes. A list of WRS applications and the waste treated are shown in Table 1.

TABLE 1. WRS INSTALLATIONS

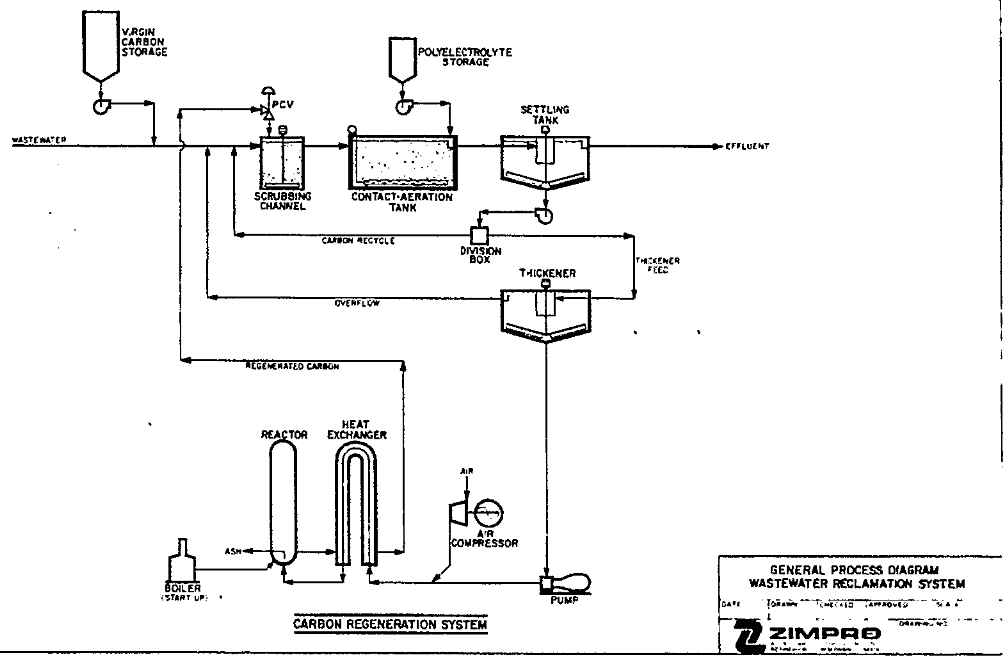
Location	Size	Wastewater	Operation
Rothschild, WI	3785 m^3/d	Domestic	1972-73 Demonstration
Kimitsu, Japan	500 KL/d	Night Soil	1975
Oga, Japan	1200 Kl/d	Night Soil	1977
Vernon, CT	24600 m^3/d	Domestic/Textile	1979
Senroku, Japan	1400 KL/d	Night Soil	1980
Oizumi, Japan	800 KL/d	Night Soil	1980
Medina, OH	37850 m^3/d	Domestic	1981
Burlington, NC (East Plant)	47300 m^3/d	Domestic/Textile	1981
Mt. Holly, NJ	18425 m^3/d	Domestic/Textile	1981
Kalamazoo, MI	204400 m^3/d	Domestic/ Pharmaceutical	Under Construction
Burlington, NC (South Plant)	35960m^3/d	Domestic/Textile	Under Construction
East St. Louis, IL	102200 m^3/d	Domestic/Organic Chemicals	Under Construction
Ibaragi, Japan	1520 KL/d	Night Soil	Under Design
El Paso, TX	37850 m^3/d	Domestic	Under Design
Bedford Heights, OH	11350 m^3/d	Domestic/ Industrial	Under Design
North Olmsted, OH	26500 m^3/d	Domestic/ Industrial	Under Design

The WRS flow scheme is presented in Figure 2. Typical major process components include aeration, clarification and optional effluent filtration. Auxiliary process components include dry carbon storage and liquid polymer addition.

When using WRS, the wastewater is aerated in the presence of a high concentration of powdered activated carbon (PAC), from 4,000 to 12,000 mg/L, depending on the influent wastewater characteristics and effluent quality required. The powdered carbon not only acts as an adsorbent, but also as a weighting agent, enhancing MLSS settling and enabling higher concentrations of volatile biological solids to be maintained under aeration. Thickened clarifier underflow solids, at concentrations typically ranging from 3.0 to 5.0 percent are recycled to the inlet of the aeration basin. Due to the high concentrations of PAC and biological solids maintained in the WRS, a high degree of reliable treatment is obtained.

The excess secondary sludge from the WRS is wasted from the aeration tank or clarifier to a gravity thickener. The thickened

Figure 2. WASTEWATER RECLAMATION SYSTEM



underflow solids, at a concentration of 6.0 percent suspended solids or greater, is pumped to the regeneration unit heat exchangers by the high pressure pump at a pressure of approximately 50 kg/cm^2 (800 psig).

Compressed air is added to the carbon slurry flow prior to the heat exchangers. The combined slurry and air mixture passes through the heat exchangers where its temperature is raised prior to entering the reactor. In the reactor, the volatile biological solids and sorbed organics contained in the carbon slurry are 'wet oxidized.'

Since a net heat gain (temperature rise) occurs during the wet oxidation reactions, autothermal (thermally self-sustaining) operation is obtained. The hot regenerated slurry is then passed through the heat exchangers to recover the produced heat. The cooled regenerated slurry flows to the pressure reducing station and returned to the wastewater flow via a distribution diffusor in the scrubbing channel. Though a nearly complete oxidation (85-95%) of chemical oxygen demand occurs during regeneration, a small amount of low molecular weight residual organics remain which are returned directly to the treatment system for biological stabilization. Since these organics are readily biodegradable and comprised of weak acids, separate sidestream treatment of the regeneration recycle stream is not required.

Control of the mixed liquor suspended ash concentration is provided by regeneration reactor blowdown. Inerts accumulate at the reactor bottom and are vented from the reactor during steady-state operation and disposed. Since these materials are inert and 'wet oxidized' during regeneration, disposal as a non-hazardous material is generally acceptable.

A steam generator is included in the regeneration system to provide start-up steam requirements.

Wet air regeneration losses of volatile PAC are less than 5 percent of throughput, substantially less than PAC oxidation losses in conventional thermal regeneration processes. Regeneration losses include both those resulting from oxidation losses and reactor inerts blowdown to disposal. Powdered carbon losses of 1 to 5 percent and autothermal regeneration system operation have been confirmed in the full scale operations at Kimitsu, Japan* and Vernon, CT.**

ADVANTAGES TO SYNFUELS WASTE TREATMENT

Major advantages of the Wastewater Reclamatiom System to the treatment of fossil fuel derived wastewaters are the excellent product water quality obtained and the reliable treatment process operation and stability that is ensured with PAC addition. Treatment process stability is of major significance to the synfuels facility since biological treatment difficulties resulting in upset conditions will likely curtail fuel production, will result in post-biological treatment difficulties in reuse applications, and will result in failure to meet discharge requirements where direct effluent discharge is practiced.

Since the treatment system effluent quality is a major consideration in most synfuels applications, for both effluent reuse in the facility and for direct discharge, optimum performance is extremely important. Residuals (COD, ammonia) are of concern in terms of fouling reverse osmosis membranes, evaporator tubes and cracking and carbonizing in boilers and superheaters. Ammonia generally presents corrosion problems in cooling water systems and boilers. Organic priority pollutants present in coal derived wastewaters (see Table 2) represent a potential health hazard in the plant and must be effectively removed before direct discharge.

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* Meidl, J.A.; Berndt, C.L. and Nomoto, K., "Experience with Full Scale Wet Oxidation of Spent Carbon from the 'PACT' Process." Presented at the 51st Annual Conference of the WPCF, Anaheim, CA, (October, 1978).

** Pitkat, C.A. and Berndt, C.L., "Textile Waste Treatment at a Municipal PACT Facility." Presented at the 35th Purdue Conference, Purdue University, West Lafayette, IN, (May, 1980).

Enhanced organics (BOD_5, COD) removals and biological nitrification are obtained when powdered carbon is added to activated sludge. In numerous treatability demonstrations, improved organic removals of chemical wastes were obtained*, efficient nitrification was obtained in the WRS whereas biological treatment was unsuccessful due to the presence of pharmaceuticals** and nitrification of toxic wastes was possible in a two stage WRS mode***.

TABLE 2. LEVEL OF ORGANIC PRIORITY POLLUTANTS DETECTED IN EPA SCREENING PROGRAM

Priority Pollutant						
No.		Name	No. of Samples	Mean (mg/L)	Minimum Value (mg/L)	Maximum Value (mg/L)
1	*	Acenapthene	18	216.8	0.013	3,000.0
39	*	Fluoranthene	21	147.7	0.011	1,400.0
81	*	Phenanthrene	36	130.2	0.010	3,200.0
80	*	Fluorene	25	80.2	0.011	1,400.0
3		Acrylonitrile	9	65.7	0.043	330.0
84	*	Pyrene	26	61.4	0.010	1,100.0
55	*	Naphthalene	59	43.4	0.010	1,200.0
64		Pentachlorophenol	35	37.5	0.012	680.0
11		1,1,1-trichloroethane	93	26.0	0.010	1,300.0
74	*	3,4-benzofluoranthene	4	24.8	0.010	99.0
76	*	Chrysene	27	24.3	0.010	440.0
49		Trichlorofluoromethane	27	22.4	0.011	290.0
75	*	Benzo(k)fluoranthene	9	22.1	0.011	99.0
59		2,4-dinitrophenol	16	17.8	0.011	230.0
72	*	Benzo(a)anthracene	23	15.8	0.010	180.0
78	*	Anthracene	35	15.1	0.010	510.0
79	*	Benzo(ghi)perylene	8	14.0	0.013	84.0

* Coal Based.

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* Sago, W.L. and Foresman, M.R., "Joint Municipal/Industrial Wastewater Treatment - Metro East St. Louis, Illinois." Presented at the 53rd Annual Conference of the WPCF, Las Vegas, Nevada (September, 1980).

** Sampayo, F.F. and Hollopeter, D.C., "The Influence of Industrial Waste on Nitrification." Presented at the 33rd Purdue Conference, Purdue University, West Lafayette, IN (May, 1978).

*** Frohlich, G., Ely, R.B. and Vollstedt, T.J., "Performance of a Biophysical Treatment Process on a High Strength Industrial Waste." Presented at the 31st Purdue Conference, Purdue University, West Lafayette, IN (May, 1976).

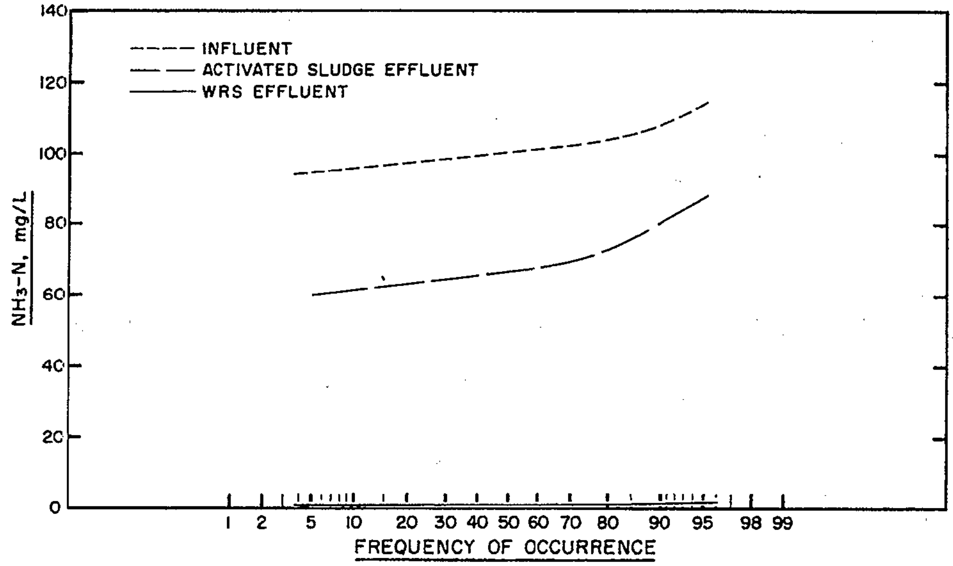

Figure 3. FREQUENCY PLOT OF AMMONIA REMOVAL

Recent performance on fossil fuel derived wastewaters wherein nitrification was required show that complete nitrification is readily obtained with PAC addition but is not obtained in a pure biological activated sludge system even at a long solids residence time and hydraulic detention time. A comparison of nitrification performance of activated sludge and WRS is shown in Figure 3. Both processes were operated in a single stage mode at an SRT of 35 days, however, the activated sludge pilot plant hydraulic detention time exceeded 50 hours more than two times the WRS.

A performance comparison of priority pollutant removals from conventional activated sludge and the powdered activated carbon/activated sludge process is shown in Table 3.* Improved priority pollutant removals were obtained with PAC addition.

Similar results, an approximate one-third greater priority pollutant removal with PAC enhanced sludge, has been demonstrated for shale oil retort wastewaters.**

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* Hutton, D.G., "Removal of Priority Pollutants with a Combined Powdered Activated Carbon - Activated Sludge Process." Presented at the 179th National AIChE Meeting, Houston, TX (March, 1980).

** Wei, op. cit.

TABLE 3. EFFLUENT PRIORITY POLLUTANT COMPARISON

Compound	Feed Concentration ppb	% Removal Activated Sludge	% Removal Powdered Carbon/ Activated Sludge
Benzene	81	98.5	99.6
Chlorobenzene	3,660	99.1	99.8
Chloroethane	667	99.8	99.9
Chloroform	72	96.7	96.9
Methyl Chloride	138	98.5	99.7
Tetrachloroethylene	33	99.5	99.5
1,2-Dichlorobenzene	18	90.6	99.0
2,4-Dinitrotoluene	1,000	31.0	90.0
2,6-Dinitrotoluene	1,100	14.0	95.0
Nitrobenzene	330	94.5	99.9
1,2,4-Trichlorobenzene	210	99.9	99.9
2,4-Dichlorophenol	19	0	93.0
2,4-Dinitrophenol	140	39.0	99.0
4-Nitrophenol	1,100	25.0	97.0

Resiliency to potential toxic upsets due to production process malfunctions is illustrated in Figure 4. Consistent WRS performance is maintained in the two stage system though the total phenol concentration reached 2000 mg/L in the coal gasification liquor feed for a 1.0 hour duration. This was preceeded by a 0.5 hour period at 1000 mg/L total phenol, to simulate actual shock phenol levels occurring in a process malfunction. The results of Figure 4 show that the WRS effluent NH_3-N and total phenol levels remained low though no WRS operational adjustments were made to compensate for the shock loading. Consistent results continued beyond that shown in Figure 4. The effluent NH_3-N levels returned to less than 0.5 mg/l following the stress tests. Improved response would be expected with SRT changes during stress conditions.

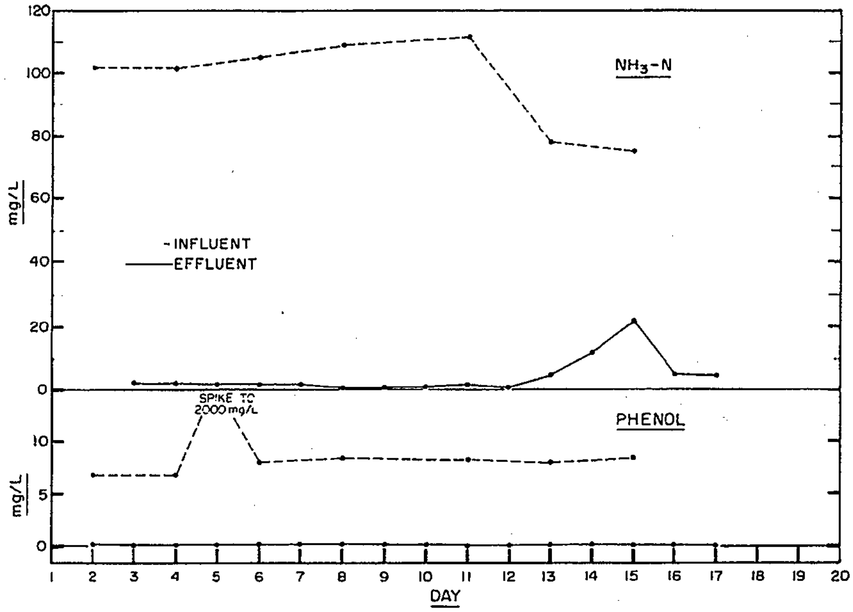

Figure 4. RESPONSE TO PHENOL SHOCK LOADING

PERFORMANCE

Initial WRS treatability investigations were conducted on coke oven gas flushing liquors -- quite similar to synfuels wastewaters. A performance comparison from studies of activated sludge and WRS treating these high strength liquors is shown in Table 4. The results indicate good performance for both processes, however, ammonia conversion to nitrate nitrogen was not obtained in the activated sludge treatment. Nitrification was obtained in the single stage WRS despite the high phenol concentration (468 mg/L total phenol) and the high waste COD level.

TABLE 4. PERFORMANCE COMPARISON: COKE OVEN GAS FLUSHING LIQUORS

	Activated Sludge		WRS	
	Influent	Effluent	Influent	Effluent
BOD_5, mg/l	650	10	1050	4
COD, mg/l	1329	436	2359	289
NH_3-N, mg/l	600	731*	13	<1
SCN, mg/l	130	3.5	279	<2
Phenol, mg/l	150+	<1	468	<1
Cyanide, mg/l	--	--	7	1.2

*SCN is biologically converted to NH_3-N, there is no nitrification.

Subsequent treatment demonstrations confirmed nitrification of coke oven flushing liquors at solids residence times as low as 7 days at approximately 25°C.* Wastewater characteristics were similar to the WRS influent data of Table 4.

More recently, Zimpro Inc. has conducted treatability studies on fossil fuel derived wastewaters. Laboratory scale treatment of coal gasification wastes were performed. Additional process wastes were added to duplicate expected full scale plant waste characteristics. Both single and two stage activated carbon/activated sludge systems were operated for organics removal. Spent carbon regeneration was provided. Since nitrification was not required, pH control and alkalinity supplement were not provided. The raw waste pH was slightly less than 5 while the mixed liquor and effluent pH levels were approximately 6.5.

Performance results, shown in Table 5, indicate good organic removals for both single and two stage systems.

TABLE 5. WRS PERFORMANCE: COAL GASIFICATION WASTEWATER

	Single Stage		Two Stage	
	Influent	Effluent	Influent	Effluent
BOD_5, mg/l	699	<12	708	<12
COD, mg/l	1580	110	1560	94
TKN, mg/l	148	110	152	116
NH_3-N, mg/l	104	88	103	93
Phenol, mg/l	6.9	<0.9	6.7	<1.0
Cyanide, mg/l	10.0	0.17	10.8	0.14

Similar laboratory scale treatment of a coal gasification wastewater in a nitrification mode with intermittent NaOH supplement for pH control provided the results shown in Table 6. The pH adjustment maintained a minimum pH of 6.5. The wastewater in this study contained a higher volatile acids fraction than the previous gasifier waste resulting in a higher BOD/COD ratio. In addition to nearly complete nitrification in both single and two stage treatment modes, substantial denitrification is demonstrated.

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* Bauer, G.L., Hardie, M.G. and Vollstedt, T.J., "Biophysical Treatment of Coke Plant Wastewaters." Presented at the 35th Purdue Conference, Purdue University, West Lafayette, IN (May 1980).

TABLE 6. WRS PERFORMANCE: COAL GASIFICATION WASTEWATER

	Single Stage		Two Stage	
	Influent	Effluent	Influent	Effluent
BOD_5, mg/l	1344	<6	1344	<4
COD, mg/l	2270	45	2270	53
TKN, mg/l	99	5.5	99	5.7
NH_3-N, mg/l	70	<1.1	70	<1.0
Phenol, mg/l	2.6	<0.1	2.6	<0.1
Cyanide, mg/l	7.5	0.08	7.5	0.11

An extensive design study on a larger scale pilot basis was conducted on the gasifier wastewater of Table 6. Performance results over the 6 month study period were excellent with a neglible effluent NH_3-N concentration from the two stage WRS.

TREATMENT COST COMPARISON

Cost comparisons (Table 7) of WRS and more conventional biological treatment processes, sponsored by the EPA, show the WRS is approximately cost equivalent to conventional activated sludge and activated sludge designed for nitrification.* Considerable cost savings is obtained employing WRS in-lieu of activated sludge followed by granular carbon adsorption.

TABLE 7. TREATMENT COST COMPARISON

	Cost, $/1000 Gallons		
Process	5 mgd	10 mgd	25 mgd
WRS*	0.52	0.40	0.30
Activated Sludge			
Conventional	0.49	0.38	0.29
Single Stage Nitrification	0.51	0.41	0.31
Two Stage Nitrification	0.59	0.46	0.35
Granular Carbon System @ 1500 lb carbon/MG	0.73	0.58	0.46

* Designed to nitrify.

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* Culp, G.L. and Shuckrow, A.J., "Appraisal of PAC Processes for Municipal Wastewater Treatment." Environmental Protection Technology Series, EPA-600/2-77-156, Contract No. 68-03-2211 (September, 1977).

Investigation of secondary treatment options for Lurgi process coal gasification liquors including the powdered activated carbon/activated sludge process and other applicable wastewater treatment processes showed the PAC/activated sludge process employing Wet Air Regeneration the most cost effective treatment option (see Table 8).* The annual operating cost of the PAC/activated sludge process is comparable to conventional biological treatment with land application of waste sludges, while considerable capital cost savings are obtained. The net energy requirements of the PAC treatment system is also equivalent to conventional activated sludge.

TABLE 8. TREATMENT COST COMPARISON FOR LURGI PROCESS WASTES*

Treatment Process	Capital Cost	Annual Operating Cost	Net Energy Requirements, KWH/yr
PAC/Activated Sludge			
Wet Air Regeneration	5,788,000	1,764,000	18,066,920
Multiple Hearth Regeneration	6,761,000	2,460,000	23,030,900
Activated Sludge			
Incineration of Sludges	9,862,000	2,347,000	26,115,400
Land Application of Sludges	6,769,000	1,799,000	18,401,500

* Based on 242 MM SCF PD SNG

The results of Table 8 show considerable spent carbon regeneration cost savings with Wet Air Regeneration over that obtained with multiple hearth regeneration.

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* Castaldl, F.J., "Application of Combined Powdered Carbon/Activated Sludge Treatment to Lurgi Process Coal Gasification Wastewaters." Application of Adsorption to Wastewater Treatment, Vanderbilt University, Nashville, TN (February, 1981).

CONCLUSIONS

The addition of powdered activated carbon to the activated sludge process, including spent carbon reactivation by Wet Air Regeneration, provides improved treatment performance and ensures stable reliable operation. The addition of PAC provides further treatment benefits including resistance to shock loading and wastewater toxicity and permits nitrification of synfuels wastewaters.

Performance of the Wastewater Reclamation System on coke oven gas flushing liquors and coal gasification process liquors is excellent. Both organic treatment and nitrification of these wastewaters were demonstrated.

Cost evaluations of the Wastewater Reclamation System on coal gasification wastewaters show the WRS cost effective compared to conventional biological treatment with land application of residuals. Wet Air Regeneration was shown more economical than multiple hearth regeneration for spent powdered carbon regeneration.

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LAND TREATMENT OF COAL CONVERSION WASTEWATERS

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ABSTRACT

This research project investigated the treatment potential of soil systems for polynuclear aromatic compounds (PNAs) present in aqueous wastes from coal conversion processes. A protocol for obtaining the soil assimilative capacities for mutagenic and recalcitrant PNA compounds was developed and, for a subset of compounds, data were obtained to describe: (1) rates of transformation, including degradation, detoxication, and possible intoxication; (2) effect of PNA structure on transformation rate; (3) effect of engineering management options, including nutrient addition, analog enrichment, surfactant addition, and pH adjustment on transformation rates; and (4) soil acclimation to PNAs.

A three-step protocol including: (1) incubation, (2) identification, and (3) determination of mutagenic potential involves interfacing high performance liquid chromatography (HPLC) for compound and metabolite identification with the Ames _Salmonella typhimurium_/mammalian microsome mutagenicity assay for determining genotoxic potential of PNA compounds and transformation products in soil. Identification (HPLC) and mutation (Ames assay) were quantified.

INTRODUCTION

This research has investigated the use of land treatment for the polynuclear aromatic (PNA) class of compounds present in wastes from the coal gasification industry. Land treatment has been demonstrated to be a cost-effective environmentally safe technology for a multitude of industrial wastes. PNA compounds have been identified as byproducts in the synfuel industry, and are of critical environmental concern due to the following specific characteristics: (1) chronic health effects (carcinogenicity), (2) microbial recalcitrance, (3) high bioaccumulation potential, and (4) low removal efficiencies in traditional wastewater treatment processes (Herbes et al., 1976). Therefore, a preliminary feasibility assessment regarding the application of land treatment technology for coal conversion wastes in general and for hazardous components in particular was undertaken.

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In a comprehensive review of the literature Sims and Overcash (1981) summarized the behavior and fate of PNA compounds in terrestrial systems, including soils and vegetation. The potential for effective treatment and safe ultimate disposal of PNA compounds is significant with regard to land application of coal gasification wastes.

Land application is defined for the purpose of this study as the intimate mixing or dispersion of wastes and the soil-plant system with the objective of microbial stabilization, adsorption, immobilization, selective dispersion, or crop recovery leading to an environmentally acceptable assimilation of the waste. In this case coal conversion wastes are applied in thin layers over land areas to provide intensive waste constituent interaction with the soil, with substantial soil zones between waste and relevant surface and ground waters, for the purpose of environmentally acceptable assimilation.

Land application of synfuel wastes is also based on a constraint of nondegradation of land. That is, the waste when considered on a constituent-by-constituent basis shall be applied to the plant-soil system at such rates or over such time spans that no land is irreversible removed from some other potential usage (agriculture, development, forestation, etc) (Overcash and Pal, 1979).

There are four major stages in the design of a total waste management system for coal conversion wastes. These stages, shown in Figure 1 are:

I. the determination of the land limiting constituent (LLC) or that parameter or class of parameters requiring the largest land area for assimilation;

II. the design evaluation of all required components for the land application system and the cost analysis based on different amounts of the LLC;

III. the selection and cost analysis of pretreatment or in-plant alternatives for reducing the total level of the LLC;

IV. the economic balance between the cost of the total land receiver and the cost of pretreatment processes such that the sum total system costs is a minimum (Overcash and Pal, 1979).

The first stage of the design methodology is the most difficult. The assimilative capacities for PNAs have not been established. An objective of this research project has been to obtain the information necessary to complete stage one for the coal gasification industry. This has required a detailed literature review of coal gasification waste characterization and plant-soil assimilative capacities for waste constituents, and laboratory studies to determine the soil assimilative capacities for relevant PNAs.

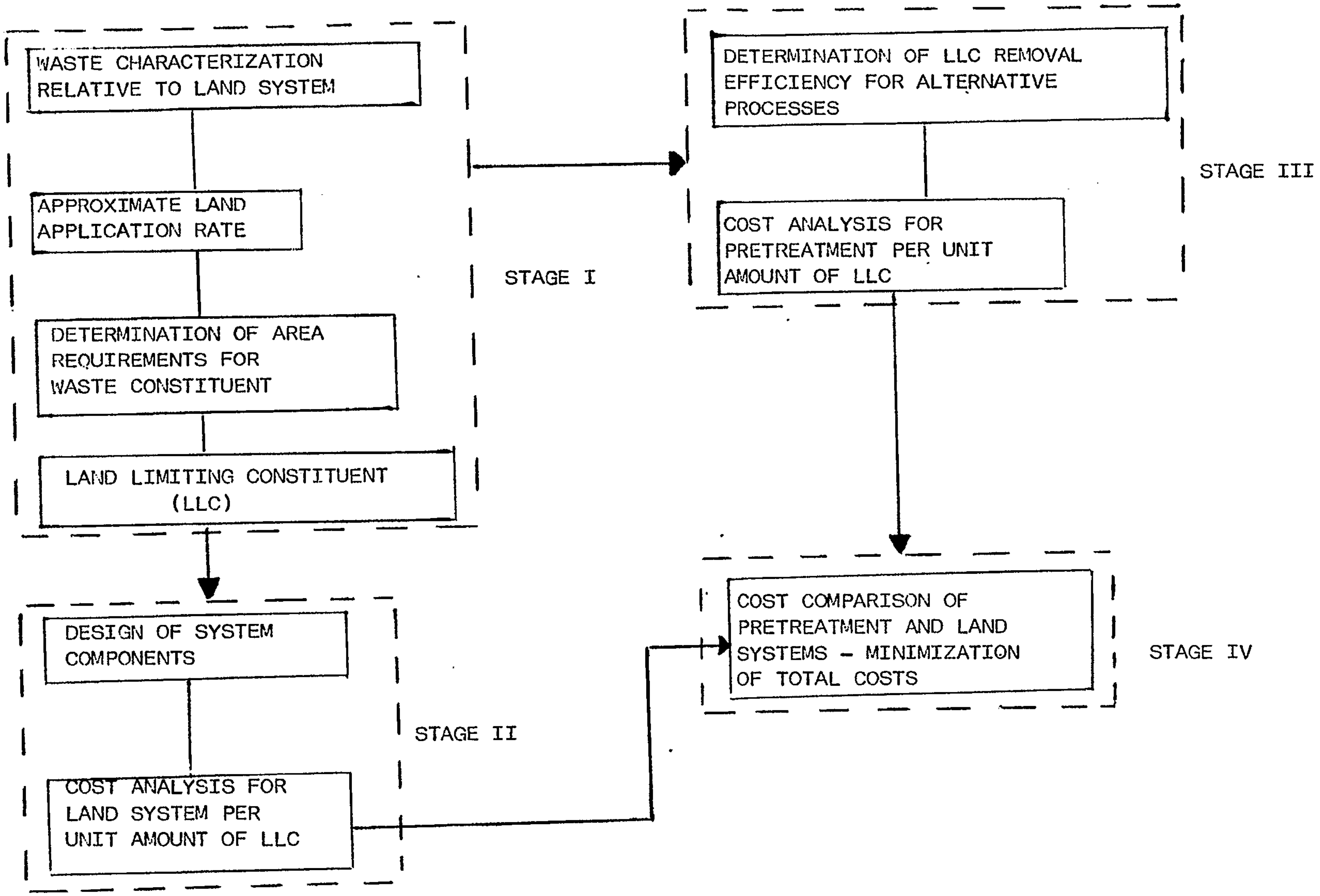

Figure 1. Stages of Unified Methodology for Design of Pretreatment-Land Application Systems.

APPROACH

Stage one of the four-stage methodology required the following information: (1) waste characterization on a constituent-by-constituent basis; (2) determination of the plant-soil assimilative capacity for each waste constituent or component; (3) determination of the land area requirements for each waste component or class of components; and (4) determination of the land limiting constituent (LLC), which is that constituent or class of constituents requiring the largest land area for safe treatment and ultimate disposal.

The waste characterization for each constituent is expressed as kg/unit time, while the assimilative capacity is expressed as kg of parameter/unit area/unit time. The ratio of waste generation to assimilative capacity is the area (hectares or acres) required for the environmentally acceptable waste application to the terrestrial system. Ranking the required land areas indicates one or more constituents as requiring the greatest land size, and this constituent or class of constituents is defined as the LLC. Using the LLC area guarantees that other waste constituents are applied at environmentally acceptable rates.

WASTE CHARACTERIZATION AND GENERATION

A review of the literature was conducted to obtain information concerning wastewater characterization in the coal gasification industry. Due to the experimental and developing nature of "the state of the art" of coal gasification, it has been impossible to obtain comprehensive information concerning:(1)coal mass flow rates, (2) water mass flow rates, and (3) concentrations of inorganic and organic species including toxic organic compounds (PNAs) in one assessment document or one coal gasification facility.

Waste constituents were identified, quantified, and waste generation rates (kg/yr) were calculated with information obtained for an expected typical full scale Lurgi coal gasification facility. That is, wastewater was characterized for a full scale Lurgi facility: 250 x 10^6 SCFD of medium to high BTU synthetic natural gas (SNG), operating at a coal feed rate of 2245 x 10^3 lb/hr and a condensate flow rate of 1897 x 10^3 lb/hr, and using North Dakota Lignite coal. Because of the dearth of information concerning PNA concentrations and mass flows in the literature surveyed, several calculational procedures were necessary to derive expected concentrations of PNAs in the wastewater addressed. Expected concentrations of PNAs were based on other waste constituents present. The result is a preliminary waste characterization including constituent identification and waste generation rates for over 90 individual constituents.

ASSIMILATIVE CAPACITIES AND LAND AREA REQUIREMENTS

Much information already exists with regard to the terrestrial assimilation capacities for several soil types for a multitude of organic and inorganic constituents identified in coal gasification wastewaters (Overcash and Pal, 1979; and Sims and Overcash, 1980). Information is especially abundant with regard to inorganic species identified. A large body of information exists indicating that PNAs are not generally biomagnified in vegetation and crops (Sims and Overcash, 1981). However, information concerning the soil assimilation of PNA constituents in coal gasification wastewaters needed to be developed for several PNA compounds.

With the information obtained an initial land limiting constituent analysis was conducted which did not take into account the PNA class of compounds. The LLC analysis for coal gasification wastewater identified cadmium as the constituent requiring the greatest land area (750 ha) for land treatment.

To determine the soil assimilative capacities (SACs) for PNAs in coal gasification wastes, it is necessary to determine realistic concentrations of PNAs that would result from the land application of a typical coal gasification waste. The land area determined in the initial LLC analysis provided the basis for calculating the resultant PNA concentrations in soil for each PNA compound. Waste generation for each PNA was calculated by multiplying the PNA concentration by the volumetric flow rate to obtain mass/time (kg/yr). The calculated waste generation was divided by the land area determined in the LLC analysis (750 ha) to obtain the resultant soil PNA concentration (mg/kg).

The effect of the presence of PNA compounds in coal gasification wastewater on land area requirements can be evaluated by experimentally determining the soil assimilative capacities. An evaluation of the SACs could determine whether an individual PNA compound or the class of PNAs required more or less land area for treatment than cadmium. With this information a design for land application for the safe treatment and disposal of hazardous and toxic components as well as other constituents in coal gasification wastes is assured by using the LLC approach.

EXPERIMENTAL DESIGN

Experiments to determine the SACs of PNA compounds present in coal gasification wastewaters were designed to obtain the following specific information: (1) rates of PNA transformation; (2) effect of PNA structure on transformation rate; (3) effect of engineering management options on transformation rate; (4) soil acclimation to PNAs; and (5) toxicity and genotoxic potential of soil-treated PNAs.

SELECTION OF PNA COMPOUNDS FOR STUDY

A subset of the total number of PNAs identified in coal gasification wastewaters was selected based on the following criteria: (1) genotoxicity, (2) molecular recalcitrance, (3) priority pollutant status, and (4) lack of information concerning fate and behavior in the environment. Soil concentrations for the PNAs considered based on the LLC analysis conducted are shown in Table 1. Waste PNA concentration, mass generation, and soil concentration resulting from land application using the LLC constraint (750 ha) are included. For those PNAs not quantified in the literature, the highest concentration on the list was used (0.57 mg/kg in soil).

TABLE 1. PNA COMPOUNDS AND SOIL CONCENTRATIONS

PNA Compound	Condensate Concentration (mg/l)	Waste Generation (kg/yr)	Soil Concentration (mg/kg)
Acenaphthylene	0.114	855	0.57
Dibenzofuran	-	-	0.57
Acridine	-	-	0.57
Anthracene	0.082	615	0.41
Benzo(b)fluoranthene	0.066	495	0.33
Benzo(k)fluoranthene	0.034	255	0.17
Benz(a)pyrene	0.072	540	0.36
Indeno(1,2,3-cd)pyrene	-	-	0.57

PNA COMPOUND APPLICATION

Each PNA compound was investigated as a separate solution applied on separate soil reactors. Compounds were applied to the soil in small volumes of solvent (methylene chloride), and were mixed thoroughly with the soil to simulate soil incorporation of applied wastes, and to obtain an even distribution of the PNA compound throughout the soil at the desired concentration. Triplicate reactors were used for each PNA.

SOIL TYPE

Norfolk fine sandy loam is a common soil type, typical of the coastal plain, used in land application systems in North Carolina. The Norfolk series is a member of the fine-loamy, siliceous, thermic family of Typic Paleudults.

ENVIRONMENTAL CONTROL CHAMBER

PNA compounds, at the indicated concentrations in 200g and 2000g soil in glass beakers, were incubated in an environmentally controlled chamber. Environmental parameters that were controlled included temperature (25 C), light exposure (dark to prevent photodegradation), and soil moisture (60-80% field capacity). Soil moisture was adjusted to 80% of field capacity with water. Water was added when the soil moisture capacity decreased to 60% of field capacity to simulate field conditions of wetting and drying.

ANALYTICAL METHODS

Soil Extraction and Sample Preparation

The extraction procedure used for extracting PNAs from soil was based on the high performance liquid chromatography procedure for analysis of PNA compounds in water samples (Federal Register, 1979). Soil moisture was adjusted to 80% field capacity prior to extraction. Methylene chloride (250 ml) was added to 200g soil. The solvent-soil mixture was homogenized for two minutes with a Tekmar Tissumizer. The supernatant was decanted from the soil reactor and filtered through anhydrous sodium sulfate. The filtrate was concentrated to a final volume of 3-5 ml.

Reverse Phase-UV HPLC Analysis

A Waters HPLC was utilized with acetonitrile-water as the mobile phase, and a C-18 Perkin Elmer Reverse Phase column was used as the stationary phase. PNA compounds were identified with a UV detector at a wavelength of 254 nm.

Sample Fractionation for Ames Assay

Soil extracts were fractionated using a C-8 preparative Lobar size A prepacked column. Polarity classes of degradation products were collected in acetonitrile-water, evaporated, and redissolved in dimethyl sulfoxide for the Ames assay.

BIODEGRADATION DETERMINATION

Kinetic parameters of interest with respect to biodegradation include half-life ($t_{1/2}$ in days), rate of transformation (r in kg PNA/ha-day), and the rate constant (k in day^{-1}). These kinetic parameters are directly related to the soil assimilative capacities for PNAs.

GENOTOXICITY

Polarity classes of soil PNA degradation products were tested with the Ames assay (Ames et al., 1975). This assay is widely used for the detection of potential carcinogenicity and mutagenicity of environmental chemicals. Toxicity and mutagenicity were determined and dose-response curves were developed. The assay was conducted with and without microsomal activation. Strain TA-98, which detects frameshift mutations, and strain TA-100, which detects base pair substitution mutations, were used.

ENGINEERING MANAGEMENT OPTIONS

Engineering management options, including analog enrichment, nutrient addition, surfactant addition, and pH adjustment are tools which the environmental engineer may use to stimulate biological activity and to increase the rate of biodegradation of recalcitrant compounds. With application of industrial wastes with low levels of substrate organics and PNAs, the level of microbial activity would be expected to be similar to that of the native soil. Engineering management options for organic constituents are potential accelerators of microbial activity. Since the soil assimilative capacity is directly related to the kinetics of degradation, increasing microbial activity may lead directly to increasing the soil assimilative capacities for PNA compounds in coal gasification wastes.

The effect of each engineering management option was tested separately. Addition of an analog-substrate (carbon and energy source) has been shown to increase general microbial activity and growth. Addition of the nutrients nitrogen and phosphorus, which influence the growth of microorganisms, to microbial cultures stabilizing compounds deficient in these elements has been demonstrated to increase the rate of stabilization. Since surfactants can be utilized to increase cell membrane permeability, surfactants may be useful in increasing the solubility and cell membrane permeability of PNAs with a resultant greater oxidation and degradation in the soil environment. These three amendments were investigated for their direct effect on PNA degradation kinetics.

Although increasing soil pH from less than seven to neutral generally increases microbial activity, it may be especially important in soil systems to encourage bacterial growth and competition vis-a-vis fungi. Major differences with respect to microbial oxidation pathways of aromatic hydrocarbons between bacteria and fungi are believed to exist with fungi, premoninant at low soil pH, possibly metabolizing PNAs to more genotoxic products than with bacteria (Dagley, 1975; Cerniglia et al., 1979). Since pH has a significant effect on soil bacterial/fungal proportions, pH may be an important engineering tool to direct the pathway of PNA degradation through a series of detoxication reactions. Soil pH was adjusted with calcium carbonate solutions to 7.0 in triplicate soil reactos.

Two PNA compounds chosen for intensive study with amendments were anthracene and benz(a)pyrene. Anthracene is a three ring aromatic hydrocarbon which serves as a carbon and energy source for microorganisms and is weakly carcinogenic. Benz(a)pyrene is a five ring aromatic hydrocarbon that has not been demonstrated to be a carbon and energy source, but is believed to be degraded through cometabolic processes. Benz(a)pyrene is a powerful carcinogen.

SOIL ACCLIMATION

Acclimation of the soil to each PNA compound was investigated by spiking the soil at zero, three, and six months. Rates of degradation were monitored for each time increment and were compared through time.

STATISTICAL ANALYSIS

Kinetic data were subjected to analysis of variance, and when significant differences at the five percent level were found among PNA compounds Duncan's New Multiple Range Test was employed to separate means. The statistical procedures were performed using standard package programs of Statistical Analysis Systems-76 (Barr et al., 1976).

RESULTS AND DISCUSSION

RATES OF PNA TRANSFORMATION

Table 2 presents results from the laboratory study for kinetic parameters for the biodegradation of PNAs during a 90-day incubation period. Results represent the average of triplicate reactors. Half-lives range from a low of 18 days for acenaphthylene and dibenzofuran to indeno(1,2,3-cd)pyrene which exhibited no measurable loss with time.

TABLE 2. LABORATORY DETERMINED KINETIC DATA FOR PNA DEGRADATION

PNA Compound	Number of Rings	Initial Concentration (mg/kg soil)	Half-life ($t_{1/2}$, days)	Rate Constant (k, day^{-1})	Rate $\left(\frac{mg}{kg\text{-}day}\right)$
Acenaphthylene	3	0.57	18^{A*}	0.039	0.022
Dibenzofuran	3	0.57	18^{A}	0.039	0.022
Acridine	3	0.57	102^{B}	0.007	0.004
Anthracene	3	0.41	34^{A}	0.017	0.007
Benzo(b)-fluoranthene	5	0.33	98^{B}	0.007	0.002
Benzo(k)-fluoranthene	5	0.17	89^{B}	0.008	0.001
Benz(a)pyrene	5	0.36	80^{B}	0.009	0.003
Indeno(1,2,3-cd)-pyrene	6	0.57	$-^{C**}$	**	**

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[*] Values represent means of three replicates. Means followed by the same letter are not significantly different at the 0.05 level.

[**] No decrease in Indeno(1,2,3-cd)pyrene could be detected by HPLC.

Kinetic parametersfor other PNAs identified in coal gasification wastes which were not included in the laboratory study are given in Table 3. The information for these compounds was obtained in a comprehensive review of the literature (Sims and Overcash, 1981).

TABLE 3. LITERATURE VALUES FOR KINETIC DATA FOR PNA DEGRADATION

PNA Compound	Number of Rings	Initial Concentration (mg/kg soil)	Half-life ($t_{1/2}$, days)	Rate Constant (k, day^{-1})	Rate $\left(\frac{mg}{kg\text{-}day}\right)$
Naphthalene	2	7.0	0.12	5.78	40.4
Indole	2	500	1.0	0.693	364.5
Fluorene	3	0.9	39	0.018	0.016
Fluoranthene	4	16.5	143	0.005	0.080
Phenanthrene	3	2.1	26	0.027	0.056

Results for PNA degradation kinetics from the laboratory study and from the literature review indicate that most PNAs addressed have reasonable, finite half-lives in soil systems.

EFFECT OF PNA STRUCTURE ON TRANSFORMATION RATES

Table 2 summarizes the results of the statistical analysis of PNA compounds by structure and half-life. Arranging PNAs by number of rings and half-life indicates that there are three distinct, statistically significantly different groups of PNA compounds. The general trend is for lower ring compounds to exhibit faster degradation kinetics i.e., there is an inverse relationship between the number of rings (PNA size) and half-life.

These results are consistent with the findings of other researchers for aquatic and soil systems for other PNAs. Information developed here adds to the list of quantitative data available for environmental engineers concerned with the design of land treatment systems for the coal gasification industry.

EFFECT OF ENGINEERING MANAGEMENT OPTIONS ON TRANSFORMATION KINETICS

Results showing the effects of environmental management options on biodegradation kinetics for the PNAs studied in the laboratory are given in Tables 4 and 5.

TABLE 4. EFFECT OF AMENDMENTS ON ANTHRACENE DEGRADATION

Amendment	Half-life ($t_{1/2}$, days)	Rate Constant (k, day^{-1})	Rate ($\frac{mg}{kg\text{-}day}$)
None	42^{A*}	0.017	0.68
Nutrients	41^{A}	0.017	0.69
pH	41^{A}	0.017	0.69
Surfactant	45^{A}	0.015	0.63
Analog Enrichment	38^{A}	0.018	0.75

*Values represent means of three replicates. Means followed by the same letter are not significantly different at the 0.05 level.

The degradation of anthracene, a three ring PNA compound which serves as a substrate (carbon and energy source) for soil microorganisms, does not appear to be influenced by the engineering management options used in this study. Statistical analysis of the laboratory data indicate that the relatively short half-life for anthracene with no amendment addition is not statistically different from the half-lives for anthracene treatment with any of the amendments.

TABLE 5. EFFECT OF AMENDMENTS ON BENZ(a)PYRENE DEGRADATION

Amendment	Half-life ($t_{1/2}$, days)	Rate Constant (k, day^{-1})	Rate $\left(\frac{mg}{kg\text{-}day}\right)$
None	90^{A*}	0.0077	0.28
Nutrients	81^{A}	0.0082	0.31
pH	64^{B}	0.0108	0.39
Surfactant	87^{A}	0.0080	0.29
Analog Enrichment	64^{B}	0.0108	0.39

*Values represent means of three replicates. Means followed by the same letter are not significantly different at the 0.05 level.

The degradation of benz(a)pyrene, a five ring PNA compound, is considered to be cometabolized i.e., cannot serve as a source of carbon and energy for the growth of microorganisms, does appear to be influenced by the engineering management options used in this study. Statistical analysis of the data indicated statistically significant **differences** among the treatments. The amendments which effected a significant decrease in the half-life of B(a)P included analog enrichment and pH adjustment.

This information has direct implications for the design of land treatment systems for coal gasification wastes. The data suggest that it may be possible to influence the degradation rates of recalcitrant and hazardous organic compounds through engineering management options.

SOIL ACCLIMATION TO PNAs

Results for the acclimation of soil systems to PNA compounds are still being analyzed. Extent of acclimation appears to vary among the PNA compounds. Indeno(1,2,3-cd)pyrene showed the greatest acclimation from no measurable degradation to 360 days half-life to 201 days half-life for 3,6, and 9 months incubation respectively. More information must await additional data collection and statistical analysis.

TOXICITY AND GENOTOXIC POTENTIAL OF SOIL-INCUBATED PNAs

PNA parent compound, benz(a)pyrene and degradation products collected as polarity classes were not found to be toxic at concentrations from 10ug/plate to 500 ug/plate to be *Salmonella typhimurium* strains TA-98 and TA-100 used in this study,

Results for mutagenesis testing for B(a)P and degradation products are presented in Table 6. Data are given for the soil control, and at six months of incubation of B(a)P in soil.

TABLE 6. MUTAGENICITY OF SOIL-INCUBATED BENZ(a)PYRENE

Sample	Time (months)	Mutagenic Ratio at 500 ug/plate[*]			
		Without Activation		With Activation	
		TA-98	TA-100	TA-98	TA-100
Soil Control	6	1.81	1.20	1.84	1.72
Parent Compound (B(a)P)	6	1.37	1.09	7.82	3.16
Polar Class Fraction	6	1.18	1.26	2.96	1.50
Nonpolar Class Fraction[**]	6	1.28	1.15	3.72	2.19

[*] Mutagenic Ratio is defined as a number of revertants with sample divided by the number of revertants without sample. A test compound or sample is considered negative if the mutagenic ratio is less than 2.0

[**] The Nonpolar class fraction was that fraction collected in preparative high performance liquid chromatography which appeared after the parent compound (B(a)P) for an elution gradient proceeding from more polar fractions to less polar fraction with increasing run time.

Results indicate that neither parent compound nor degradation products are mutagenic without mammalian microsomal activation. This is well known for B(a)P, but is not known for soil metabolites of B(a)P.

Results also indicate that the mutagenic potential of degradation products of soil incubated B(a)P are much less than the parent compound. The highest mutagenic potential (3.72) is associated with the Nonpolar class fraction.

This information suggests that after six months of soil incubation, the products of biodegradation of B(a)P are much less mutagenic than the parent compound. A detoxication pathway is therefore indicated for B(a)P biodegradation in soil.

CONCLUSIONS

Results from this preliminary study indicate that land application technology for fossil fuel wastes is promising. A protocol has been established for obtaining the soil assimilative capacities for recalcitrant and mutagenic PNA compounds, and for determining genotoxic potential of parent compounds and metabolites in soil. With the significant cost benefit for land treatment and the demonstrated potential to actually decompose recalcitrant and hazardous organics, it would apppear reasonable to proceed to further evaluations. Using this protocol a more detailed design based on specific waste characterization and site-specific analyses would follow for a particular sunfuel facility.

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Session III: AIR-RELATED ENVIRONMENTAL CONSIDERATIONS

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Research Triangle Park, NC

PB83-126322

REMOVAL OF ACID GASES AND OTHER CONTAMINATES FROM COAL GAS † USING REFRIGERATED METHANOL

by

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ABSTRACT

The steam-oxygen gasification of a New Mexico subbituminous coal was carried out in a pilot-scale fluidized bed gasifier. Gas cleaning was accomplished by a hot cyclone, a water quench-venturi scrubber, filters, and an acid gas removal system using refrigerated methanol as the solvent. Results of both gasification and gas cleaning are described. Refrigerated methanol proved to be effective in cleaning the gasifier make gas, however, the presence of several reduced sulfur species and hydrocarbons was detected in the absorber, flash tank, and stripper exit gas streams over a wide range of operating conditions. While a variety of simple aromatics accumulated in the recirculating methanol, essentially no polynuclear aromatic compounds were detected. Most polynuclear aromatic compounds were evidently removed in the gas quenching process.

INTRODUCTION

As a part of a continuing research program on the environmental aspects of fuel conversion, the U. S. Environmental Protection Agency has sponsored a research project on coal gasification at North Carolina State University in the Department of Chemical Engineering. The facility used for this research is a small coal gasification-gas cleaning pilot plant. The overall objective of the project is to characterize the gaseous and condensed phase emissions from the gasification-gas cleaning process, and to determine how emission rates of various pollutants depend on adjustable process parameters.

A complete description of the facility and operating procedures is given by Ferrell et al., Vol I, (1980), and in abbreviated form by Felder et al. (1980). A schematic diagram of the Gasifier, the Acid Gas Removal System (AGRS), and other major components is shown in Figure 1.

In an initial series of runs on the gasifier, a pretreated Western Kentucky No. 11 coal was gasified with steam and oxygen. The results of this work are given by Ferrell et al., Vol II, (1981), and were presented at the EPA Symposium on Environmental Aspects of Fuel Conversion Technology V, held in St. Louis, Mo., September, 1980.

The second major study carried out on the facility was the steam-oxygen gasification of a New Mexico subbituminous coal (from the Navaho mine of the Utah International Co.) using refrigerated methanol as the AGRS solvent. This paper presents a brief summary of the gasifier operation using this coal, shows examples of analyses of some of the gasifier effluent streams, and presents a summary of the results of the operation of the AGRS using the gasifier make gas as feed.

SUMMARY OF GASIFIER OPERATION

The fluidized bed gasifier and raw gas cleaning system (cyclone, venturi scrubber, filters and heat exchanger) used for these studies was originally designed for the gasification of a devolatilized coal char with a very low volatile matter content. Extensive modification of the upper part of the gasifier, the venturi scrubber system, and the heat exchanger was required for operation with the high volatile matter New Mexico coal. Table 1 shows an analysis of the char and coal used in studies to date. After modification, the system functioned well in providing a clean, dry gas to the acid gas removal system.

All of the experimental work so far has been carried out with the solid coal particles fed into the reactor several feet above the top of the fluidized bed. The particles are thus in contact with the hot product gases for several seconds before mixing into the fluidized bed, a mode of operation

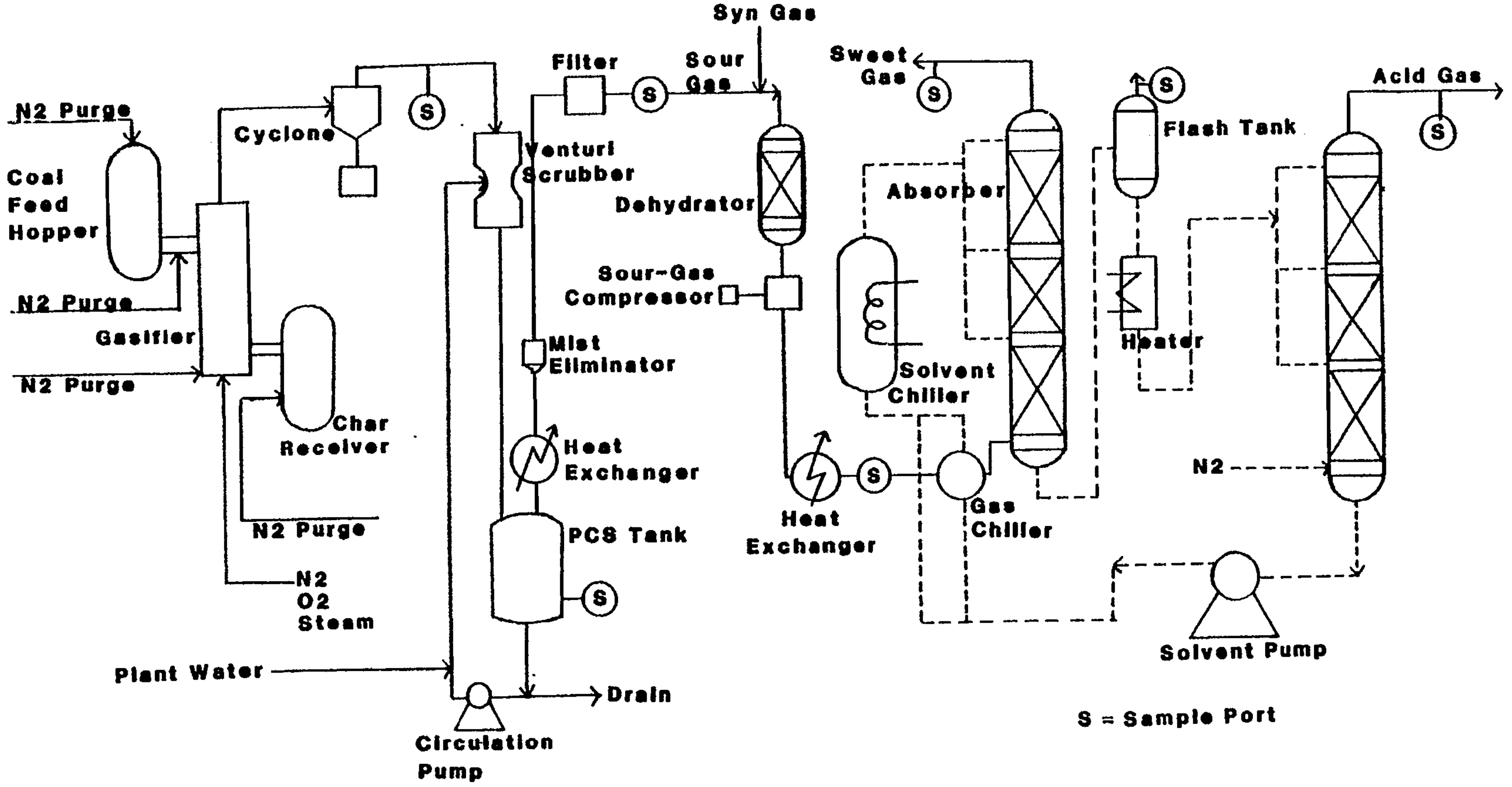

Figure 1. Pilot Plant Facility

that tends to maximize the production of tars and other organic liquids from the coal. It is an excellent mode of operation for our present purpose since it produces relatively high concentrations of environmentally important elements and compounds.

TABLE 1
COAL AND CHAR ANALYSIS

	Coal Char	New Mexico Coal
Proximate Analysis		
Fixed Carbon	86.0	42.0
Volatile Matter	2.4	35.4
Moisture	0.9	10.5
Ash	10.7	22.6
Ultimate Analysis		
Carbon	83.8	52.5
Hydrogen	0.6	4.8
Oxygen	2.2	18.3
Nitrogen	0.1	1.2
Sulfur	2.6	0.6
Ash	10.7	22.6

A total of 15 gasifier runs were made covering a range of reactor parameters. For this series of runs, the average temperature of the fluidized bed was varied from about 1600°F to 1800°F, and the molar steam to carbon ratio was varied from about 1.0 to 2.0. The coal feed rate and the reactor pressure were kept nearly constant. Several of the first reactor runs were made with mixtures of coal and char, but all integrated runs reported on later were made with 100% coal.

At the lower temperatures the production of methane and of tars and other hydrocarbons is maximized. As the temperature is increased, the make gas rate increases, the production of methane and other hydrocarbons decreases, and the concentration of CO_2 increases. As an example, conditions and mass balances for run GO-76 are shown in Table 2.

GASIFIER MODELING RESULTS

To aid in the formulation of gasifier performance correlations, a simple model has been developed which considers the gasification process to occur in three stages: instantaneous devolatilization of coal in a zone above the fluidized bed, instantaneous combustion of carbon at the bottom of the bed, and steam-carbon gasification and water gas shift reaction in a single perfectly mixed isothermal stage. The model is significant in and of itself,

Table 2

```
*******************************************
*                                         *
* NCSU DEPARTMENT OF CHEMICAL ENGINEERING *
*                                         *
* FLUIDIZED BED COAL GASIFICATION REACTOR *
*                                         *
*******************************************

          RUN GO-76  4-28-81  13:30-16:15


      REACTOR SPECIFICATIONS .                         FEED RATES AND RATIOS

PRESSURE     = 100.6 PSIG ( 794.9 KPA)          COAL       = 50.86 LB/HR (23.07 KG/HR)
TEMPERATURE  = 1711.6 DEG.F ( 933.1 DEG.C)      STEAM      = 57.37 LB/HR (26.02 KG/HR)
BED HEIGHT   = 38.0 IN. (0.97 METERS)           OXYGEN     = 12.62 LB/HR ( 5.72 KG/HR)
BED DIAMETER =  6.0 IN. (0.152 METERS)          NITROGEN   =  6.74 LB/HR ( 3.06 KG/HR)
ESTIMATED BED VOIDAGE = 0.80                    PURGE N2   = 10.33 LB/HR ( 4.69 KG/HR)
SOLIDS HOLDUP = 10.4 LB ( 4.7 KG)               STEAM/CARBON = 1.54 MOLES STEAM/MOLE C
                                                O2/CARBON    = 0.19 MOLES O2/MOLE C
                                                N2/O2        = 0.61 MOLES N2/MOLE O2


                  ELEMENTAL MATERIAL BALANCES : FLOWS IN LB/HR

                  MASS      C        H        O        N        S

          COAL    50.9    24.81     2.01    11.53     0.51    0.422
         GASES    87.1     0.00     6.42    63.56    17.07    0.000
   TOTAL INPUT   137.9    24.81     8.43    75.09    17.58    0.422

          CHAR    13.3     6.10     0.12     0.00     0.07    0.074
          DUST     0.1     0.03     0.00     0.00     0.00    0.000
         GASES   121.6    18.38     8.44    76.97    17.52    0.263
    WASTEWATER     0.0     0.00     0.00     0.00     0.00    0.000
  TOTAL OUTPUT   135.0    24.51     8.56    76.98    17.59    0.337

  % RECOVERY     97.9%    98.8%   101.6%   102.5%   100.0%    80.0%


                        OUTPUT VARIABLES

        CARBON CONVERSION (PERCENT)                 74.1

        DRY MAKE GAS FLOW RATE (SCFM)               19.2

        HEATING VALUE OF SWEET GAS (BTU/SCF)       373.7

        EFFLUENT FLOW RATES (LB/HR)
                  CO                                15.65
                  H2                                 2.06
                  CH4                                3.40
                  CO2                               33.42
                  N2                                17.52
                  H2S                                0.271
                  COS                                0.015
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but its particular importance to the project is that it enables the specification of gasifier conditions required to produce a feed to the acid gas removal system with a predetermined flow rate and composition.

In a previous report (Ferrell et al., 1981), the structure of the model was presented, and the ability of the model to correlate data on the gasification of a devolatilized bituminous coal was demonstrated. The model was subsequently extended to include the evolution of volatile gases in the pyrolysis stage of the gasification process, and used to fit the data from the present series of runs with the New Mexico subbituminous coal. The model takes as input the average reactor bed temperature and pressure, the bed dimensions, feed rates of coal, steam, oxygen, and nitrogen, solids holdup in the bed, and ultimate analysis of the feed coal, and calculates carbon conversion and make gas flow rate and composition. A complete description of the model in its present form will be given in an EPA report now in preparation. Plots of model predictions vs measured values of carbon conversion and dry make gas flow rate are shown in Figures 2-3. The reasonably close proximity of most points to the 45 degree line is gratifying in view of the simplicity of the model. The proximity of the points corresponding to the "best" runs (from the standpoint of satisfying mass balances) is even more satisfying.

The model also does a good job of correlating data on the evolution of individual species. Figure 4 shows predicted versus measured values of the rate of production of CO from the gasifier. Similar plots have been obtained for the production of H_2 and CO_2. The good correspondence seen in these plots suggests that the model can be used to predict the composition of the gasifier make gas for a specified set of reactor conditions, and also to study the effects of individual reactor variables on yield.

AGRS OPERATION AND RESULTS

As previously mentioned, top feeding coal into the gasifier allows a substantial amount of devolatilization to take place before the coal enters the fluidized bed. While most commercial fluidized bed gasifiers will use a deep-bed injection method of feeding coal into the fluidized bed, it was decided not to modify our system in order to maximize the formation of tars, oils, and other hydrocarbons and to provide a more complete test of the AGRS.

It should also be noted that the relatively simple acid gas removal system used in this study lacks the complexity of the selective systems found in many physical absorption processes. These systems, which use more than one absorber and stripper, and often several flash tanks, separate sulfur gases from carbon dioxide before further processing of the acid gas. This is done to concentrate the sulfur gases before they are fed to a sulfur recovery unit, and to recover the CO_2 or vent the CO_2-rich stream to the atmosphere. While the AGRS used in this study could have been modified to emulate an

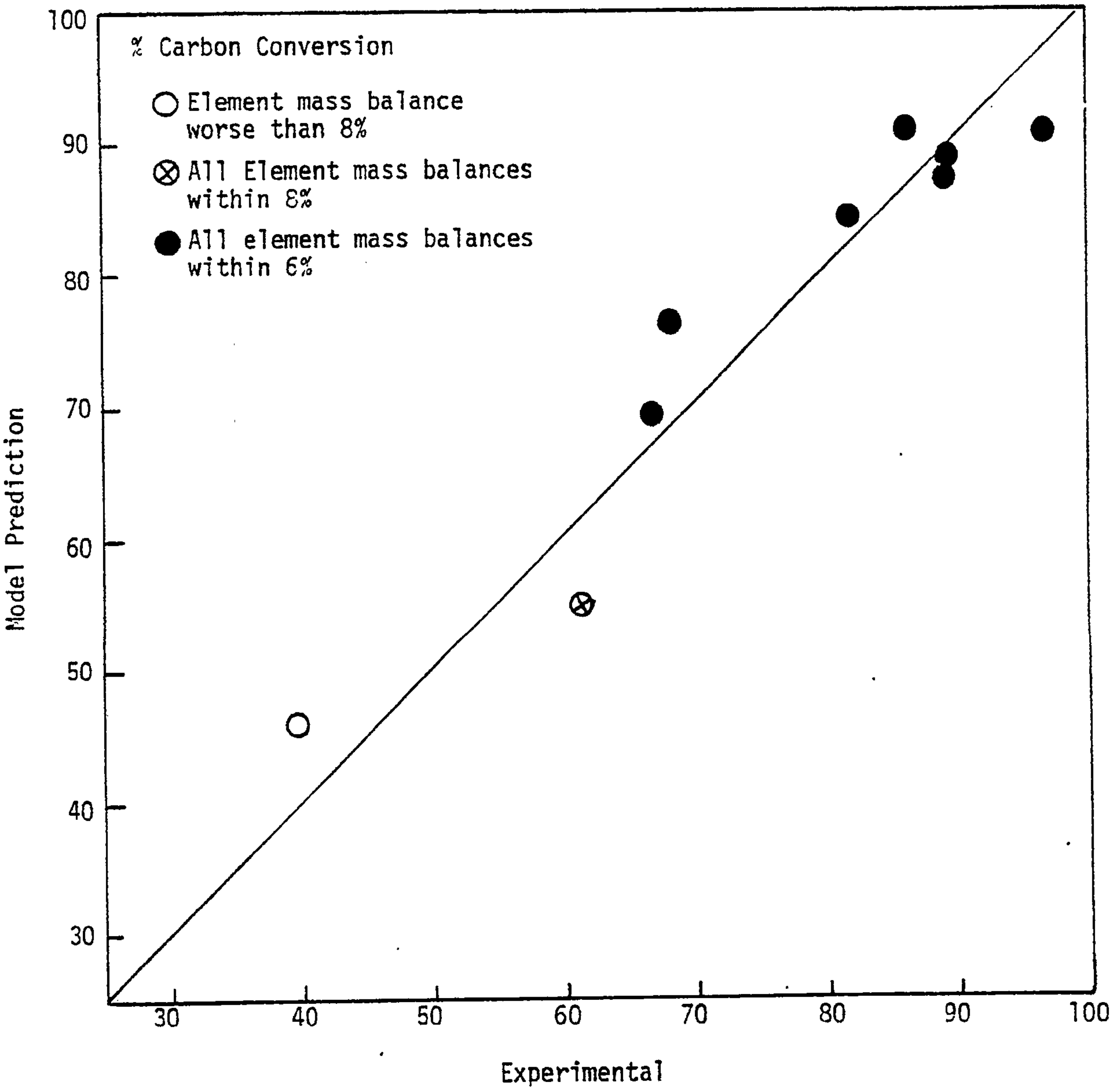

Figure 2. Predicted vs. Experimental Carbon Conversion, Gasification of New Mexico Coal

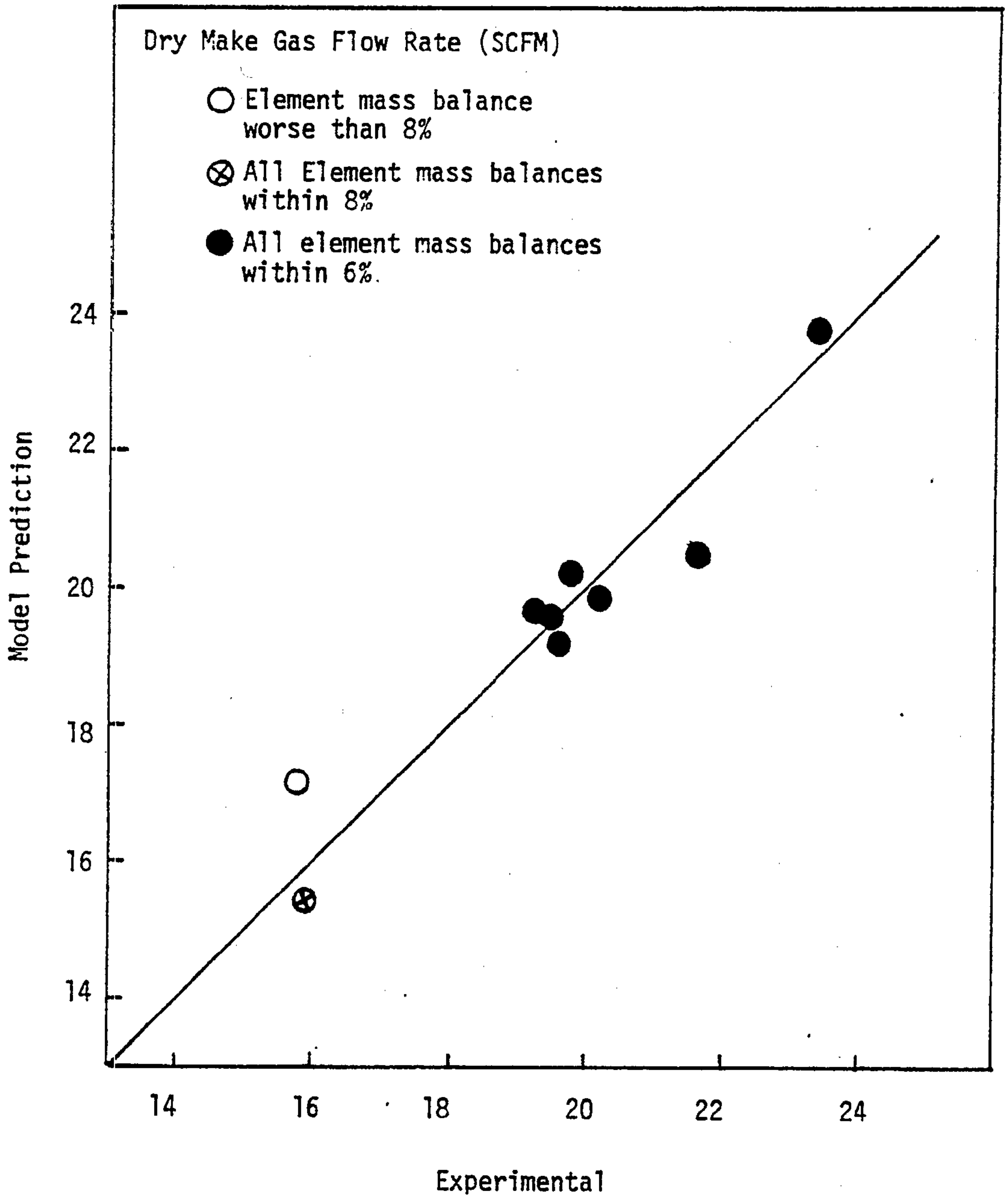

Figure 3. Predicted vs. Experimental Dry Make Gas Flow Rate, Gasification of New Mexico Coal

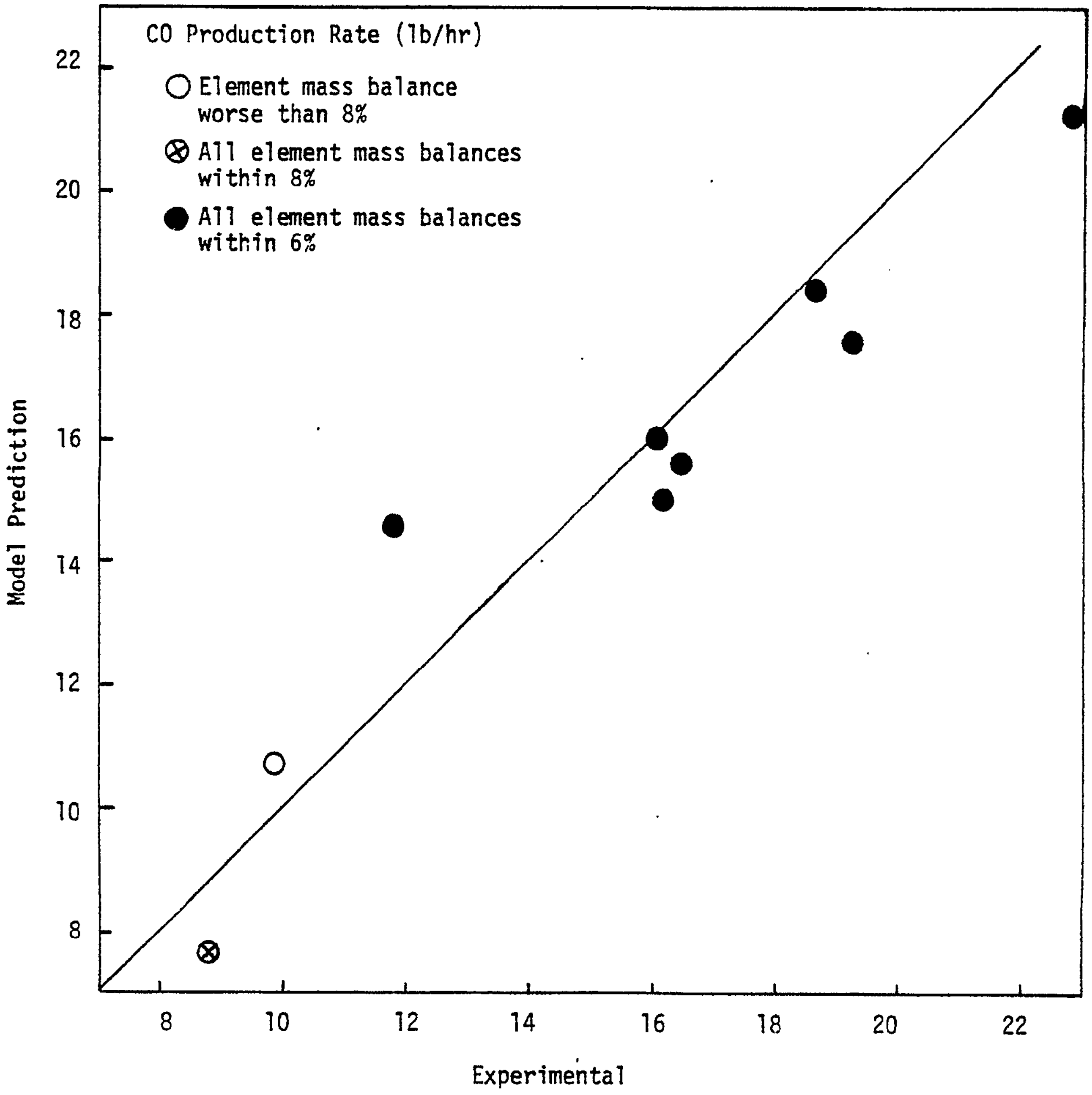

Figure 4. Predicted vs. Experimental Production Rate of CO from Gasification of New Mexico Coal

existing selective absorption process, it was decided that data obtained from a relatively simple but well-characterized system would be of more use than data obtained from a fairly complex system, similar but not identical, to existing commercial systems. Through judicious use of computer simulation and engineering calculations, the data obtained from our system should be extrapolatable to more industrially significant situations.

EXPERIMENTAL PROGRAM

In designing the experimental program to be used in these studies, the use of a full factorial experimental design was not believed to be necessary. The program was designed to cover the broadest range of operating conditions possible for the system of New Mexico coal and refrigerated methanol. Effects of variations in important process variables were examined by comparing all runs to a base case. Although this approach is not exhaustive, it provides a framework with which to examine the environmental consequences of acid gas removal with methanol. In addition, the work done in this study will be useful in developing experimental programs for other coals and acid gas removal solvents to be studied in our facility.

Table 3 shows the operating conditions used for the nine runs made in this part of the study. Also shown are inlet and outlet gas concentrations for the major acid gases in the absorber.

DISCUSSION

From an environmental perspective, operation of the acid gas removal system in a coal gasification process becomes important when harmful compounds or pollutants may be discharged to the atmosphere. Although there are a wide variety of extremely toxic materials released from coal during gasification, as long as they remain within the gas cleaning system or are properly processed, they pose little problem. However, while these harmful materials are seldom purposely discharged to the atmosphere from the acid gas removal system under normal operating conditions, several of the AGRS gas streams are fed to downstream processes. There, inability to handle toxic compounds and pollutants may result in their discharge to the atmosphere. It is therefore important to know what compounds enter the AGRS, and how they distribute in the system under various processing conditions.

Of the runs shown in Table 3, run GO-76, AMI-57 will be used to illustrate AGRS performance results. Gas analyses from the six different locations shown in Figure 1 are given in Table 4.

TABLE 3
OPERATING CONDITIONS FOR COAL GASIFICATION RUNS

Run Number	AMI- 43	44	45	47	52	53	57	59	60
	GO- 68B	69B	70	71B	72	73B	76	78	79
Absorber									
Pressure Atm	18.0	18.0	31.6	31.6	31.6	18.0	31.6	18.0	24.8
Packing Height Ft	7.1	7.1	7.1	7.1	21.3	7.1	7.1	7.1	7.1
Inlet Liquid Flow	63.6	63.5	129.3	130.5	127.9	127.5	61.7	127.3	100.8
Inlet Solvent Temp	-36.1	0.8	-36.3	-34.9	-35.7	-5.4	-36.2	-3.5	-21.0
Inlet Gas Flow	18.1	17.0	17.1	16.8	16.8	17.9	15.4	14.9	16.0
Inlet Gas Temp F	40.1	47.6	22.3	36.3	38.1	42.5	50.4	44.2	56.4
H_2S in ppm	2950	2900	2550	4682	3023	1710	2868	3180	2139
H_2S out ppm	220	280	260	151	105	172	48	190	260
COS in ppm	119	112	79	133	67	60	76	81	84
COS out ppm	12	10	5	7	6	7	1	4	19
CO_2 in %	20	22	21	22	23	22	22	23	22
CO_2 out %	--	1	3	--	--	--	--	--	--
Flash Tank									
Pressure Atm	4.2	10.9	11.0	11.0	11.0	10.8	11.0	10.8	10.7
Stripper									
Pressure Atm	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Packing Height Ft	21.3	21.3	21.3	21.3	21.3	21.3	21.3	21.3	21.3
Stripping N_2 Flow	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Inlet Gas Flow	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0
Inlet Solvent Temp F	8.4	14.6	-5.6	48.0	48.0	48.1	48.1	48.1	37.6
Overall Mass Balance Closure									
Gasifier %	98.0	96.6	95.3	103.5	98.6	97.8	97.9	98.3	100.6
AGRS %	103.8	102.3	103.0	104.8	101.4	103.1	99.2	101.8	95.5

All Flows in lb-mole/hr-ft^2

The sample train sample is taken downstream from the cyclone separator and is the closest sampling point to the gasifier. Unreacted steam in the gas is first condensed and removed before the sample is taken. The PCS tank sample is taken after the gas quenching step but before the dehydrating towers and sour gas compressor. The sour gas sample is taken after the PCS tank and after the gas has been dehydrated, compressed, and cooled to remove the heat of compression. The high levels of several hydrocarbon and sulfur species in the sour gas sample may be attributed to the presence of condensate in the gas sampling lines. A trap located near this sampling station accumulated small amounts of a condensed hydrocarbon phase which was analyzed by GC/MS after run AMI-60. It is thought that this sample provides qualitative information on the variety of trace compounds entering the AGRS.

When the system is operating at steady state, the compositions of the sample train, PCS tank and sour gas samples will be nearly the same. This is some indication of the quality of the run. More detailed descriptions of the sampling and analytical procedures can be found in Ferrell et al. (1981).

TABLE 4
GAS ANALYSIS SUMMARY FOR AMI-57/GO-76

Species	Sample Train	PCS Tank	Sour Gas	Sweet Gas	Flash Gas	Acid Gas
H_2	31.60	31.11	31.29	42.38	15.58	0.00
CO_2	23.51	23.91	21.98	-----	25.99	64.74
C_2H_4	0.52	0.53	0.56	0.0242	1.28	1.54
C_2H_6	0.72	0.72	0.76	0.0164	1.92	2.13
H_2S	0.250	0.284	0.287	0.0048	0.090	0.66
COS	0.0078	0.0076	0.0076	0.0001	0.0041	0.027
N_2	19.36	19.61	19.93	26.79	19.27	23.06
CH_4	6.56	6.46	6.57	7.54	14.20	2.36
CO	17.29	17.47	17.92	23.35	21.55	1.80
Benzene	0.087	0.097	0.234	TRACE	0.0031	0.15
Toluene	0.031	0.034	0.534	0.0054	0.0033	0.030
Ethyl Benz.	0.0016	0.0017	0.0450	-----	-----	-----
Xylenes	0.0080	0.0094	0.1557	-----	-----	-----
Thiophene*	44	44	127	-----	-----	-----
CH_3SH*	16	29	28	TRACE	5	TRACE
C_2H_5SH*	TRACE	-----	8	-----	-----	-----
CS_2	TRACE	3	TRACE	TRACE	TRACE	TRACE
Propylene*	1505	1521	1811	107	995	4640
Propane*	208	198	253	301	172	2203
Butane*	185	150	143	54	91	71
Methanol**	-----	-----	-----	-----	-----	3.68

*Parts per Million (volume) **Estimated

Acid Gas Removal

The primary function of the AGRS is to remove CO_2 and sulfur compounds from the gases produced during coal gasification. When using refrigerated methanol, the absorber also acts as an excellent trap for any other compound which condenses or disolves in the methanol at absorber conditions. Table 3 shows the concentrations of H_2S, COS and CO_2 for the nine coal gasification runs. Using AMI-47 as the base case, the effect of process conditions on acid gas removal can be seen.

Because the acid gas content of the solvent entering the absorber has a pronounced effect on removal efficiencies, ineffective solvent regeneration in the stripper can be a problem. In run AMI-45, the stripper was operated at $-5.6^{\circ}F$ rather than at $48^{\circ}F$ as in AMI-47. Comparing the results from AMI-47 and AMI-45, the former shows a significantly better acid gas removal efficiency as a result of the higher operating temperature in the stripper.

The effect of packing height on removal efficiency can be seen by comparing AMI-47 with AMI-52. In AMI-52, 14.2 feet of additional packing was used with only a marginal improvement in the outlet H_2S levels. The acid gas removal efficiencies for the two runs are almost the same.

From the results of these three runs and the other runs in Table 3, it appears that for the range of conditions studied here, the most significant factor in high acid gas removal efficiencies is stripping efficiency. With the use of more extreme operating conditions and "cleaner" methanol fed to the absorber, the levels of CO_2, COS and H_2S in the sweet gas can be reduced to acceptable levels. This is a particularly important point in the case of COS removal which poses problems for many coal gas cleaning systems. From the data collected in this study, it appears that refrigerated methanol is effective in removing COS and no unusual solubility characteristics were evident at moderate pressures and low liquid temperatures.

Trace Sulfur Compounds

There are also several other sulfur compounds besides H_2S and COS present in the gas fed to the AGRS which must be removed. Table 4 shows the distribution of several of these compounds in the AGRS. While there is some scatter in the analyses for methyl mercaptan, thiophene, CS_2, and ethyl mercaptan/dimethyl sulfide, it appears that in most runs they are removed to very low levels in the absorber.

A point of potential environmental significance is that while these compounds are removed to low levels, they are not completely accounted for in the flash and acid gas streams. This can be seen for methyl mercaptan and thiophene, which are present in relatively high levels in the feed gas. These compounds will accumulate in the recirculatory solvent and most likely eventually leave the system in one of three exit streams: sweet gas, flash gas, or acid gas. Because most sulfur recovery systems cannot treat mercaptans and thiophene, they will present emission problems if some additional method of treating these gases is not used. This can be a significant problem because the total sulfur from mercaptans, organic sulfides, CS_2, and thiophene is approximately half of the total sulfur associated with COS. If these compounds appear with the sweet gas, they are likely to affect adversely downstream methanation catalysts. The presence of these compounds in the sweet gas stream is also a problem if the gas is to be burned for immediate use because the sulfur in these compounds will be converted to SO_2.

In examining the results from all runs, there appears to be some pattern of trace sulfur species distribution. The increase in stripper temperature from the low levels of AMI-45 to $48^{\circ}F$ for AMI-47 resulted in substantially greater amounts of mercaptan and thiophene in the acid gas stream. The results from AMI-44, which represents the "worst case" for absorber performance, show an increase in mercaptan levels in the sweet gas. Apparently, the conditions used in the absorber for this run were not sufficient to remove the mercaptans to low levels. CS_2 seems to distribute to all exit streams in most of the runs despite the differences in process conditions.

Perhaps the most significant finding here is that over a wide range of processing conditions, the presence of at least small amounts of several different sulfur species is to be expected in all AGRS exit streams, and provision must be made for handling the associated problems.

Aliphatic Hydrocarbons

As the amount of volatile matter present in a particular coal increases, the production of aliphatic, aromatic, and polynuclear aromatic compounds produced during gasification also increases. Over the range of conditions studied here, the most significant point to be made about the distribution of aliphatic hydrocarbons is their presence in significant quantities in the flash and acid gases. Although flashing of the methanol down to atmospheric pressure prior to stripping would release most of the hydrocarbons, the CO_2-rich flash gas would still contain substantial amounts of several hydrocarbon species. This stream would require further processing before it could be vented.

In run AMI-57, in which the gasifier was operated at a lower temperature to increase the production of hydrocarbons, the aliphatics (excluding methane) make up almost 4.5% of the acid gas stream and 3.5% of the flash gas stream. While staging the flashing operations may result in a better distribution of these compounds, the total product from the flashing and stripping operations must be either recovered as product, fed to a sulfur recovery unit, or vented to the atmosphere. Since it is unlikely that all of the aliphatic hydrocarbons will appear in the sweet gas stream, as evidenced by the data collected here, additional treatment will be necessary to prevent their eventual appearance in a vent stream.

There appears to be no unusual pattern of distribution of aliphatic hydrocarbons in the AGRS. The lighter hydrocarbons-- methane, ethylene, and ethane-- seem to distribute as would be indicated from an examination of their pure-component solubilities in methanol. The magnitude of their solubilities, however, are greater than would be expected from Henry's law, especially at the high pressures used in the absorber. This is evident from the lower than predicted levels of ethane and ethylene in the sweet gas in several of the runs.

Aromatic Hydrocarbons

Because large amounts of aromatic hydrocarbons are produced during coal gasification, the potential for environmental problems is great. These compounds, which range from benzene to polynuclear species of many forms, must be prevented from escaping from the gas cleaning process and their distribution throughout the gas cleaning system is of great concern.

Table 3 summarizes the information obtained from a single run. The simpler aromatics, benzene, toluene, and xylene, typically make up 0.1% (by volume) of the gas stream entering the AGRS.

Analyses performed for selected runs indicate that significant quantities of these compounds are found in the solvent leaving the stripper. Results from two runs are reported in Table 5. These compounds will build up in the solvent to the point of saturation. If the solvent is not effectively purged of these compounds periodically, they will begin to appear in several of the process streams.

TABLE 5
METHANOL ANALYSIS FOR STRIPPER EXIT
ALL ANALYSES REPORTED IN PPM (VOLUME)

	AMI-44/GO-69B	AMI-57/GO-76
Benzene	190	157
Toluene	200	196
Ethylbenzene	30	87
Xylenes	70	203

Methanol Analysis

In order to identify the various hydrocarbon species that accumulate in the methanol, samples of the methanol leaving the stripper were taken for several runs. These samples were then analyzed by gas chromatography/mass spectrometry.

Initial samples taken of the stripped methanol were analyzed by the Research Triangle Institute, Research Triangle Park, North Carolina. The results from AMI-44/GO-69B and AMI-57/GO-76 are shown in Figures 5 and 6 and in Tables 6 and 7. The gasifier conditions for AMI-57/GO-76 were designed to result in the production of larger amounts of heavy organics and tar than the other runs made in this study. The spectra from Figures 5 and 6 show that this result was achieved. The presence of several siloxanes and phthalates were probably related to some contamination of the sample during processing.

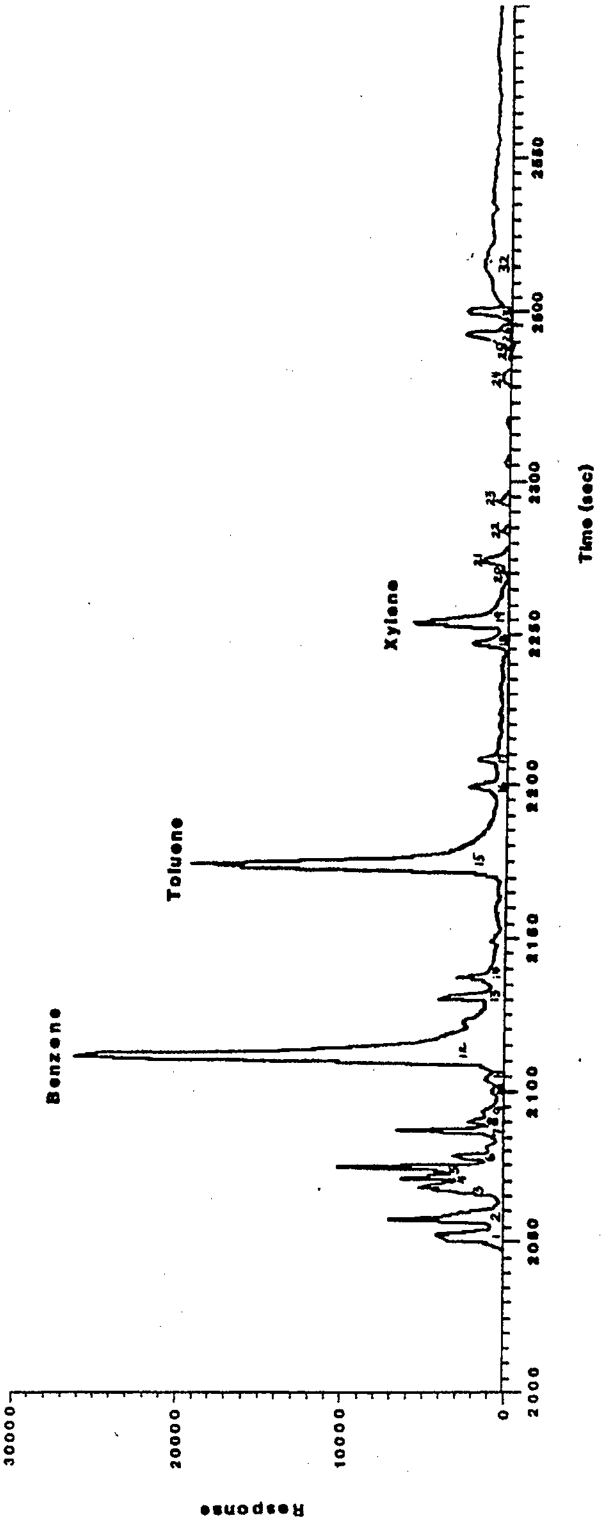

Figure 5. Analysis of Stripper Exit Methanol from AMI-44/GO-69B

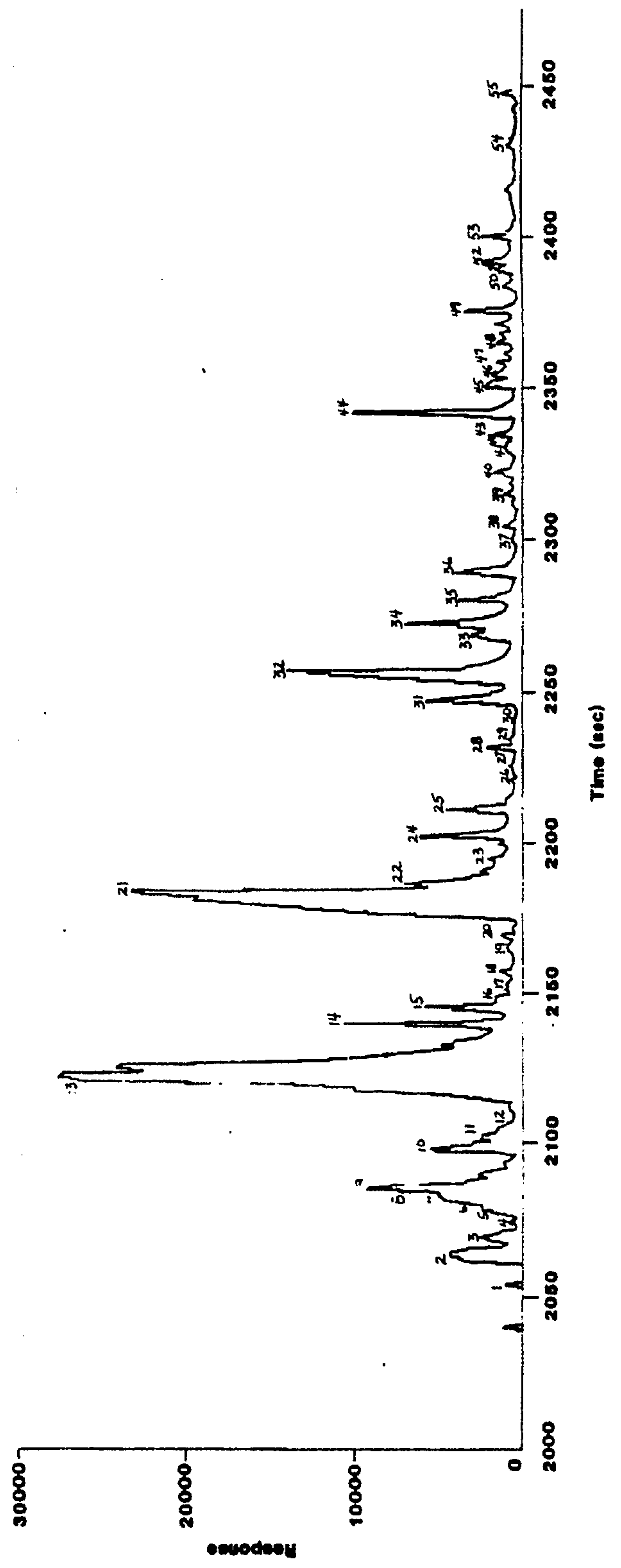

Figure 6. RTI Analysis of Methanol at Stripper Exit

Results from these runs indicate that most of the compounds accumulating in the methanol are simple aromatics, primarily substituted benzenes. A few C_{10} and C_{11} isomers were identified, indicating that napthalene is probably present but at trace levels. The presence of trace amounts of C_{14} and C_{15} isomers were found in AMI-57 but they could not be better identified. These may be polynuclear aromatics but they were present in very small amounts relative to the simpler aromatics.

Later in the sampling program, samples from AMI-60/GO-79 were analyzed by the GC/MS facility at North Carolina State University. The results from these analyses are shown in Figures 7 and 8. These Figures show the mass spectra for the stripped methanol before and after the run. Although compound identification was not performed for these analyses, comparison of the two spectra shows the relative changes in the levels of hydrocarbons. This methanol had been used for several previous runs and had accumulated significant quantities of a variety of organics. The spectra for the sample taken at the end of the run show that the locations of most peaks have not changed but the relative sizes of several peaks have. This indicates that these hydrocarbons were in fact, accumulating and will continue to do so until they saturate the solvent.

TABLE 6
STRIPPER EXIT METHANOL FOR AMI-44/GO-69B

Peak Number from Figure 5					
1.	CO_2	12.	benzene	24.	C_9H_{20} isomer
2.	butene isomer	13.	C_7H_{14} isomer	25.	$C_{10}H_{20}$ isomer
3.	pentene isomer	14.	C_7H_{16} isomer	26.	$C_{10}H_{22}$ isomer
4.	2-methyl-2-butene	15.	toluene	27.	$C_{10}H_{22}$ isomer
5.	cyclopentadiene	16.	C_8H_{16} isomer	28.	----------
6.	cyclopentene	17.	C_8H_{18} isomer	29.	$C_{11}H_{24}$
7.	C_6H_{12} isomer	19.	ethyl benzene	30.	methyl undecane
8.	C_6H_{14} isomer	20.	xylene (M,P)	31.	$C_{11}H_{24}$ isomer
9.	C_6H_{10} isomer	21.	styrene	32.	Sat'd hydrocarbon
10.	methyl cyclopentane	22.	xylene (O)	33.	phthalate
11.	methyl cyclopentadiene	23.	C_9H_{18} isomer	34.	Sat'd hydrocarbon

Samples of liquid condensing in the knockout tank downstream from the sour gas compressor were collected and analyzed by GC/MS. This condensate contains most of the heavier hydrocarbons fed to the AGRS. Results of these analyses are presented in Figure 9 and Table 8, and show that the compounds identified are very similar to those found in the stripped methanol from AMI-44 and AMI-57. Again, mostly simple aromatics were found. No polynuclear aromatics were present, which supports the findings of the earlier analyses.

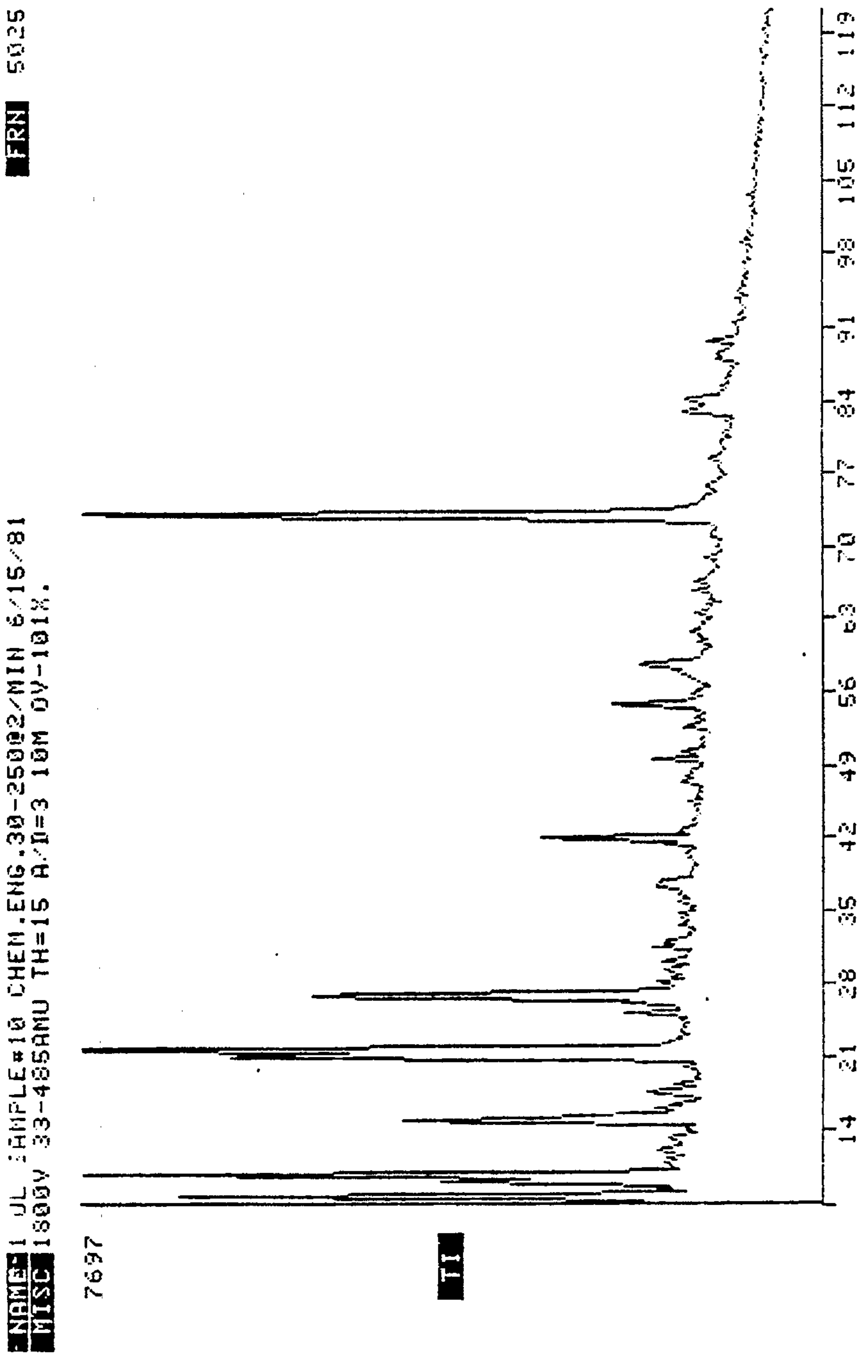

Figure 7. Stripper Exit Methanol Before Integration for AMI-60

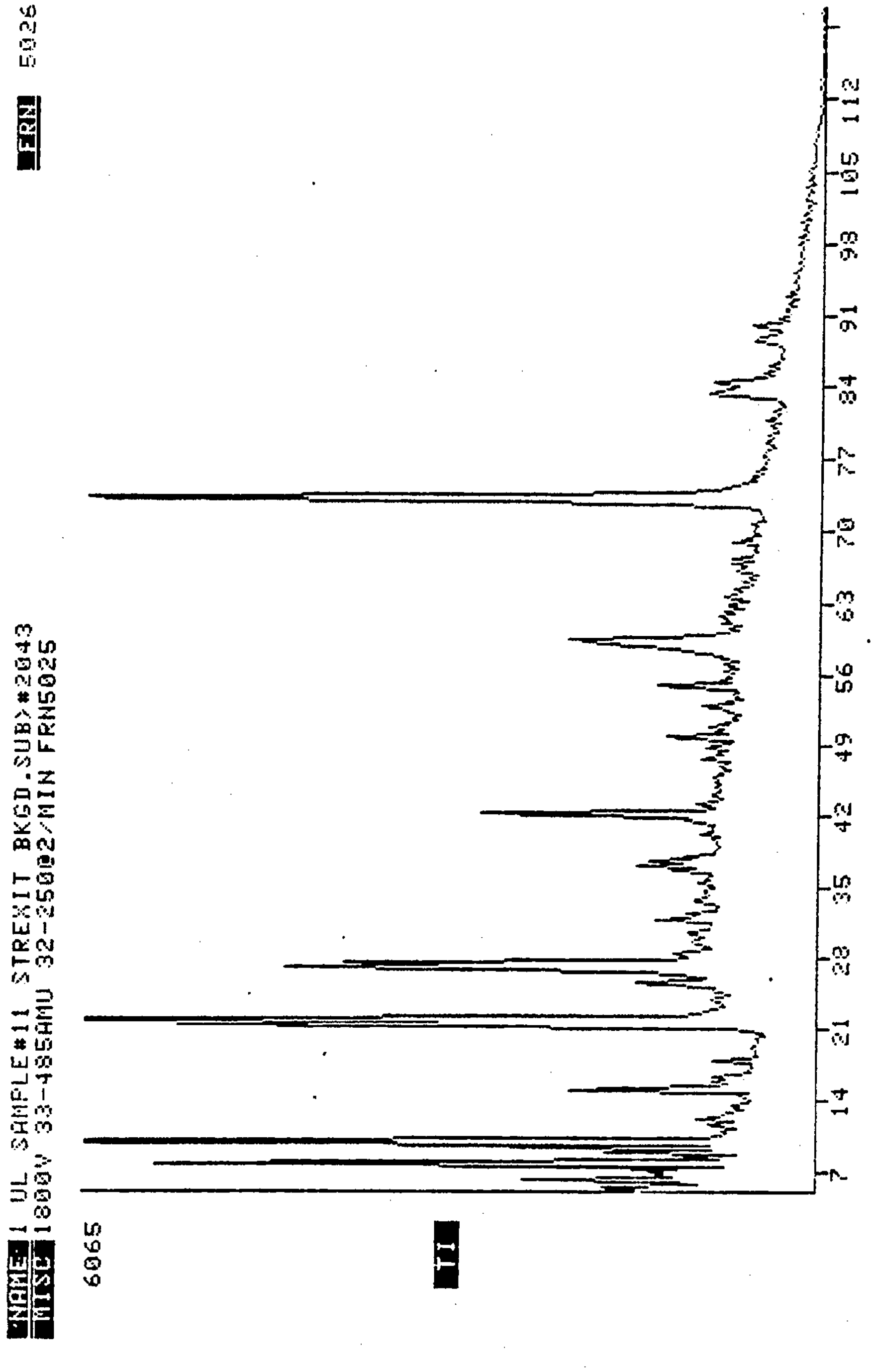

Figure 8. Stripper Exit Methanol Taken at the End of AMI-60

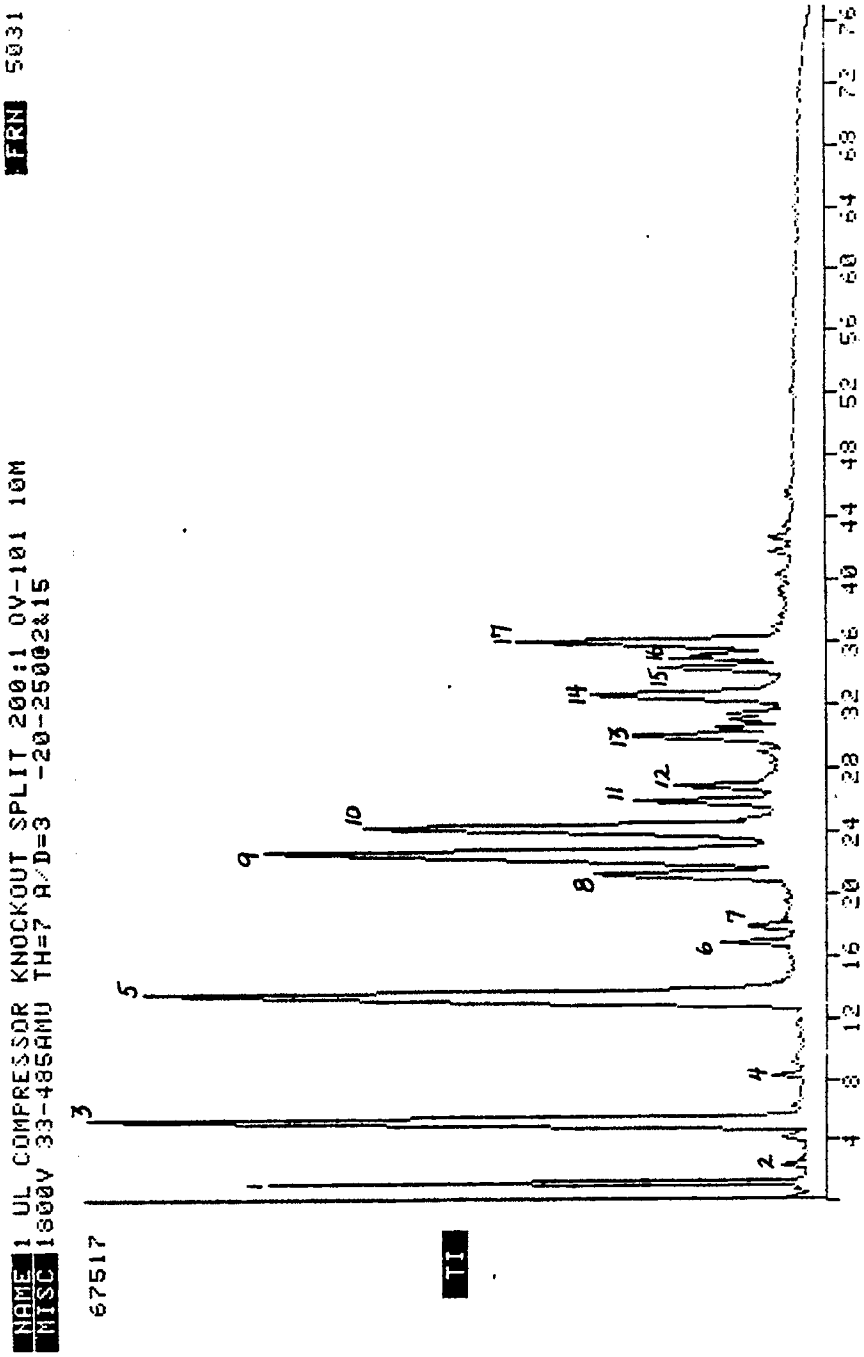

Figure 9. GC/MS Scan of Compressor Knockout Condensate for AMI-60

TABLE 7
AMI-57/GO-76 STRIPPER EXIT METHANOL

Peak Number from Figure 6

1. sat'd hydrocarbon
2. CO_2
3. C_4H_8 isomer
4. tetramethylsilane
5. trichlorofluromethane
6. C_5H_{10} isomer
7. unknown
8. Freon 113
9. cyclopentadiene
10. C_6H_{12} isomer
11. C_6H_{14} isomer
12. C_6H_{10} isomer
13. benzene
14. C_7H_{14} isomer
15. C_7H_{16} isomer
16. C_7H_{16} isomer
17. C_7H_{12} isomer
18. C_7H_{12} isomer
19. C_7H_{12} isomer
20. unknown hydrocarbon
21. toluene
22. methyl thiophene isomer
23. C_8H_{16} isomer
24. C_8H_{16} isomer
25. C_8H_{16} isomer
26. C_8H_{16} isomer (trace)
27. C_8H_{14} isomer (trace)
28. hexamethyl cyclotrisiloxane
29. C_9H_{20} isomer
30. C_9H_{18} isomer
31. ethyl benzene
32. xylene (M,P)
33. styrene
34. xylene (O)
35. C_9H_{18} isomer
36. C_9H_{20} isomer
37. C_3 alkyl benzene
38. $C_{10}H_{22}$ isomer
39. unknown hydrocarbon
40. unknown hydrocarbon
41. $C_{11}H_{24}$ isomer
42. C_3 alkyl benzene
43. C_3 alkyl benzene
44. $C_{10}H_{22}$ isomer
45. $C_{10}H_{22}$ isomer
46. C_4 alkyl benzene
47. $C_{10}H_{22}$ isomer
48. $C_{10}H_{20}$ isomer
49. unknown hydrocarbon
50. C_9H_{10}
51. C_9H_8 isomer
52. alkyl benzene isomer
53. $C_{11}H_{24}$ isomer
54. $C_8H_{10}O$ isomer
55. $C_{11}H_{24}$ isomer
56. C_8H_{100} isomer
57. unknown siloxane
58. unknown siloxane
59. unknown siloxane
60. $C_{14}H_{30}$ isomer
61. $C_{14}H_{30}$ isomer
62. unknown
63. $C_{15}H_{32}$ isomer

TABLE 8
COMPRESSOR KNOCKOUT SAMPLE FROM AMI-60/GO-79
PEAK NUMBER FROM FIGURE 9

1. 1-pentene
2. hydrocarbon
3. benzene
4. hydrocarbon
5. Toluene
6. cyclo C4-C5
7. hydrocarbon
8. ethyl benzene
9. dimethyl benzene
10. substituted benzene
11. C_8 hydrocarbon
12. C_9 hydrocarbon
13. propyl or ethyl methyl substituted benzene
14. propyl or ethyl methyl substituted benzene
15. 1-decene
16. 2-propyl benzene
17. 1-ethyl-4-methyl benzene

Results from these analyses indicate that very little, if any, polynuclear aromatic compounds were present in the gas fed to the AGRS. This is a particularly important finding. Analyses of the water used to quench the gasifier product gas stream showed that a substantial amount of polynuclear aromatics were present. Evidently, scrubbing of the raw product gas with water effectively removes these compounds.

Although polynuclear aromatics are removed by the quenching process, substantial amounts of simpler aromatics will be present in the sour gas fed to the AGRS. The use of cold traps may remove some of these compounds but provision must be made to prevent their release to the atmosphere through vent streams or through the sulfur recovery unit. The accumulation of these compounds in the methanol further complicates the problem because of the increased likelihood of their distribution to a number of process streams. Achievine efficient solvent regeneration is, therefore, a key step in avoiding environmental problems.

SUMMARY

A cyclone, a cold water quench scrubber, and a refrigerated methanol absorber have been used to clean the make gas from the steam-oxygen gasification of a New Mexico subbituminous coal in a pilot-scale fluidized bed ractor. A model developed for the gasifier provides the capability of predicting the make gas amount and composition as a function of gasifier operating conditions. The methanol functioned effectively for acid gas removal. Removal ot CO_2, COS, and H_2S to sufficiently low levels was achieved with proper choice of operating conditions and effective solvent regeneration.

The presence of several trace sulfur compounds--mercaptans, thiophenes, organic sulfides, and CS_2--complicates the gas cleaning process because these compounds were found to distribute among all exit streams from the AGRS. Since no provision is made to specifically treat these forms of sulfur, the possibility of their emission into the atmosphere exists and must be dealt with to avoid significant environmental problems.

A wide variety of aliphatic and aromatic hydrocarbons are present in the gas stream fed to the AGRS. The aliphatic hydrocarbons, ranging from methane to butane, cover a wide range of solubilities. Their presence in all AGRS streams must be anticipated to prevent their emission to the atmosphere.

While a wide range of simple aromatics were identified in the gas stream fed to the AGRS, essentially no polynuclear aromatic compounds were found. Apparently, the water quenching process effectively removes these compounds from the gasifier product gas. However, significant quantities of simple aromatics were found to accumulate in the recirculating methanol, indicating a potential for their eventual discharge to the atmosphere. Provision must be made to periodically purge the solvent of these compounds and/or remove them prior to the AGRS through cold traps.

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ADVANCED TECHNIQUES FOR FLUE GAS DESULFURIZATION†

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ABSTRACT

In 1979 the combustion of sulfur-bearing fuels accounted for more than 80 percent of the SO_2 emissions in the United States. These emissions can be controlled to a degree by burning low-sulfur fuels or by pretreating the fuel to lower its sulfur content. Currently the most widely-practiced technological control involves scrubbing the combustion flue gases to remove the SO_2. Flue gas desulfurization systems can be categorized as nonregenerable or "throwaway" and regenerable or producing a saleable product. Several systems in each category will be discussed as to their advantages and disadvantages. In addition, several recent developments regarding waste disposal and enhanced SO_2 removal will be presented.

INTRODUCTION

Sulfur dioxide (SO_2) is one of a number of sulfur-containing pollutants found in the atmosphere. It enters the air primarily from the combustion of coal and oil, but also from various other industrial processes. The combustion of sulfur-containing fuels accounts for more than 80 percent of the SO_2 emissions in the United States(1,2). These emissions can be controlled to a degree by burning low-sulfur fuels or by pretreating the fuel to lower its sulfur content. Currently the most effective control involves scrubbing the combustion flue gases to remove SO_2 by flue gas desulfurization (FGD) technology.

This paper briefly discusses methods for controlling these emissions, related waste disposal, and process costs. Since most FGD technology has been developed in relation to coal-fired steam electric generating plants, the major emphasis will be advanced FGD systems for these plants. Such systems, however, are being used at industrial sites and may be adaptable to commercial gasification facilities. Sulfur oxides (SO_x) are pollutants of major environmental concern, and their formation in power generation units of commercial medium- and high-Btu gasification plants may be at levels requiring control. Several proposed gasification plants include FGD systems on coal-fired power generation units for these plants.

While SO_x are not the major pollutant in raw product gases from coal gasifiers, commercial processes for cleaning these gases or upgrading the quality of the synthetic gas produced may produce SO_x at levels requiring control to meet air quality constraints. For example, the production of sulfur from sulfur compounds in raw product gases can lead to tail gases containing reduced levels of sulfur compounds and other combustible gases. Combustion of the tail gases along with coal in the power-producing component of a medium- or high-Btu gasification plant may generate SO_x at levels requiring FGD, but would reduce fuel requirements through combustion of the tail gases. Thus the integrated control of SO_x in flue gases from the incineration of pollutant-bearing tail gases and the combustion of coal in connection with power or steam production may be more cost effective than treating separate pollutant streams.

FGD systems are classified into two categories: nonregenerable or "throw-away" systems and regenerable systems which produce a saleable product. They may be further classified into wet and dry FGD systems, the distinction being that saturated (with water) and unsaturated flue gas, respectively, result from the gas cleaning process. A brief discussion of these categories of advanced FGD systems will now be presented.

NONREGENERABLE FGD SYSTEMS

Presently, nonregenerable FGD systems can be classified into two types, wet and dry. Each type of process will be discussed.

Most commercial wet FGD systems, that are either operating or planned for use in utility applications, are lime or limestone based systems. The major driving force for using these "throwaway" systems rather than regenerable FGD technology is one of economics. Wet limestone systems are slightly more economical than wet lime systems because of the cost and energy requirements associated with calcination of the limestone to produce lime. This cost difference is expected to increase with rising energy costs. Although these calcium-based systems are in wide use, their performance to date has been limited by reagent reactivity which results in low soluble alkalinity, relatively higher liquid-to-gas (L/G) ratio requirements, and larger reaction tanks than other FGD processes.

Wet Lime/Limestone(3)

Wet lime/limestone FGD processes (Figure 1) employ a scrubbing slurry of lime or limestone to remove SO_2. As a side benefit, these processes can also be designed to remove fly ash and chlorides simultaneously. Because lime/limestone processes are nonregenerable, they produce large quantities of waste solids. This characteristic could place them at a disadvantage compared with regenerable processes where disposal costs are high. Regenerable processes, however, still require disposal of waste fly ash and chlorides by environmentally acceptable methods, and these waste products can amount to more than 50 percent (high ash fuels) of the volume of solid waste produced by lime/limestone processes.

Lime/limestone systems are usually less complex than regenerable systems, and they generally cost less to install and operate than other wet FGD processes. Consequently, lime/limestone FGD processes are the most widely used wet FGD systems in operation.

Lime/limestone FGD processes consist of four steps:

1. Feed material processing.
2. Absorption.
3. Solids precipitation.
4. Solids concentration and disposal.

Flue gas enters the absorber (Figure 1) where it contacts the circulating scrubbing slurry containing calcium ions from dissolved lime or limestone. SO_2, fly ash, and chlorides contained in the flue gas are removed by the

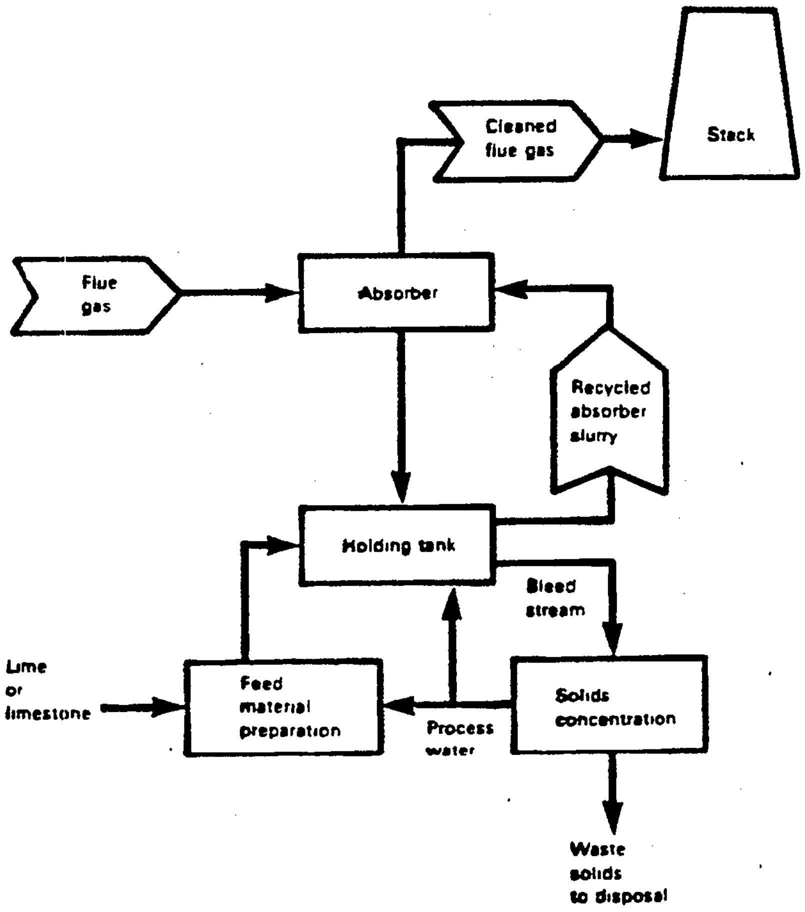

Figure 1. Typical Lime/Limestone FGD Process Flow(3)

circulating slurry. Alkaline species in the liquor neutralize the absorbed SO_2, promoting the formation of ions of sulfite and sulfate. Water droplets are removed from the cleaned flue gas by mist eliminators as they leave the absorber. The clean, water-saturated, flue gas is reheated, if necessary, to counter material corrosion and/or plume dispersion problems and then is exhausted through the stack to the atmosphere.

The scrubbing slurry, which may be supersaturated with solids of calcium sulfite and calcium sulfate, flows to an effluent holding tank or precipitation vessel. In the holding tank, fresh makeup lime or limestone is added, and reaction products are precipitated. One effluent stream from the holding tank is recycled to the absorber; another is bled off for concentration and disposal of waste solids.

Solids in the bleed stream may be concentrated in a thickener, filter, or centrifuge, or may be sent directly to a holding/settling pond. Clarified process water is returned to the system. Concentrated solids may be disposed of in ponds or used for landfill and may or may not be chemically stabilized. It is also possible to convert the solids to gypsum for use in portland cement or wallboard manufacture. This, however, requires the additional process operations of oxidation and purification.

Wet Lime/Limestone with Adipic Acid Enhancement(4)

IERL-RTP has sponsored extensive laboratory, pilot, prototype, and commercial scale studies on an adipic acid enhanced wet limestone system which shows significant improvement in operation over non-adipic acid enhanced wet limestone systems. Addition of relatively small quantities of adipic acid (approximately 1500 ppm), in either conventional or forced oxidation limestone FGD systems, provides these important benefits:

- Significantly enhanced SO_2 removal efficiency in either conventional or forced oxidation modes (compared with additives such as MgO which may be of little benefit in forced oxidation systems).

- Increased limestone utilization; hence, decreased waste solids disposal requirements and improved scrubber reliability.

- Lower projected capital and operating costs than conventional limestone FGD systems.

- Not adversely affected by chloride as is the limestone/MgO process; thus, it is especially attractive for closed-loop operation.

- Less expensive and less energy intensive limestone rather than lime is used.

Adipic acid is a weak dicarboxylic acid which buffers the slurry pH and thus enhances the SO_2 solubility and limestone dissolution rate. An important advantage of adipic acid as compared with other scrubber additives is that its ability to improve SO_2 removal is not affected by chlorides. Adipic acid significantly enhances SO_2 removal over a range of operating conditions (with scrubber slurry pH's of 5.0 to 5.5). Operation at the lower end of the typical pH range increases limestone utilization and may reduce scaling and mist eliminator fouling. Improved limestone utilization in turn reduces both the amount of limestone required and the quantity of solid wastes produced by the FGD system. These improvements represent an estimated 6 percent reduction in capital investment and 7 percent reduction in operating costs.

Figure 2 shows enhanced SO_2 removal due to adipic acid addition. For example, a scrubber feed with a pH of 5.5 and an adipic acid concentration of approximately 1600 ppm resulted in 95 percent SO_2 removal, as opposed to 70 percent SO_2 removal at the same operating conditions without adipic acid. Adipic acid addition also improved limestone utilization, increasing it to over 90 percent.

Research and development activities have focused on adipic acid to enhance the performance of the limestone FGD process. However, other organic acids will also enhance the process. One of the most intriguing alternatives is dibasic acid (DBA) material which is a by-product of the adipic acid manufacturing process. This material has been tested at IERL-RTP's pilot plant and at a full scale scrubber installation. The results show that the DBA material enhances the performance of the scrubbers similar to pure adipic acid. Since the DBA material is projected to cost only one-third to half the cost of adipic acid, this alternative is particularly attractive.

The testing to date has found that the adipic acid or DBA additive reduces energy requirements of the process over conventional limestone scrubbing processes. This results primarily from operating at a lower L/G and from reducing the solid waste handling requirements. The environmental impact of the enhanced process is about the same as conventional limestone scrubbing, except that the solid waste loading is less from the enhanced process. There is no significant difference in the toxicity of the wastes from the two processes.

Wet Lime/Limestone with Forced Oxidation(5)

A major advancement in the wet lime/limestone scrubbing process is the stabilization of the waste material by forced oxidation (e.g., air sparging into slurry hold tank). In the past, a disadvantage of lime/limestone scrubbing processes has been the large volume of waste solids produced. This waste slurry, consisting of predominantly calcium sulfite, could only be dewatered to about 50 to 60 percent solids, thus

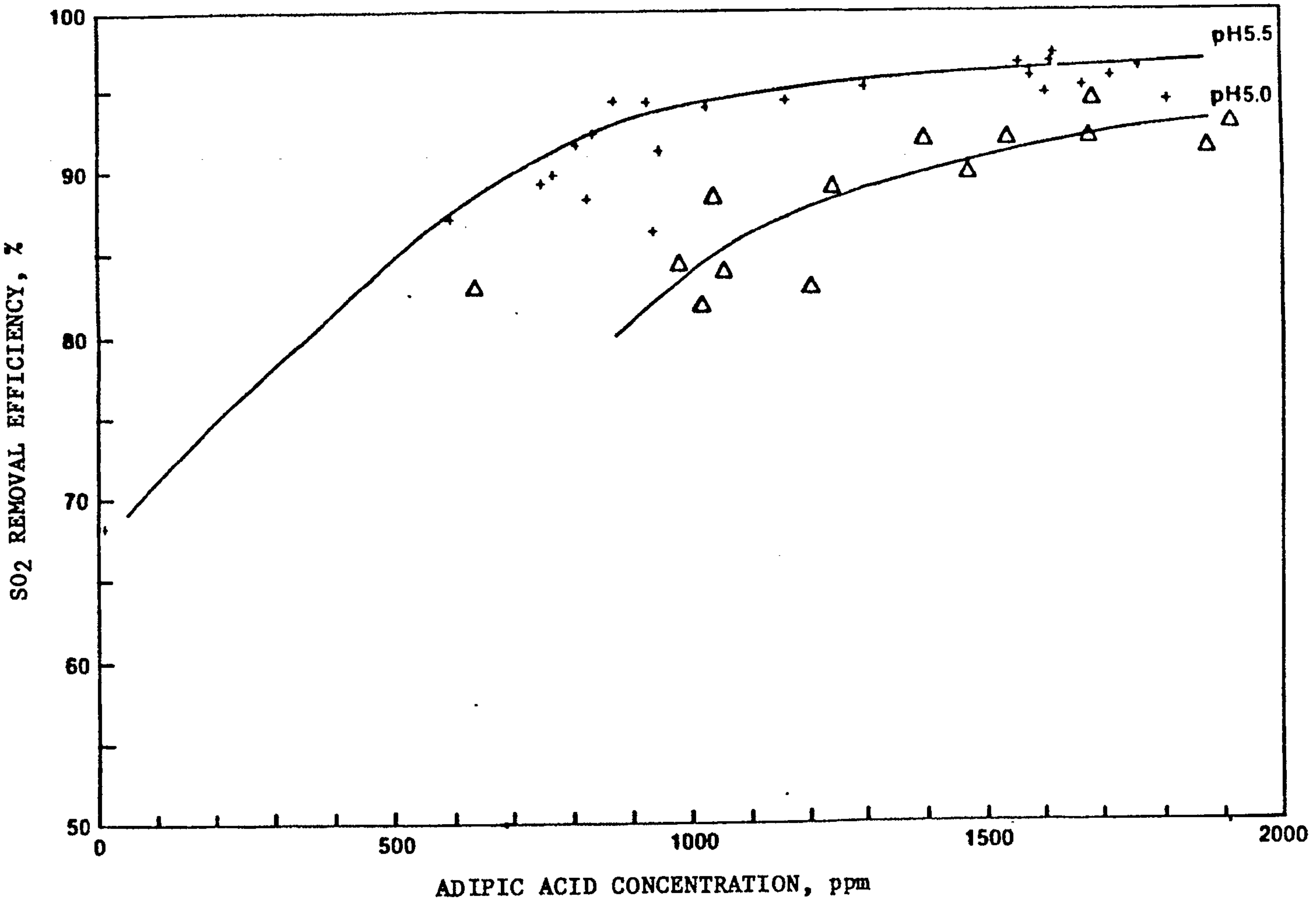

Figure 2. Effect of Adipic Acid Concentration and pH on SO_2 Removal Efficiency in Limestone Wet FGD(4)

producing a material which may be unsuitable for landfill. In the past, the primary utility practice involved the use of lined ponds for containment in order to prevent contamination of ground and surface waters. Although less expensive than other disposal options compatible with landfill, such as chemical fixation and fly ash blending, ponding of this material represented as much as 20 to 25 percent of the overall scrubbing process costs. Furthermore, the large land areas required for these disposal ponds were difficult to reclaim for other productive use due to the poor mechanical stability and load bearing strength of the waste material. One solution to the situation is the forced oxidation of the calcium sulfite produced to calcium sulfate (gypsum), a material easily dewatered to greater than 80 percent solids. Since, in the United States, by-product gypsum may be unable to compete with the widely available natural gypsum, the incentive has been to develop simplified low-cost forced-oxidation procedures directed primarily toward improving waste solids handling and disposal properties while minimizing waste disposal costs.

Wet ponding, landfilling, and mine disposal are three current means of disposal. Ponds can be designed based on diking or excavation and can even be engineered on slopes. A special case of wet ponding is FGD gypsum stacking. Gypsum slurry from the forced oxidation system is piped to a pond and allowed to settle, and the supernate recycled. Periodically the gypsum is dredged and stacked around the embankment. For disposal in a landfill, dewatered wastes are transmitted to the disposal site where they are spread on the ground to a thickness of about 0.3 to 1 meter. Compaction by heavy equipment follows, and a layering process proceeds at the site. A disposal method that is receiving increased attention is mine disposal, particularly in the West. Surface coal mines are the most likely candidates for FGD waste disposal. Coal mines offer the greatest capacity for disposal, and they frequently have direct transportation (e.g., rail) connections tied to power plants. In fact, many new coal-fired power plants are "mine-mouth" (located within a few kilometers of the mine), and the mine provides a dedicated coal supply. Since the amount of FGD wastes produced is considerably less than the amount of coal burned, such mines usually would have the capacity for disposal throughout the life of the power plant.

Surface mines have basically three options for the disposal of FGD wastes:

- In the working pit, following coal extraction, and prior to return of overburden.
- In the spoil banks, after return of overburden, but prior to reclamation.
- Mixed with, or "sandwiched" between, layers of overburden.

The latter two options appear to be more environmentally sound and are expected to show strong growth in the future.

Dual Alkali(6)

The dual alkali FGD process consists of four basic steps:

1. Flue gas pretreatment (optional).
2. SO_2 absorption.
3. Absorbent regeneration.
4. Solid/liquid separation and solids dewatering.

Figure 3 illustrates the process flow for a typical dual alkali FGD system.

During pretreatment, flue gas from the boiler can be routed through an electrostatic precipitator (ESP) to remove particles (fly ash) upstream of the absorber. Pretreatment can also involve wet scrubbing, alone or in series with the ESP, for particle and chloride removal. Pretreatment is not always necessary in dual alkali FGD; its use depends on site-specific conditions such as fuel characteristics and cost considerations.

The flue gas then flows to an absorber and is brought in contact with a recirculating solution containing an equilibrium mixture of sodium sulfite (Na_2SO_3), sodium bisulfite ($NaHSO_3$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$). SO_2 is absorbed by this solution and reacts with the alkali in solution to form soluble sulfur salts.

Desulfurized flue gas leaves the absorber, is reheated if necessary, and is exhausted through the stack to the atmosphere. A portion of the circulating absorbent solution is routed to the absorbent regeneration system to be reacted with lime, to precipitate the absorbed SO_x as:

- Calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$).
- Gypsum ($CaSO_4 \cdot 2H_2O$) (only in dilute dual alkali systems).
- A mixed crystal of hydrated calcium sulfite/sulfate.

The precipitation reaction also regenerates soluble alkali for recycle to the absorber.

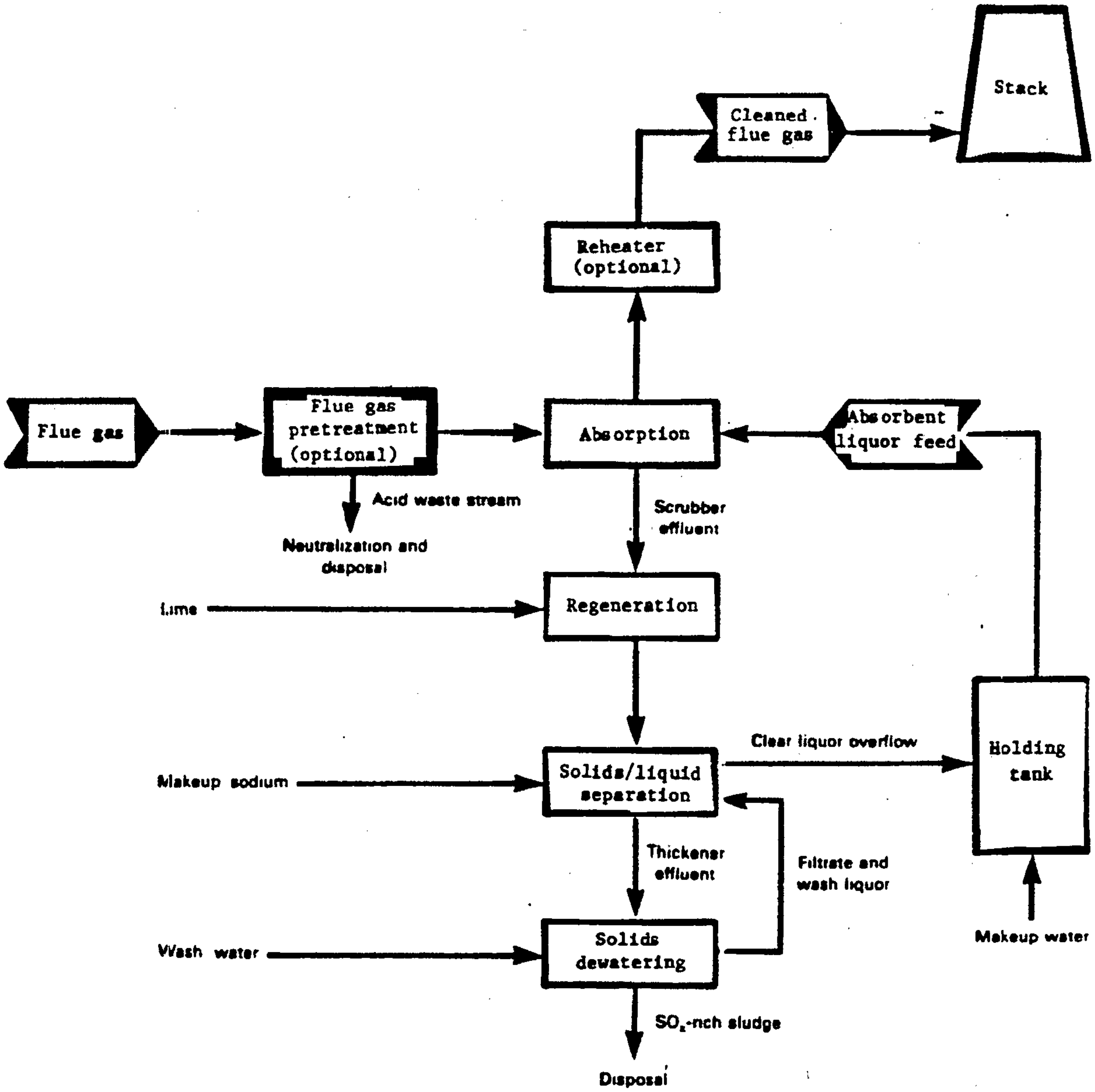

Figure 3. Dual Alkali FGD Process(6)

The precipitated SO_x salts are separated from the scrubbing liquor and concentrated for disposal in the solid/liquid separation and solids dewatering steps. The solids settle out of the slurry in a clarifier-thickener; they are dewatered further in a vacuum filter or centrifuge and are washed to recover sodium salts before disposal. The clear liquor overflow from the clarifier-thickener is combined with makeup soda ash solution and returned to the absorption system.

Spray Drying(7)

Nonregenerable spray drying processes are presently the only commercially applied dry FGD processes in the United States. Other dry FGD processes under development include dry injection and combustion of coal/alkali-fuel mixtures. Several factors, including increases in coal use and the 1979 new source performance standards (NSPS) for utility boilers, have promoted increased research and development and commercial application of the dry FGD technology.

Interest in spray drying FGD has primarily been spurred by the potential cost savings dry FGD offers over conventional wet FGD, particularly for low-sulfur coal (less than 1.5 percent sulfur) applications. In addition to the production of a dry waste, advantages of spray drying FGD over wet FGD systems include potentially lower initial capital investment, lower operating costs for up to moderate fuel sulfur content (possibly 3 percent), and less process complexity, which may lead to greater system reliability.

The major disadvantage of spray drying FGD relative to wet FGD systems is the higher absorbent cost, which results from the higher priced absorbent (lime versus limestone) and the higher stoichiometric ratios necessary. The applicability of spray drying FGD for high-sulfur coal-fired installations is limited by the lack of data on the SO_2 removal capability and the higher costs of this technology.

The spray drying FGD process (Figure 4) consists of three steps:

1. Absorbent preparation.

2. SO_2 absorption drying.

3. Solids collection.

For economic comparison of wet and dry FGD systems, waste disposal cost should also be included. In this regard, waste disposal would be the last step of each of the process steps for FGD systems.

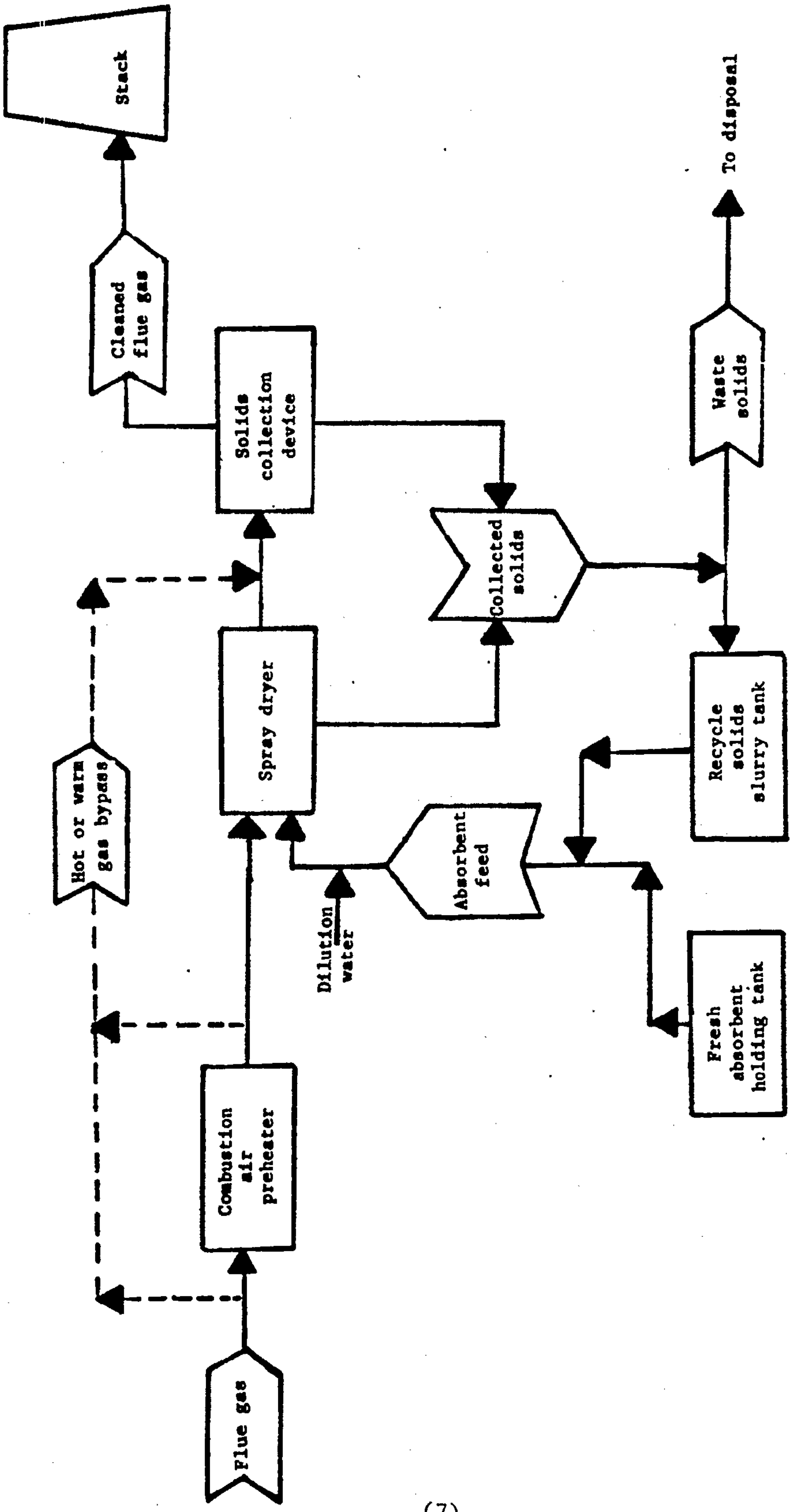

Figure 4. Spray Drying FGD Process(7)

Flue gas exiting the combustion air preheater is contacted with an alkaline solution or slurry in a spray dryer. In the spray dryer, the flue gas passes through a contacting chamber, and the solution or slurry is sprayed into the chamber with a rotary or nozzle atomizer. The heat of the flue gas dries the atomized droplets, while the droplets absorb SO_2 from the flue gas. The SO_2 reacts with the alkaline reagent to form solid-phase sulfite and sulfate salts.

Most of these solids (and any fly ash present) are carried from the dryer in the exiting flue gas. The rest fall to a hopper at the bottom of the dryer. In contrast to wet FGD systems, the flue gas is not saturated with moisture after the absorption step but is within 11 to 28°C (20 to 50°F) of the saturation temperature(8).

The solution or slurry is pumped to the dryer from an absorbent holding tank. Fresh absorbent and dilution water are added to this tank as needed. (In some systems, dilution water for temperature control in the spray dryer is added to the absorbent feed just upstream of the spray dryer.) Recycle solids from the spray dryer hopper or downstream solids collection equipment contain unreacted absorbent and may be used to supplement the fresh absorbent feed. Recycle solids are either slurried separately and added to the absorbent feed just upstream of the spray dryer or are added directly to the fresh absorbent holding tank.

Flue gas may be reheated after it leaves the spray dryer to prevent condensation in downstream solids collection equipment. Reheating may be desirable and economically justifiable: SO_2 removal in the spray dryer is greatly improved as the flue gas temperature approaches the saturation temperature of the gas at the spray dryer exit. Reheat may be accomplished by mixing the flue gas from the spray dryer with either hot flue gas from upstream of the combustion air preheater or warm flue gas from upstream of the spray dryer. Other methods of reheat could be used such as heating air and injecting it into the cleaned flue gas, heating part of the cleaned flue gas and re-injecting it into the remainder of the gas stream, or heating all the treated flue gas in a surface heat exchanger upstream of the particle collection device. Also note that using dirty flue gas (either warm or hot) for reheating means that higher SO_2 removal is required of the spray dryer to meet given emission limits. The reheated flue gas then flows to the solids collection device where the dry solids (which consist of reaction products, unreacted absorbent, and fly ash) are collected. A fabric filter (baghouse) is the most common solids collection device, but electrostatic precipitators (ESPs) are also used. When a baghouse is used, significant absorption of SO_2 may occur during the solids collection step. Absorbent in the solids collected on the surface of the bags reacts with SO_2 remaining in the flue gas, and the desulfurized flue gas is exhausted to the atmosphere through a stack.

While sodium compounds may serve as absorbents, most nonregenerable spray dryer FGD applications use lime because of its lower cost and the more stable wastes produced through its use(9). Since dry waste solids are generated in dry FGD processes, their disposal is typically by landfill. With sodium compounds (e.g., soda ash) as absorbents, the high water solubility of the resulting sodium salt wastes could require expensive lined landfills to control leaching into the ground water.

REGENERABLE FGD SYSTEMS

There are two primary regenerable wet FGD systems currently available for commercial applications: Magnesium Oxide and Wellman-Lord. Two other processes, the aqueous carbonate and citrate processes, are under development. These systems are capable of removing 90 to 95 percent of the flue gas SO_2(10).

The principal advantages of regenerable FGD systems over nonregenerable systems are the economic advantages gained from the reduction of waste disposal problems and the sale of recovered by-products. Wastewater streams are collected and can be neutralized by standard treatment systems, and most of the spent solution can be recirculated to the process. Solid waste loads are also considerably reduced. On the other hand, regenerable systems are more complex than current nonregenerable systems and generally involve higher capital investment and higher operating costs.

Wellman-Lord(11)

The Wellman-Lord process consists of four basic steps:

1. Flue gas pretreatment.
2. SO_2 absorption.
3. Purge treatment.
4. Sodium sulfite regeneration.

A fifth step, the processing of SO_2 into by-product sulfur, is not a part of the Wellman-Lord process but is generally associated with Wellman-Lord installations. Figure 5 illustrates the process flow for a typical Wellman-Lord system installed on a coal- or oil-fired boiler.

Boiler flue gas is pretreated by contact with water, usually in a venturi scrubber. This step cools and saturates the gas, absorbs corrosive chlorides, and removes some of the particles remaining in the gas after upstream particle removal efforts.

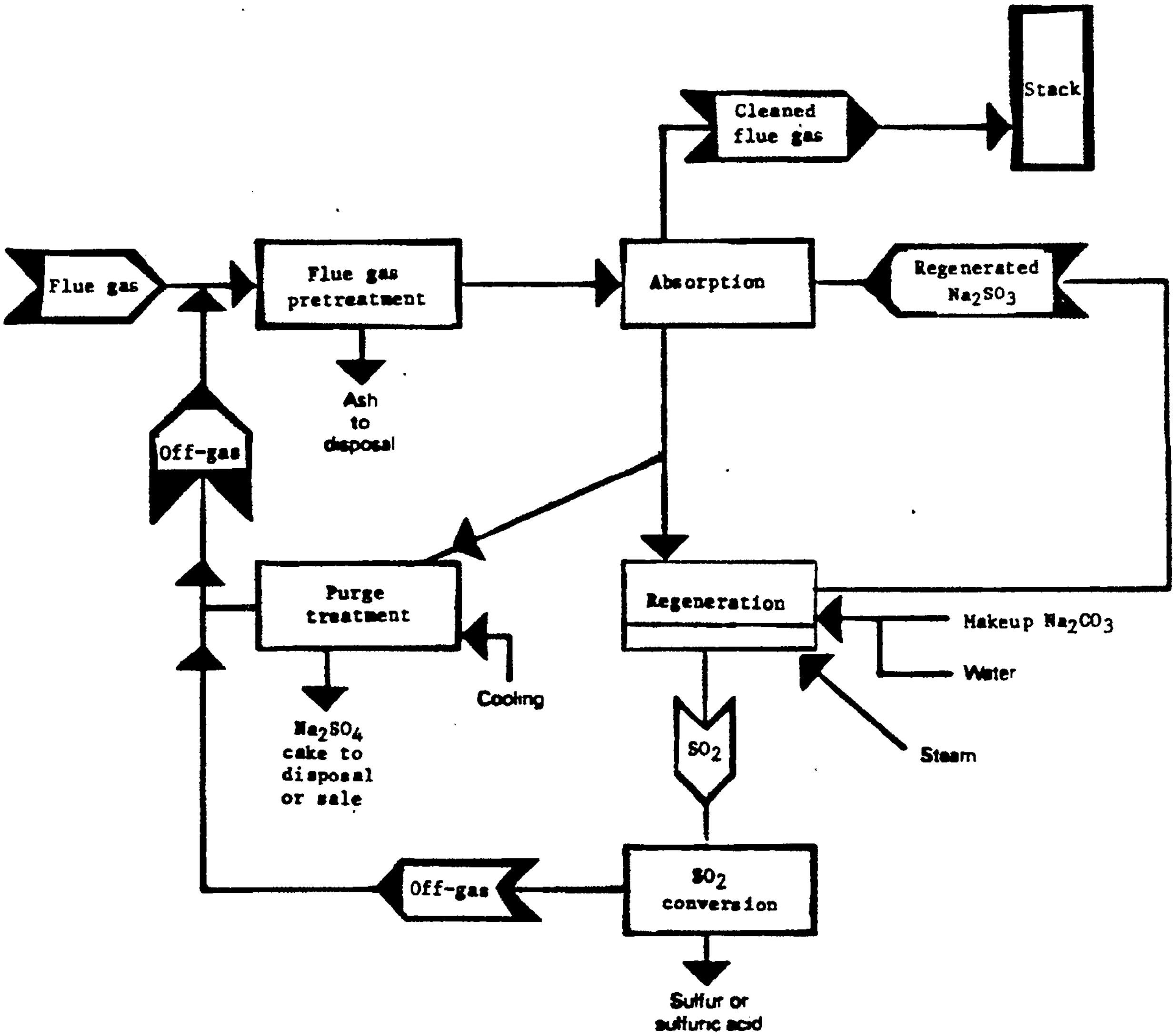

Figure 5. Typical Wellman-Lord Process(11)

The flue gas then flows to an absorber where it is contacted with a sodium sulfite (Na_2SO_3) solution. The SO_2 in the flue gas reacts with the Na_2SO_3 to produce sodium bisulfite ($NaHSO_3$). In a side reaction, some sodium sulfate (Na_2SO_4) is formed by direct oxidation of Na_2SO_3.

Desulfurized flue gas leaves the absorber, is reheated to improve plume buoyancy and to vaporize any liquid droplets present, if necessary, and is exhausted through the stack to the atmosphere. If reheat is not used, then protective linings in stacks and acid-corrosion-resistant material in ducts are generally used in wet FGD applications. The effluent from the absorption tower, rich in $NaHSO_3$ and also containing some Na_2SO_3 and Na_2SO_4, is split into two streams. Approximately 15 percent of the effluent is routed to a purge treatment for sulfate removal. The remaining 85 percent goes to a regeneration process.

The purge stream is cooled in a chiller and a mixture of Na_2SO_4 and Na_2SO_3 is crystallized out of the solution. This crystalline mixture is removed from the process and dried for sale or disposal.

Regeneration is accomplished in an evaporator where the remainder of the SO_x absorber effluent is heated to convert $NaHSO_3$ to Na_2SO_3 and to drive off SO_2. The regenerated Na_2SO_3 crystallizes and then is redissolved and recycled to the absorber. Sodium lost during the process, primarily from the purge operation, is replenished by adding sodium carbonate (Na_2CO_3) to the feed dissolving tank.

The fifth step, SO_2 processing, uses the SO_2 by-product from the Wellman-Lord process. The output of the Wellman-Lord process is a gas stream of about 85 percent SO_2; the remainder is mostly water vapor. This concentrated SO_2 stream may be dried and marketed without further processing, reduced to elemental sulfur, or oxidized and reacted with water to form sulfuric acid (H_2SO_4).

Magnesium Oxide(12)

The magnesium oxide (MgO or Mag-Ox) FGD process consists of four major processing steps:

1. Flue gas pretreatment.
2. SO_2 absorption.
3. Solids separation and drying.
4. Regeneration.

SO_2 processing may be considered a fifth step because it is often associated with the MgO FGD process. Figure 6 illustrates the process flow for a typical MgO FGD system.

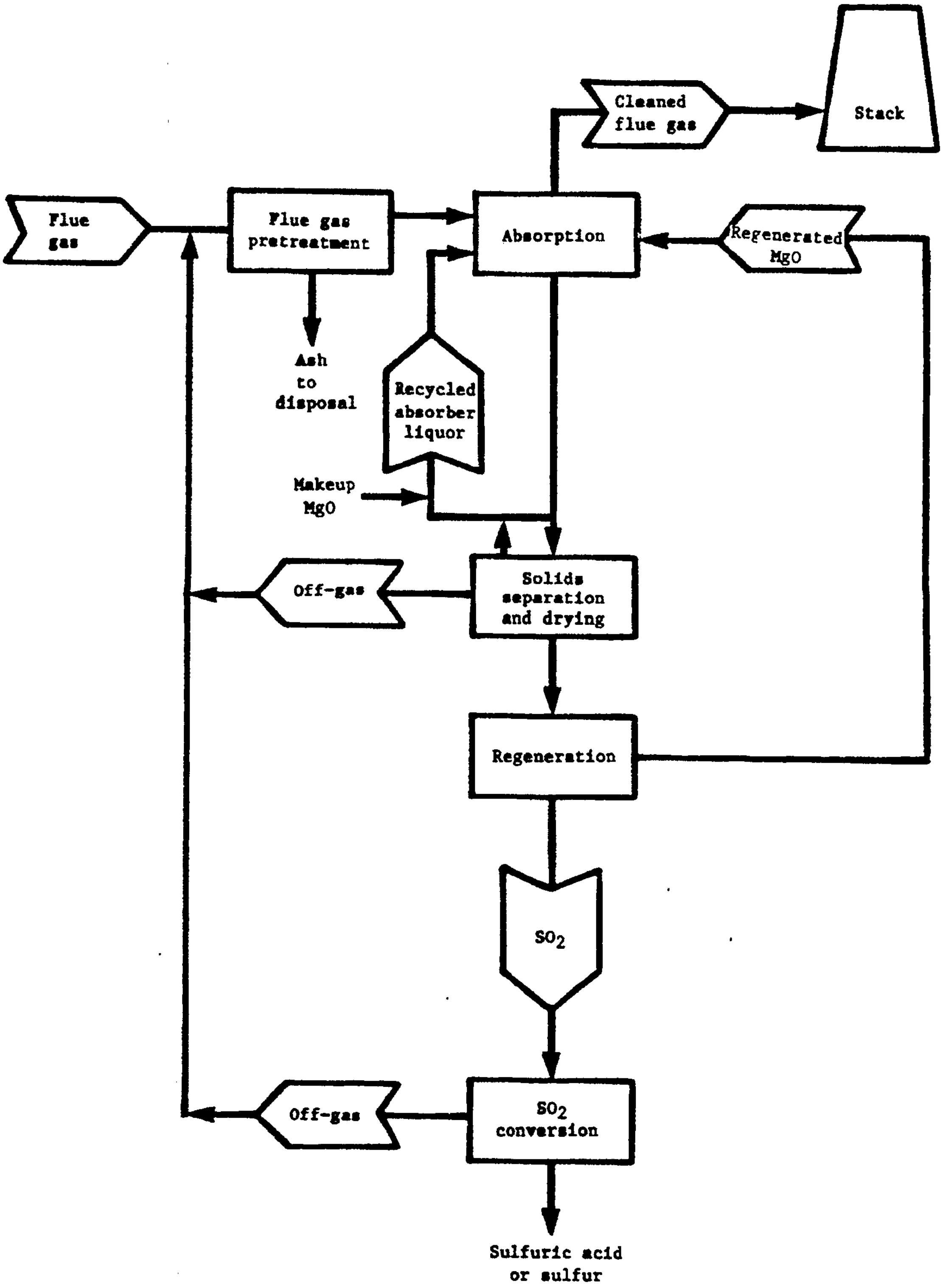

Figure 6. Magnesium Oxide FGD Process with Regeneration and SO_2 Conversion(12)

In the first step, water scrubbing cools and saturates the boiler flue gas and removes fly ash and chlorides upstream of the absorber. While flue gas from oil-fired boilers generally does not require pretreatment by quenching, this step is necessary in coal-fired applications.

In the absorber (Step 2), SO_2 is removed from the flue gas by contact with a recirculating slurry of magnesium oxide (MgO), magnesium sulfite ($MgSO_3$), and magnesium sulfate ($MgSO_4$). Flue gas SO_2 is absorbed by this slurry and reacts with MgO to form $MgSO_3$, some of which reacts with oxygen (O_2) present in the flue gas to form $MgSO_4$. Additional $MgSO_4$ is formed when flue gas sulfur trioxide (SO_3) reacts with MgO.

Desulfurized flue gas leaves the absorber, is reheated if necessary, and is exhausted through the stack. The scrubbing liquor is continuously recycled to the absorber after a continuous bleed stream has been withdrawn from the recirculation loop for solids separation and regeneration processing. Fresh MgO slurry is added to the recirculation loop to replace the scrubbing liquor removed by the bleed stream.

In the third step, the bleed stream is routed to a centrifuge where it is concentrated to 60 percent solids by weight, and the mother liquor is recycled to the absorber recirculation loop. The concentrated solids flow to a dryer where surface moisture and most of the water of hydration are removed, producing a dry powder of $MgSO_3$, $MgSO_4$, unreacted MgO, and inert materials.

Calcination of the dry powder in the regeneration processing stage (Step 4) converts $MgSO_3$ and $MgSO_4$ to MgO, which is recycled to the absorber recirculation loop. $MgSO_4$ is reduced with coke during the calcination process. Calcination also produces an SO_2-rich by-product stream that may be processed further to form sulfuric acid or elemental sulfur.

Thus, the MgO FGD process not only regenerates the essential absorbent, MgO, but also produces SO_2 at concentrations practical for conversion to sulfuric acid or elemental sulfur.

Aqueous Carbonate(13)

The aqueous carbonate process can be divided into four major operations: flue gas handling, SO_2 absorption and product collection, absorbent regeneration, and sulfur production. Figure 7 is a process flow diagram of a typical aqueous carbonate system.

Flue gas is contacted with sodium carbonate solution in a spray dryer, and SO_2 is absorbed. The solid sodium sulfite and sodium sulfate formed is collected in cyclones and an ESP. The flue gas, which is only partially quenched, is emitted to the atmosphere without reheating. Overall reactions in the spray dryer are:

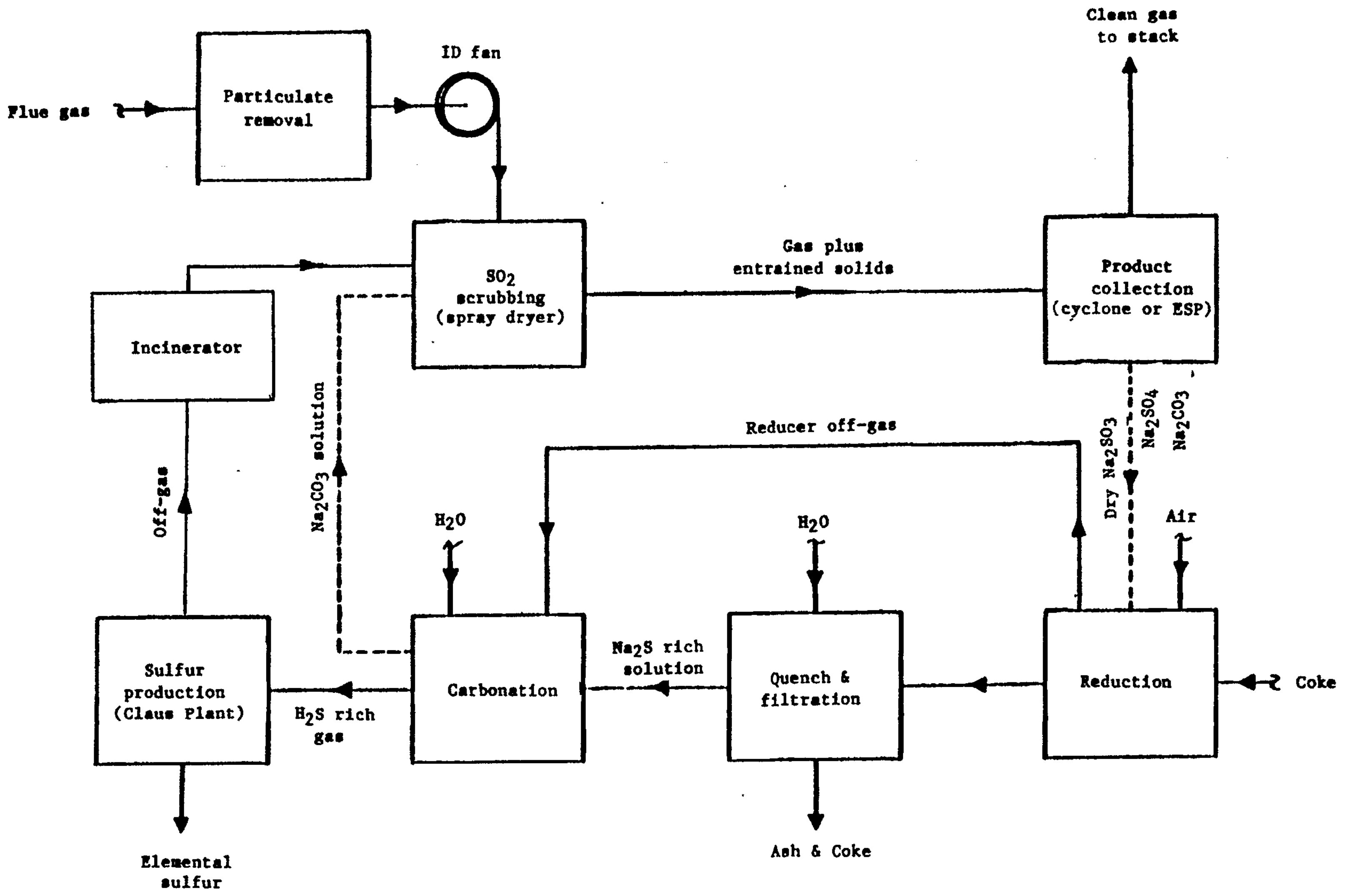

Figure 7. Aqueous Carbonate FGD Process(13)

$SO_2 + Na_2CO_3 \rightarrow Na_2SO_3 + CO_2 \uparrow$ (1)

$Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4$ (2)

In the regeneration area, spent absorbent is melted, mixed with coal or petroleum coke, and sparged with air in the reducer vessel. The following reactions occur:

$Na_2SO_3 + 2\ C + 1/2\ O_2 \rightarrow Na_2S + 2\ CO_2$ (3)

$Na_2SO_4 + 3\ C + O_2 \rightarrow Na_2S + 3\ CO_2$ (4)

A portion of the smelt is continuously withdrawn to a quench tank and dissolved in water. The "green liquor" thus produced is clarified, filtered, and contacted with the cooled reducer off-gas in a series of tray towers to regenerate sodium carbonate and evolve hydrogen sulfide by the following reactions:

$Na_2S + 2\ CO_2 + 2\ H_2O \rightarrow H_2S + 2\ NaHCO_3$ (5)

$2\ NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$ (6)

The regenerated liquor is filtered and recycled to the spray dryer/absorber. Solids, mainly composed of ash and miscellaneous impurities, from the green liquor filters and from the regenerated liquor filters are disposed of.

Sulfur production involves the conversion of H_2S to elemental sulfur in a three-stage Claus unit. The tail gas from the unit is incinerated and recycled to the spray dryer/absorber.

Currently no dry FGD systems use regeneration, although those using Na_2CO_3 in spray dryers duplicate the absorption step of the aqueous carbonate process.

ECONOMIC COMPARISONS

Cost estimates for most wet FGD processes are readily obtained from the wealth of design and operating experience for these processes. Cost projections for the only dry FGD (spray dryer) process yet commercialized are based on pilot- and demonstration-scale tests and vendor estimates. As TVA has performed comprehensive studies for EPA on the economics of FGD, costs from these studies are the bases for the comparisons reported here.

The state-of-the-art wet FGD system is considered to be the non-regenerable limestone spray tower process. Other wet FGD systems are compared with this system, the costs for each system having been determined using the same design and economic premises(14,15,16). Since the costs of the processes ranked in Table 1 are being updated to conform to the 1979 NSPS for utility boilers and revised design and economic premises, no numerical values are listed. Table 1 ranks these processes in order from lowest to highest costs.

A comparison of dry FGD (spray dryer) costs with wet limestone FGD (spray tower) costs is given in Table 2(9). The costs include particulate matter removal and waste disposal because particulate matter removal is an inherent part of the dry FGD process. While wet FGD costs are founded on extensive design and operating experience, only limited pilot- and demonstration-scale data are available for dry FGD. Since the same estimation basis and methods were used for each process evaluated, the accuracy for comparison is reasonable for preliminary studies.

Table 2 shows that the capital investment and first year revenue requirements for dry FGD are less than those for wet FGD for all cases compared. For high sulfur coal (3.5 percent sulfur), however, the lifetime cost for wet limestone FGD is about 2 percent less than for lime spray drying. While the capital investment advantage for the lime spray dryer over the wet limestone process ranges from about 14 to 30 percent, the annual revenue requirement advantage for the spray dryer over the wet limestone process falls from about 28 to 2 percent for increasing sulfur content of the eastern coals. This is attributed to the higher unit cost and the higher stoichiometric ratio for the lime system relative to the limestone system. By increasing the sulfur content of the coal from 0.7 to 3.5 percent, the absorbent costs increase about 10-fold and represent about 27 percent of the first year revenue requirements for the lime spray dryer, while corresponding values for the wet limestone FGD system are 7-fold and 3 percent.

Table 2 also indicates that the lime spray dryer would be the economic choice over soda ash spray drying for low-sulfur western coal. Because of the higher unit cost of soda ash relative to lime, the expected sources for soda ash being in the West, and high disposal costs for sodium salt wastes, the economic advantage of the lime over the soda ash spray dryer is expected to be even greater at eastern sites.

As noted earlier, the addition of adipic acid to the wet limestone FGD process improves both SO_2 removal and limestone utilization. Both of these improvements lead to decreased lifetime cost, and the quantification of their effects is underway. Limited pilot plant testing also showed adipic acid to improve both SO_2 removal and sorbent utilization when either lime or limestone are used in spray drying with partial recycling of waste solids(17). However, the low reactivity of limestone at the usual flue gas conditions in spray drying apparently limits SO_2 removal

TABLE 1. COMPARATIVE ECONOMICS OF ALTERNATE WET FGD PROCESSES IN ORDER OF INCREASING COSTS(14,15,16)

Lifetime Cost	Capital Investment	First Year Annual Revenue Requirements	Waste or By-product
Limestone	Lime	Limestone	Waste
Dual alkali	Limestone	Dual alkali	Waste
Lime	Dual alkali	Lime	Waste
Aqueous carbonate	Aqueous carbonate	Aqueous carbonate	By-product
Magnesium oxide	Wellman-Lord/acid	Magnesium oxide	By-product
Wellman-Lord/acid	Magnesium oxide	Wellman-Lord/acid	By-product
Wellman-Lord/RESOX	Wellman-Lord/RESOX	Wellman-Lord/RESOX	By-product
Citrate	Citrate	Citrate	By-product

NOTES:

1. Credit is taken for the sale of by-products for the last five processes listed.

2. Particulate matter removal and waste disposal costs are not included for any process listed.

3. Design and economic premises are: new 500-MWe midwestern plant firing eastern bituminous coal (3.5% S, 12% ash, 5833 kcal/kg (10,500 Btu/lb), 30-year plant life, and SO_2 emissions meeting 1971 NSPS).

TABLE 2. COMPARATIVE ECONOMICS FOR DRY (SPRAY DRYER) AND WET LIMESTONE FGD PROCESS FOR SEVERAL COALS AND SULFUR CONTENTS(7,9)

Process	Fuel	Lifetime Cost, $\$10^6$	Capital Investment $\$10^6$	First Year Annual Revenue Requirements, $\$10^6$
Lime spray dryer	Lignite	860.8	82.6	20.9
Limestone wet FGD	0.9% S	1069.5	107.4	26.3
Soda ash spray dryer	Subbituminous (western) coal	844.4	79.4	20.4
Lime spray dryer	0.7% S	774.7	77.1	19.0
Limestone wet FGD		885.5	88.1	21.7
Lime spray dryer	Bituminous	757.1	75.3	18.6
Limestone wet FGD	(eastern) coal 0.7% S	936.4	92.6	23.9
Lime spray dryer	Bituminous	1413.3	100.1	31.9
Limestone wet FGD	(eastern) coal 3.5% S	1355.8	121.9	32.4

BASIS: A new 500 MWe plant is assumed to be located in Wyoming, Colorado, Nebraska, North Dakota, or South Dakota when lignite or low sulfur western coal is the fuel. A midwestern plant site (Kentucky, Illinois, or Indiana) is used for the eastern coal estimates. TVA design and economic premises were applied with capital investment expressed in 1982 dollars. Investment costs include those for control of SO_2 emissions and disposal of scrubber waste via landfilling 1.6 km (1 mi) from the plant site. The plant has an operating life of 165,000 hours over a 30-year period (equivalent to full load over 5500 hr/yr). The boiler heat rate is 2394 kcal/kWh (9500 Btu/kWh) for coal and 2948 kcal/kWh (11700 Btu/kWh) for lignite. Revenue requirements are in 1984 dollars, while the total evaluated cost is based on a fixed charge rate of 14.7 percent and a levelized operation and maintenance factor of 1.886, which account for inflation and the cost of money over the plant life.

FUEL DATA:

	As Fired				Dry Basis
	Heating Value kcal/kg	Heating Value Btu/lb	Ash %	Moisture %	Sulfur %
Lignite	3667	6600	7.2	36.3	0.9
Western Coal	5390	9700	9.7	16.0	0.7
Eastern Coal	6501	11700	15.1	4.0	0.7
Eastern Coal	6501	11700	15.1	4.0	3.5

to about 30 to 35 percent. While the apparent improved performance using adipic acid in the wet FGD system may exceed that in the spray dryer, the impact this additive has on lifetime cost may be greater for the dry FGD system because of the relative effect of sorbent cost on revenue requirements (as noted earlier). Consequently, further work is needed to definitize the cost effect of adipic acid additive on both of these FGD processes.

SUMMARY

Wet FGD processes can effectively and reliably control SO_2 emissions from coal-fired boilers. Among the available wet processes, the nonregenerable (throwaway) wet limestone system predominates the power plant applications because of its cost advantage. A recent improvement to the wet limestone/lime FGD process is the use of forced oxidation to produce a more suitable waste product (gypsum) for landfill disposal. Currently, the addition of adipic acid to limestone is demonstrating improved SO_2 removal (consistently above 90 percent) and sorbent utilization (over 95 percent) and appears to offer significant performance improvement and cost savings.

Dry FGD has recently emerged as a potentially more economical and reliable option for low-to-moderate-sulfur coal applications. Its viability remains to be demonstrated in full-scale applications: the first utility system is slated for operation this year. The lime-based spray dryer appears to offer capital investment savings due to its simpler design, but it requires lime which is more expensive than limestone. The application of dry FGD to high-sulfur coal may be enhanced by using adipic acid in the lime spray dryer method.

Regenerable FGD processes offer sulfur or sulfuric acid as by-products. The Wellman-Lord process is being used at several power plants and a 100-MWe demonstration of the aqueous carbonate process is in the construction phase. Generally, the higher lifetime costs and the markets for these by-products have not encouraged widespread selection of regenerable FGD processes.

Wastes from nonregenerable FGD processes are classed as nonhazardous, with disposal by landfill becoming the general practice. Forced oxidation has improved the disposal characteristics of wastes from the wet limestone FGD process, making these wastes more suited to landfill disposal. Dry wastes from lime spray dryers are well-suited to landfill disposal, but the use of sodium compounds in dry FGD may require lined landfills to limit the leaching of sodium salts into ground water.

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HEALTH AND ENVIRONMENTAL STUDIES OF COAL GASIFICATION PROCESS STREAMS AND EFFLUENTS

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ABSTRACT

The Synfuels Environmental Research Program at Argonne National Laboratory is investigating the impact of high-BTU coal gasification on health and the environment. Activities include a toxicologic and chemical characterization of process streams in the gasifier and pretreater sections of the HYGAS coal gasification pilot plant, and process streams and workplace air from the Grand Forks Energy Technology Center's slagging fixed-bed gasifier facility. Cellular assays for mutagenicity, cytotoxicity, and functional impairment are performed to determine relative toxicity. Various acute and chronic whole animal toxicological evaluations, including skin tumorigenesis, are performed for streams found to contain potential toxicants (e.g. oils and tars). The chemical characteristics of vapor phase and airborne particulate-associated organics, as well as biologically active materials isolated from process streams, are investigated by physical and chemical fractionation of the samples, with biological monitoring and detailed GC and GC/MS analyses of the fractions. Present data indicate that toxicants are present, but their levels of activity are relatively low. As a result of these studies, we tentatively conclude that with appropriate control technology and industrial hygiene procedures there appear to be no serious health or environmental problems associated with coal gasification.

INTRODUCTION

A thorough evaluation of the potential impact on human health and the environment is a prerequisite to implementation of new fossil fuel conversion technologies. The Department of Energy (DOE), through its Offices of Energy Research and Fossil Energy, sponsors several research programs to provide this evaluation. Argonne National Laboratory has the major responsibility in the area of high-BTU coal gasification, and thus has the obligation to develop:

- A comprehensive health and environmental data base for coal gasification

- A reliable assessment of the risks associated with large-scale coal gasification

Projects within Argonne's Synfuels Environmental Research Program include a completed study of the HYGAS pilot plant at the Institute of Gas Technology (IGT) Energy Development Center (Chicago, IL) and ongoing studies of the slagging fixed-bed gasifier at the Grand Forks Energy Technology Center (GFETC) (Grand Forks, ND), and a bench scale gasifier at the Carnegie-Mellon Institute of Research (Pittsburgh, PA). This report discusses the HYGAS pilot plant studies and gives initial results from GFETC. Experiments with the Carnegie-Mellon gasifier samples were only recently initiated and will not be presented.

The Argonne program employs an integrated multidisciplinary approach to sample characterization. Sample preparation and fractionation activities, toxicological characterization, and identification of specific chemical components required interaction and collaboration among personnel in three Argonne Divisions:

Analytical Chemistry Laboratory (Chemical Engineering Division)
Biological and Medical Research Division
Energy and Environmental Systems Division

BACKGROUND

The end product of high-BTU coal gasification is a substitute natural gas (SNG), essentially indistinguishable from natural gas, and therefore presents no new health or environmental issues. However, most gasification processes also produce by-product oils and tars known to contain a variety of noxious chemicals, including carcinogens. These oils and tars are extremely complex mixtures and are at present chemically illdefined. Although these potentially toxic by-products are readily removed from the product gas and can be completely consumed on site, potential routes of human exposure do remain - namely, direct contact with solids and liquids, or inhalation of fugitive vapor, aerosol and particulate emissions. This program emphasizes the toxicological and chemical characterization of the organic components of process streams. This report summarizes our activities to date at IGT and GFETC. Additional more detailed information has appeared elsewhere (1-5).

PROCESS DESCRIPTIONS

HYGAS

This advanced process for high-BTU coal gasification was developed by IGT with support from the Gas Research Institute and DOE. An 80 ton per day pilot-plant gasifier has operated for several years on a variety of coal types. A detailed description of the process, the operating conditions during sampling, and the samples that were collected is included in a recent report presented at the Second International Gas Research Conference (6).

Emphasis in this report is placed on the pilot plant process streams deemed to be of environmental importance in commercial facilities. Samples from the low temperature reactor (LTR) provide a reasonable approximation of the organic compounds formed during coal gasification. Not all of these organic compounds leave the gasifier, but those that do enter the recycle oil. The recycle oil system, which accounts for the largest mass flow of organics within a plant, has the greatest potential for leaks and fugitive emissions. It is also the most significant environmentally, since it will represent a steady-state composition of high molecular weight organic compounds leaving the gasifier. Organics formed in the coal pretreatment process also could be a major source of fugitive emission in the commercial plant. In the pilot plant these organic compounds are found in the pretreater quench water. Finally, organic compounds present in the gasifier quench water, if not removed in the water treatment system, could enter the atmosphere through cooling tower water desorption. Although spent char is a significant plant discharge stream, it would be incinerated in a commercial plant and thus is not considered to be environmentally important.

SLAGGING FIXED-BED GASIFIER

The gasifier operated by GFETC is a 25 ton per day slagging fixed-bed pressurized gasifier which differs from other fixed-bed gasifiers in that a lower steam:oxygen ratio is used for the gasification reaction, and operating temperatures are high enough to melt the ash for discharge as a molten slag. This gives the slagging process several advantages, including higher throughput, lower steam consumption, and lower wastewater production. A detailed description of the process was presented at the 1981 Lignite Symposium (7).

Waste effluent streams from a fixed-bed gasification process consist of (a) gaseous contaminants (chiefly H_2S, CO_2, and light hydrocarbons), which are cleaned from the product gas by commercially available processes to meet end use requirements; and (b) solid and liquid effluent streams consisting of slag, slag quench water, and the gas liquor, composed of condensed tar, oil, water, and coal dust entrained in the product gas. Additional solid wastes may also be generated by wastewater treatment processes. Emphasis in our studies has been placed on what is considered to be potentially the most noxious gasifier waste stream, the gas liquor obtained from the condensation of tars, oils, and water in the spray cooler. While the GFETC gasifier is slightly different from a commercial design, the chemical nature of the tar and oil should be more dependent on the nature of the feed coal than of gasifier design.

METHODOLOGY

SAMPLING

All process stream samples were collected by the plant operators under conditions of steady operation. Following collection, the samples were refrigerated (4°C) and shipped to Argonne. At Argonne a locked refrigerated storage vault was used. Detailed records were systematically maintained to document sample preparation, transfer to and from storage, fractionation, and subsequent distribution.

The HYGAS samples studied were from the final four HYGAS test runs, all of which used a Western Kentucky feed coal. Samples from GFETC came from a test run that used North Dakota Indian Head lignite. Samples were collected from the tar-oil separator and consisted of process oil, tar, and water.

Samples of airborne particulates and fugitive organic vapors were collected by Argonne personnel in collaboration with GFETC process and environmental engineers at various locations in the gasifier building. Vapor samples were collected on XAD-2 resin at level 2 (steam injection and control room) and level 7 (lockhopper) during a run with Indian Head lignite. The resin was extracted with methylene chloride and the organic compounds present in the extract were identified by GC/MS and quantified by GC. Procedures and techniques have been reported in an earlier study concerning sampling at the HYGAS facility (5).

Particulate sampling was conducted during shutdown operations and operation of the gasifier following an aborted start up. A size-fractionated particle sample collected with a Sierra high-volume impactor was subjected to analysis by GC/MS and scanning electron microscopy; aerosols collected with an Anderson low-volume impactor were subjected to flameless atomic absorption analysis.

TOXICOLOGY

Three cellular tests were used to establish relative toxicities of all process samples. This battery of procedures was required to provide the variety of toxicological end points and systems necessary to evaluate the broad chemical spectrum of compounds present in the sample materials. The Ames *Salmonella* plate incorporation assay was used to determine mutagenicity. Strain TA98 was used exclusively because it was found to be the most sensitive of the five commonly used strains. Metabolic activation of samples with rat liver S9 enzymes was essential for expression of mutagenicity. Mouse myeloma cells were used to measure both genotoxicity (by sister chromatid exchange) and cytotoxicity (by growth inhibition). Finally, two additional measures of cytotoxicity, a gross measure (cell death) and a subtle measure (loss of normal cell function), were obtained using the rabbit alveolar macrophage (RAM) assay. The functional loss was evaluated by determining the inhibition of normal phagocytic activity in these cells.

In addition, whole animal toxicological assays were performed on HYGAS recycle oil. The assays included measurement of the effects of both acute and chronic dermal exposures and acute ocular exposures. Dermal effects were studied in SKH hairless mice (carcinogenicity), albino guinea pigs (hypersensitivity), and New Zealand albino rabbits (acute effects).

Ocular tests were performed in New Zealand albino rabbits.

BIO-DIRECTED CHEMICAL CHARACTERIZATION

Chemical characterization of samples was always performed in support of toxicological determinations. Table 1 gives the procedures employed. Many of the process samples were heterogeneous and not suited for direct testing in the cellular assay systems. Materials were physically separated and the organic components were extracted from the aqueous and solid phases. The resulting extracts and oils were then fractionated on the basis of volatility. In our experience only the nonvolatile organic (NVO) fractions containing components boiling at greater than ≈ 200°C exhibited mutagenic activity and thus were the materials entered in the toxicity screening tests. Materials found to show significant toxicity in the test screen were further fractionated on the basis of acidity and polarity. Mutagenic activity in the various fractions was monitored with the Ames *Salmonella* assay. Chemical fractionation procedures included both liquid/liquid partitioning and high efficiency column chromatography. GC/MS was used for identification of the components in a given fraction and fused silica capillary column GC was used for quantification (1).

TABLE 1. BIO-DIRECTED CHEMICAL CHARACTERIZATION

- Physical Fractionation
  - Phase
  - Volatility

- Chemical Fractionation
  - Acidity
  - Polarity

Biomonitoring (Ames assay)
Chemical Testing (Nitrous acid)
Compound Identification (GC/MS)
Compound Quantification (GC)

RESULTS

Information is available for scores of samples and fractions of HYGAS materials and is rapidly accumulating for the GFETC gasifier. Presentation of HYGAS results is restricted to average toxicities observed in process streams deemed to be significant, either by the degree of toxicity or the potential for human exposure. GFETC data, being preliminary in nature, is restricted to process tars and oils, which are the putative major toxicants.

The streams that are discussed, and their approximate mass flow rates relative to feed coal are shown in Table 2.

TABLE 2. SIGNIFICANT PILOT PLANT STREAMS

Stream	Mass Flow (coal = 1)
HYGAS	
Recycle Oil	3
Pretreater Quench Water	3
Gasifier Quench Water	1
Low Temperature Reactor Gas	1.4
GFETC Gasifier	
Tars and Oils	0.05
Water	0.6

It is important to emphasize that the mutagenicities of HYGAS process samples were too low to measure directly and the toxicity data presented applies only to the NVO fraction. These fractions always constitute a very small part of the process stream (0.1 to 4 weight percent of the sample). Process stream toxicities (calculated as the product of NVO toxicity and its weight fraction) are accordingly quite low. Tars and oils from the GFETC gasifier have relatively greater weight percent of NVO's: approximately 90% NVO for tars and 50% for oils but only 5% of the coal is converted to tars. Because these tars and oils are not recycled, total toxicity of the raw product gas stream remains relatively low.

Results observed in the Ames Salmonella Assay of NVO fractions of HYGAS samples (Table 3) show that the greatest specific mutagenic activity is in the low temperature reactor condensate. Its specific mutagenicity is about 15% of the known carcinogen benzo(a)pyrene (BaP), but material balance studies have shown that not all of this mutagenicity leaves the gasifier. The most important HYGAS stream, the recycle oil, has an average NVO mutagenic activity less than 3% of BaP. Low or insignificant specific mutagenicity is observed with quench waters from the pretreater and gasifier and no mutagenicity could be detected in the spent char. Extrapolated specific mutagenicity of all process streams is less than 1 revertant/μg.

TABLE 3. MUTAGENICITY OF HYGAS PROCESS STREAMS (AMES SALMONELLA ASSAY)

Sample	Mutagenicity, rev/μg NVO Fraction	 Process Stream
Recycle Oil	7	0.17
Pretreater Quench Water	2.4	0.007
Gasifier Quench Water	0.7	0.0005
Low Temperature Reactor Condensate	35	0.37
Spent Char	<0.1	neg.
Benzo(a)pyrene	260	

Cytotoxicity and genotoxicity measurements in mouse myeloma cells support the general conclusion that on a process stream basis toxicity is low. However, untreated quench waters contain significant toxicity (Table 4). They are the most toxic sample type, being threefold more genotoxic than LTR condensates or recycle oil. This test does not require metabolic activation but when the LTR condensate is activated with rat liver S9 enzymes, genotoxicity increases tenfold and approximates the relative activity of LTR condensate to BaP seen in the Ames Assay.

TABLE 4. TOXICITY OF HYGAS PROCESS STREAMS (MOUSE MYELOMA CELLS)

Sample	Cytotoxicity* L/g	Genotoxicity** L/g
Recycle Oil	16.5	15.5
Pretreater Quench Water	19.3	31.4
Gasifier Quench Water	55.7	47.3
Low Temperature Reactor Condensate	12.3	17.7
Methyl Methane Sulfonate	36.0	370
Low Temperature Reactor Condensate with Activation	20.8	175
Benzo(a)pyrene with Activation	112	1230

*The reciprocal of the NVO concentration for 50% growth inhibition.

**The reciprocal of the NVO concentration for a twofold increase in sister chromatid exchanges.

In the RAM assay HYGAS materials are approximately equivalent within a given end point (Table 5). There is however a clear indication of subtle toxicity (functional loss) at concentrations of HYGAS materials significantly lower than those required for cell killing.

TABLE 5. TOXICITY OF HYGAS PROCESS STREAMS (RAM ASSAY)

Sample	Cytotoxicity* L/g NVO	Functional Impairment** L/g NVO
Recycle Oil	7.1	9.8
Gasifier Quench Water	4.1	10.8
Pretreater Quench Water	6.1	8.1
Low Temperature Reactor Condensate	7.4	11.4
Vanadium Oxide	153	208

*The reciprocal of the NVO concentration for 50% cell killing.

**The reciprocal of the NVO concentration causing a 50% reduction in the phagocytic activity of viable cells.

Ocular toxicity tests in rabbits have demonstrated that recycle oil NVO is a severe irritant according to National Academy of Science criteria (NAS publication 1138, 1977). We observed inflammatory reactions, corneal ulcers, and panus that persisted for 21 days. Likewise, rabbit skin exposure results in mild to severe inflammatory reactions with some skin necrosis. Marked skin hypersensitivity is detected in guinea pigs. We found that raw recycle oil is a mouse skin carcinogen, inducing tumors in SKH hairless mice following chronic exposure (weekly 150 μl doses). The tumorigenic response is considerably less than that for BaP (.03 μg/week); however, 105 μg of the recyle oil NVO approximates the BaP tumor response. Tumor response is based on gross observation, but histologically confirmed squamous cell carcinomas of the skin have been observed, some with metastatic nodules. Thus while it is clear that recycle oil is toxic, it is important to emphasize that the potential for human exposure is limited. The nature of the stream and normal industrial hygiene protocols should make hazards associated with recycle oil totally manageable.

Table 6 gives preliminary toxicological evaluations of GFETC tars and oils. Results are for unfractionated samples and should not be confused with the toxicity of NVO fractions. Mutagenicity is insignificant in oils but present at a level 5% that of BaP in tars. Samples are cytotoxic and genotoxic but again not at high levels. The toxicity of untreated process water while relatively low is significant when the large volume of this stream is considered (Table 2).

TABLE 6. TOXICITY PRESENT IN THE GRAND FORKS ENERGY TECHNOLOGY CENTER'S SLAGGING FIXED-BED GASIFIER PROCESS STREAMS

	Tar	Oil	Water	Reference* Standards
Mutagenicity, rev/ g	4	<1	0	260
Cytotoxicity*, L/g	11	11	0.7	36
Genotoxicity*, L/g	16	12	1.4	370
Functional loss*, L/g	14		9	208

*As in assay of HYGAS samples, see Tables 3-5.

AIR MONITORING

The organic vapor concentrations we observed in the GFETC gasifier facility ranged from approximately 1-500 μg/m^3 for individual components with an overall organic vapor concentration of from 2-3.5 mg/m^3. One- to three-ring aromatic hydrocarbons accounted for the bulk (50-70%) of the material with aliphatic hydrocarbons (30-40%) accounting for most of the remainder. Phenols and heterocyclic compounds each accounted for about 2% of the total organic fraction. The concentrations of individual compounds (e.g., benzene) were well below TLV limits in all cases.

The bulk of the particulate-associated trace organic material was associated with particles having an aerodynamic size of $\leq$3.1 μm. The particulate phase organics contained significantly higher proportions of aliphatic and phenolic compounds than the vapor phase samples and this is consistent with published data for ambient air. Particle morphologies resembled those of lignite fly ash from combustion, and particle types included smooth spheres, vesicular spheres, agglomerated masses and crystalline fragments. Trace element size distributions were bimodal and resembled those for ambient air. Lead particle sizes were predominantly submicron, while particles of Al, Fe, and other crustal species were mostly of supermicron size. Aluminum-based aerosol enrichment factors calculated from Indian Head lignite showed that the composition of the aerosol resembled that of the coal, with the exception of modest enrichment of Mg, Na, As, and Pb in the submicron size range. Aerosol enrichment factors based on the earth's crustal composition were somewhat greater than those based on coal composition for several elements, suggesting potential errors in using crustal enrichment data to investigate chemical fractionation during aerosol formation.

CHARACTERIZATION OF TOXIC COMPOUNDS

Because toxicity was confined to nonvolatile materials, it was possible to fractionate and concentrate without evaporative loss of toxic material. As previously mentioned, the components of recycle oil were fractionated by acidity and polarity. Separation by polarity was accomincreasing proportions of benzene, accounted for half of the sample weight but were only slightly mutagenic despite the fact that they contained polyaromatic hydrocarbons such as BaP. Virtually all of the mutagenicity recovered was contained in the fourth most polar fraction, (eluted with methanol).

In the initial pH fractionations, methylene chloride samples were partitioned between an aqueous acid or base. The base fraction contained more than 70% of the recovered mutagenicity. Although the base fraction contained only 4% of the initial weight, its specific mutagenicity was more than tenfold higher than that of the original sample. The neutral fraction contained the remainder of the recovered mutagenicity with the acid fraction (exclusively phenolic) being nonmutagenic. The neutral and acidic fractions accounted for 50% and 30% of the initial weight, respectively.

Chemical analysis showed that the base fraction contained azaarenes (AA) and primary aromatic amines (PAA) in the ratio of 4:1. Since members of both classes of compounds are known to be toxic, further analyses were performed to determine which components were mutagenic. The loss of mutagenicity following mild nitrous acid treatment (which modifies PAA but not AA) suggests that the PAA are responsible for the mutagenicity. More conclusive evidence was obtained by applying a new procedure for cation exchange high performance liquid chromatography (8). This procedure separates PAA (weaker bases) from AA and resolves members of each class having pK_a values differing by less than 0.2 pK_a units. Chromatography of the LTR base fraction revealed that most of the mutagenicity is concentrated in a few fractions containing 2- to 4-ring PAA as demonstrated by GC/MS. Azaarenes which elute in the later fractions contain little of the mutagenicity.

CONCLUSIONS

The results of this study on the toxicological and chemical characterization of two high-BTU coal gasification pilot plants demonstrate that while toxicants are present, they are a minor component of the process streams. The toxicity is largely confined to the nonvolatile components of the by-product tars and oils. These materials will not leave the commercial plant site because they are ultimately consumed in the process. On-site emissions can be controlled through appropriate control technology. Occupational exposures can be minimized through effective industrial hygiene procedures. These considerations allow the general assessment that no apparent serious health or environmental problems are associated with coal gasification.

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GASEOUS FUGITIVE EMISSIONS FROM SYNFUELS PRODUCTION - SOURCES AND CONTROLS†

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ABSTRACT

Fugitive emissions are generally defined as emissions that are not released through an enclosure such as a duct or vent pipe. This definition includes sources of fugitive particulate emissions and sources of gaseous fugitive emissions. In this paper, the potential sources and control options for gaseous fugitive emissions from synfuels production facilities are described. Gaseous fugitive emissions are caused by process fluid leakage from seals (valves, pumps, flanges), process fluid purges (sampling, equipment cleaning), and secondary emission sources (drains, wastewater systems, cooling towers). The majority of sources of fugitive emissions in the U.S. are currently found in petroleum production and refining facilities, organic chemical manufacturing plants, and coke by-product plants. Synfuels production facilities will also have fugitive emission sources.

Fugitive emission regulations have been applied to California petroleum refineries for several years and U.S. New Source Performance Standards (NSPS) are currently under development for several industries. These regulations are based on the need to reduce emissions of volatile organic compounds (VOC), because VOC are photochemical ozone precursors. Some fugitive emissions also need to be controlled because compounds released in the emissions may be harmful. U.S. National Emission Standards for Hazardous Air Pollutants (NESHAP) have been developed for controlling fugitive emissions of vinyl chloride and benzene. Fugitive emissions from synfuels production facilities may require control because they contribute to atmospheric ozone formation and/or because the emissions contain harmful compounds. The nature of potentially harmful compounds will be dependent on variables such as the type of process, feedstock characteristics, and operating parameters.

Fugitive emission controls can be categorized as either work practices or engineering controls. Work practices include leak detection/leak repair programs and "housekeeping" practices. Leak detection and repair programs involve periodic testing to locate significant leaks and subsequent repairs to reduce or eliminate the leakage. Housekeeping practices would include procedures to minimize process fluid spills and to expedite spill cleanup. Engineering controls are generally equipment substitution strategies. For example, closed loop sampling connections eliminate process fluid purge emissions, and double mechanical pump seals can be operated to minimize seal

emission potential. These types of equipment could be substituted for equipment with a greater potential to leak process fluids.

Because the emission sources (pumps, valves, flanges, etc.) in synfuels plants will be similar to those in existing U.S. industries, emission control techniques used in existing industries will also be applicable to synfuels facilities. The experience that has been gained in applying fugitive emission controls will be valuable in developing emission control strategies for synfuels plants.

INTRODUCTION

Gaseous fugitive emissions are the result of process fluid leakage and process fluid purges. Secondary emission sources such as cooling towers and wastewater systems may also be classified as fugitive emission sources. In contrast to process emissions, which are released through ducts or vent pipes, fugitive emissions are released from numerous discrete sources such as valves, pumps, and flanges located throughout a process unit. Process emissions are amenable to application of emission control devices that either recover or destroy the emissions conveyed to the device by a duct or pipe, but fugitive emission sources require a completely different type of emission control strategy. The purpose of this paper is to identify the potential sources of gaseous fugitive emissions in synfuels production facilities and to discuss the types of controls that can be applied to reduce emissions from those sources.

Fugitive emissions have received rapidly increasing attention in the last five years and there are several reasons for this increased awareness of a need to control fugitive emissions. Because process emissions are released through an enclosed pipe or duct, it is fairly straightforward to convey these emissions to a control device. Furthermore, process emission sources generally contribute a much larger portion of the total emissions compared to fugitive emission sources. For these reasons, process emission sources have been selected for application of controls first. As more controls are applied to process sources, fugitive emissions become a significant contributor to the remaining controllable emissions from a process unit. In addition, fugitive emission sources may be the major contributor to the total emissions of specific compounds that require control.

The compounds released from fugitive emission sources may require control because they are volatile organic compounds (VOC), which have been linked to photochemical atmospheric ozone formation. Other compounds such as benzene and hydrogen sulfide may require control because the compounds themselves are health hazards. Regulations to control fugitive emissions have been applied to the petroleum industry in California for VOC control for several years, and other states are developing regulations. Federal New Source Performance Standards (NSPS) are currently being developed for VOC control in several industries. National Emission Standards for Hazardous Air Pollutants (NESHAP) have been developed for fugitive emissions of benzene and vinyl chloride. These regulatory activities have resulted in increased awareness of the need to learn more about the sources and controls of fugitive emissions.

SOURCES OF FUGITIVE EMISSIONS

Fugitive emissions are caused by process fluid leakage, process fluid purging and atmospheric exposure of process fluids by secondary emission sources. Any type of process equipment that is capable of allowing process fluids to come in contact with the atmosphere is a potential fugitive emission source. These sources of fugitive emissions are shown in Table 1.

PROCESS FLUID LEAKAGE

Sources of process fluid leakage include valve packings, seals on pumps, compressors and agitators, flange gaskets, relief valve seats, and valve seats on open-ended lines. An open-ended line is defined as a process valve that is installed with one side of the valve in contact with process fluid and the other side in contact with the atmosphere, such as purge valves, drain valves and vent valves.

All process valves, except relief valves and check valves, are activated by a valve stem which may have either a rotational or linear motion, depending on the specific design. The moveable stem requires a sealing element to resist fluid leakage while permitting movement of the stem. In most valves, this seal is achieved with a packing compression gland. Other valves may have elastomeric O-rings or grease-filled lantern rings to prevent leakage of process fluid. Although these types of seals are satisfactory for preventing gross leakage of process fluids, they can allow a significant amount of fugitive leakage. Corrosive or toxic process fluids may require the use of a valve with a diaphragm or flexible bellows to isolate the stem sealing element from the process fluid, and these valves would also provide increased resistance to fugitive leakage.

Packed seals on pumps, compressors, and agitators are similar to packed seals on valves. Because the shafts on these devices rotate constantly, periodic adjustment of the packing is required. Mechanical seals consist of stationary and rotating elements that are machined to a very close tolerance. The mechanical contact of the two elements resists fluid leakage. As with packed seals, leaks can occur where the shaft protrudes through the seal. Double mechanical seals and oil film seals have a barrier fluid system that resists seal leakage. However, seal leakage can be entrained in the oil system and can be released to the atmosphere by degassing from the oil reservoir.

Leaks from flange gaskets can be caused by loose bolts, improper specification of materials, thermal stresses, and deterioration of the gasket material. Although they are the most numerous type of fugitive emission source, flanges contribute a small portion of total fugitive emissions.

Relief valves are designed to open at a predetermined pressure in order to protect process equipment from damage due to overpressure. The discharge that occurs when these valves open is considered a process emission. Fugitive emissions from relief valves are the result of leakage through the valve when it is closed. This leakage can be caused by improper reseating after an

TABLE 1. FUGITIVE EMISSION SOURCES

Source Type	Location of Emission Release
<u>Sources of Fluid Leakage</u>	
Valves	Stem/body junction
Pumps and Agitators	
Packed seals & single mechanical seals	Shaft/case junction
Double mechanical seals	Shaft/case junction; oil reservoir degassing vent
Compressors	
Packed seals & single mechanical seals	Shaft/case junction
Double mechanical seals & oil film seals	Shaft/case junction; oil reservoir degassing vent
Flanges	Face/gasket junction
Relief Valves	Disc/seat junction
Open-ended lines (valves)	Valve disc/seat junction
<u>Sources of Process Fluid Purges</u>	
Sampling Operations	Purge/atmosphere contact
Equipment Emptying Operations	Purge/atmosphere contact
<u>Secondary Emission Sources</u>	
Cooling Towers	Cooling tower plume
Wastewater Systems	Drains, open sewers or canals, collecting basins, separators, aeration ponds.

overpressure, deterioration of the valve seat, and operation of the process at or near the set pressure that causes the valve to open.

Open-ended lines are found on valves used for draining equipment, for purging or venting equipment, and for obtaining process fluid samples. A faulty valve seat or incomplete closure of the valve would allow process fluid to leak to the atmosphere through the open-ended line.

PROCESS FLUID PURGES

The sources of process fluid purges are sampling operations and equipment draining and venting operations. In order to obtain a representative sample of process fluid, the sample line is purged with the process fluid. If this purge is allowed to contact the atmosphere, fugitive emissions may be created. Process fluids are also purged from equipment prior to removing the equipment from service for inspection, repair, replacement, etc. Atmospheric contact with these purges can also result in fugitive emissions.

SECONDARY EMISSION SOURCES

Cooling towers and wastewater systems are considered as secondary sources of fugitive emissions because they are not the initial source of the process fluids. Process fluids may enter a cooling tower water system due to leakage in heat exchangers or from the use of contaminated process water as cooling tower make-up water. As the contaminated water is circulated through the cooling towers, process fluid components are stripped from the water and are released to the atmosphere with the evaporated cooling water.

Wastewater systems consist of drains, collection basins, canals, separators, and water treatment facilities. Because these systems have numerous locations where the wastewater contacts the atmosphere and the wastewater is frequently in a state of turbulent mixing, process fluids in the wastewater can readily become atmospheric fugitive emissions.

SEVERITY OF FUGITIVE EMISSIONS

The degree of environmental severity associated with fugitive emissions is dependent on two variables: 1) species emitted and 2) the total emission rate. The relative importance of these variables depends on the type of environmental impact that is being evaluated. With respect to the impact of fugitive emissions on atmospheric ozone formation, the total emission rate of VOC is the most significant consideration. Impacts on industrial hygiene would be dependent on the types of substances emitted and the proximity of emission release points to workers. Some of the less volatile process fluids may also accummulate over a period of time, and workers may come into contact with harmful species at any time after the initial release of the process fluid.

The contribution of fugitive emission sources must also be accounted for in considering the need for Prevention of Significant Deterioration (PSD) review due to emissions in excess of De Minimis levels. The provisions of 40

CFR 51-52 allow exemption from PSD review if the annual controlled pollutant mass emission rate from a plant is less than the established De Minimis value.

Emission control cost effectiveness is closely related to the total number of sources and the emission factor for each type of source. It is less expensive to control a few sources with high emission rates than to control many sources with low emission rates, although the total uncontrolled emission contribution of the two groups may be equal.

ASSESSMENT OF POTENTIALLY HARMFUL SPECIES

One of the first criteria that can be used in evaluating pollutants of concern in the process stream is to identify compounds covered by existing regulations. These would include "criteria pollutants" covered by National Ambient Air Quality Standards (NAAQS, 40 CFR 50) and "regulated pollutants" covered by National Emission Standards for Hazardous Air Pollutants (NESHAP, 40 CFR 61). Some compounds of potential environmental concern may be present in synfuels streams, but have not been the subject of specific regulations. Such cases arise when there are insufficient or inconclusive data available for the promulgation of enforceable regulations. One method of identifying those compounds that need additional evaluation is to compare their Multimedia Environmental Goals (MEG's).

Multimedia Environmental Goals (MEG's) have been established for over 650 chemical substances and physical agents (e.g., noise, heat). These goals (in air, water, and solid waste streams) are the maximum discharge concentrations (DMEG's) and maximum ambient concentrations (AMEG's) which will avoid potentially hazardous risks for public health or the ecology. These goals are intended to be used in prioritizing research efforts, not in establishing discharge limits. Most of the MEG's are derived using models that translate toxicological data (threshold limit values, water quality criteria, carcinogen test results, etc.), dispersion assumptions, and federal standards or criteria into discharge and ambient level goals. In many cases the models translate data from one medium to goals for another medium. Despite their obvious limitations, the MEG's do provide a method (and often the only method) of identifying pollutants of potential concern.

In order to prioritize the need for concern about specific substances, their MEG values can be compared. In Table 2, maximum ambient concentrations (AMEG's) are shown for several species that could be present in synfuels process streams. The AMEG values are in micrograms of pollutant per cubic meter of ambient air; however, the actual numerical values are not directly applicable to fugitive emission sources. These AMEG values are shown here in order to give an indication of what ambient concentrations may be of concern for some species which may be present in synfuels plant fugitive emissions.

Except for the benzene and vinyl chloride NESHAP, fugitive emission regulations have been developed in the U.S. because of the need to reduce VOC emissions. Synfuels facilities will also have sources of fugitive VOC emissions and the presence of harmful species in these fugitive emissions will

TABLE 2. HARMFUL SPECIES POTENTIALLY PRESENT IN SYNFUELS PROCESS STREAMS

Pollutant	AMEG*
Sulfur Compounds	
Hydrogen sulfide	36
Carbonyl sulfide	800
Carbon disulfide	143
Mercaptans	2.4
Thiosulfates	-
Nitrogen Compounds	
Ammonia	43
Cyanides	26
Thiocyanates	-
Nitrates, Nitrites	-
Organic Compounds	
Carbon monoxide	10,000
Benzene and other aromatics	7.1
Polynuclear aromatics (PNA's)	0.00005 to 119
Phenols	24 to 45
Organometallic compounds	-
Methanol	619
Trace Metals	
Antimony	1.2
Arsenic	0.005
Beryllium	0.01
Cadmium	0.02
Lead	0.36
Mercury	0.01
Nickel	0.035
Selenium	0.03

* Ambient Multimedia Environmental Goal ($\mu g/m^3$) from References 1, 2, and 3.

depend on the type of process, feedstock characteristics, and operating conditions. In the first phase of an environmental assessment program, the major process discharge streams are characterized. Except for the fugitive emission sources that contain (and therefore have the potential to emit) the species in these discharge streams, very little of this characterization is applicable to fugitive emissions. Because fugitive emissions are composed of the process fluid, it is necessary to know what harmful species are in these process fluids. Process stream characterization data for synfuels processes are frequently unavailable, especially for developing technologies. This information may be deemed proprietary by the process developer because the purpose of most of these process stream analyses is to determine the effects of process variables on the yield of the primary reaction products, not to characterize potentially harmful species in the streams.

Although limited test data are available, it is possible to estimate the harmful species that are likely to be present in a process stream. In Table 2, several general categories of harmful substances that could be found in synfuels processes are shown. This list does not include all possible harmful compounds, and each type of process would have a different distribution of harmful species. Some general conclusions can be reached when comparing different types of synfuels processes. For example, a process that produces organic liquids either as primary products or as by-products is more likely to have some streams containing phenols, aromatics, and polynuclear aromatics (PNA's) compared to a process that produces only a gaseous product primarily composed of carbon monoxide and hydrogen. Since trace metals are introduced into the synfuels processing facility in the coal feedstock, analysis of the feedstock would show which elements need to be considered for a particular feedstock.

ASSESSMENT OF EMISSION RATES

The average emission rate for a particular type of source is called the emission factor. The total number of sources multiplied by the emission factor equals the total emission rate from that type of source. For assessment of the severity of VOC emissions, the total emission rate is the main factor to consider. Other factors become significant when evaluating VOC emission control strategies, as discussed in the section on fugitive emission controls.

The total emission rate of harmful species is also important, but the emission rate of individual sources may also be significant. The effect on the environment beyond the boundaries of the synfuels plant is primarily determined by the total emission rate from the plant, but industrial hygiene considerations within the plant boundaries are also dependent on individual emission factors for sources. For example, if a particular type of source has a very high emission factor but there are very few sources present, the emission contribution may be a small fraction of the total hazardous fugitive emissions from the plant. However, if plant workers are frequently required to be in close proximity to this type of source, additional emission controls or protective equipment for workers may be needed.

Each synfuels process will have unique characteristics, and therefore process-specific (or even site-specific) evaluation of the severity of fugitive emissions will be necessary. Extensive fugitive emission testing has been conducted in petroleum production and refining facilities, coke byproduct plants and organic chemical plants in the U.S., and a limited fugitive emission test has been performed at a European coal gasification plant (Ref. 4). The results of these tests show that emission factors for the same type of source (valve, pump, flange) can vary over several orders of magnitude for different types of processes, and significant variations exist for the same type of process at different locations. Because of this variability, it is difficult to estimate emissions from one type of process based on data obtained from a different process. The primary benefit that these tests results provide for synfuels processes pertains to development of emission control strategies as described in the section on fugitive emission controls.

Because of the two types of tests that can be performed, there are two types of results that are generated in fugitive emission testing; leak screening and leak rate measurement. Leak screening consists of a method to identify the relative magnitude of leakage from fugitive emission sources. Leak rate measurement involves enclosure of a leaking source and measurement of the pollutant mass emission rate from the source. These two types of testing results can be combined to develop emission factors. In Table 3, emission factors are shown for fugitive emission sources in several industries. These emission factors have units of kilograms per day per source. Therefore, the total emissions from a particular type of source can be estimated by multiplying the number of sources by the emission factor.

In Table 3, the 95 percent confidence intervals for the emission factors are also shown. It is important to consider these confidence intervals since they indicate that the true emission factor is expected to be found within these confidence intervals 95 percent of the time. If confidence intervals (for different sources or processes) overlap, it is not possible to state that the true emission factors for the different sources or processes are significantly different.

In addition to their contribution to emissions of harmful substances, fugitive emissions also need to be included in De Minimus calculations. If the total controlled emission rate from a plant exceeds the De Minimus level for a particulate pollutant, PSD review is required. De Minimus levels for several pollutants are shown in Table 4 in metric tons (Mg) per year. As an example of how fugitive emissions might contribute to De Minimus levels, the total hydrocarbon and carbon monoxide emission rates estimated for the Kosovo coal gasification plant are shown in Table 5. Hydrocarbon emissions of 5.72 kg/day would be 2.1 metric tons/year, which is approximately 6 percent of the De Minimus level of 36 tons/year of volatile organic compounds.

FUGITIVE EMISSION CONTROLS

Fugitive emission controls can be categorized as either work practices or engineering controls. Work practices are specific work activities whose objective is to prevent emissions, to reduce the potential for emissions, to

TABLE 3. COMPARISON OF EMISSION FACTORS

Source Type Service	Emission Factor (95% confidence interval) for Various Types of Industrial Processes (kg/day-source)					
	Kosovo coal gasification plant*	Organic Chemicals Manufacturing**			Refineries***	Natural Gas Plants****
		Vinyl Acetate	Cumene	Ethylene		
Valves						
Hydrogen	-	-	-	-	.20(.076,.49)	-
Gas/Vapor	.0019(.0002,.016)	.05(.011,.33)	.12(.033,.54)	.26(.087,.76)	.64(.33,1.2)	.48(.2,1)
Light Liquid	.0026(.0008,.01)	.0033(.001,.022)	.061(.022,.22)	.22(.076,.65)	.26(.18,.39)	
Heavy Liquid		-	-	-	.0054(.0022,.016)	-
Aqueous	.0012(Neg*****,.12)	-	-	-	-	-
Pumps						
Light Liquid	.005(.009,.03)	.047(.001,1.1)	.57(.011,2.9)	.75(.065,8.7)	2.7(1.7,4.0)	1.5(.5,4)
Heavy Liquid		-	-	-	.50(.21,1.2)	-
Aqueous	.0012(Neg,.0021)	-	-	-	-	-
Compressors						
Hydrogen	-	-	-	-	1.2(.54,2.5)	-
Gas/Vapor	-	-	-	-	15(7.2,32)	4.9(.7,30)
Flanges	.00036(Neg,.02)	-	-	-	.0061(.0022,.027)	.026(.01,.05)
Open-ended lines	-	-	-	-	.054(.017,.17)	.53(.2,1)
Relief Valves	-	-	-	-	2.07(.76,5.3)	4.5(.1,100)
Drains	-	-	-	-	.76(.25,2.2)	-

* Total hydrocarbons from Reference 4

** Nonmethane hydrocarbons from Reference 5

*** Nonmethane hydrocarbons from Reference 6

**** Total hydrocarbons from Reference 7

*****Negligible = $<3 \times 10^{-5}$ kg/day-source

TABLE 4. DE MINIMIS LEVELS TRIGGERING PSD REVIEW

Pollutant	De Minimis Level* metric tons/yr
Carbon monoxide	91
Nitrogen oxides	36
Sulfur dioxide	36
Ozone	36 (as volatile organic compounds)
Lead	0.5
Asbestos	0.006
Beryllium	0.0004
Mercury	0.09
Fluorides	2.7
Sulfuric acid mist	6
Hydrogen sulfide (H_2S)	9
Total reduced sulfur (including H_2S)	9

* 40 CFR 51-52.

TABLE 5. TOTAL EMISSION RATES FROM KOSOVO FUGITIVE EMISSION SOURCES (from Ref. 4)

Source Type/Service (Emission Factor - kg/day-source)	Process Unit											
	Rectisol		Phenosolvan		Tar Separation		Gas Cooling		Gasification		Total	
	Number Sources	Emissions	Number Sources	Emissions	Number Sources	Emissions	Number Sources*	Emissions	Number Sources**	Emissions	Number Sources	Emissions***
Hydrocarbon Emissions												
Valves/gas (0.0019)	169	0.32	37	0.07	33	0.06	85	0.16	99	0.19	423	0.80
Valves/hydrocarbon liquid (0.0026)	544	1.41	112	0.29	176	0.46	68	0.18	0	0	900	2.34
Valves/aqueous (0.0012)	78	0.09	209	0.25	56	0.07	0	0	140	0.17	483	0.58
Flanges/gas (0.00024)	558	0.13	133	0.03	151	0.04	263	0.06	355	0.09	1460	0.35
Flanges/hydrocarbon liquid (0.00048)	1459	0.70	494	0.24	524	0.25	292	0.14	0	0	2769	1.33
Flanges/aqueous (< 3 x 10^{-5})	208	<0.006	916	<0.03	165	<0.005	0	0	273	<0.008	1562	<0.05
Pumps/hydrocarbon liquid (0.005)	33	0.17	8	0.04	6	0.03	0	0	0	0	47	0.24
Pumps/aqueous (0.0012)	2	<.003	7	0.01	8	0.04	0	0	6	0.01	23	0.03
TOTAL	-	2.83	-	0.96	-	.92	-	0.54	-	0.46	-	5.72
Carbon Monoxide Emissions												
Valves/gas (0.0012)	169	0.20	37	0.04	33	0.04	85	0.10	99	0.12	423	0.51

* Based on two of three cooling trains in operation.
** Based on two of six gasifiers in operation.
*** Does not include emissions from open-ended lines, sampling purges, or wastewater systems.

identify emitting sources and to mitigate emissions from these sources. Engineering controls include equipment design, equipment operation, and equipment specification procedures that either reduce emission potential of sources or capture and control emissions from the sources. The effectiveness of fugitive emission controls can be dependent on many variables, and in some cases effectiveness cannot be assessed before applying the controls.

WORK PRACTICES

Work practices that can prevent or reduce the potential for fugitive emissions are sometimes called "housekeeping" practices. The procedures are implemented in all types of industrial plants in order to reduce safety and fire hazards, and they can also be applied to reduce fugitive emissions. Specific procedures regarding process fluid spills and spill cleanup can be used to minimize fugitive emissions from these sources. Fugitive emissions from equipment draining, purging and venting operations can be minimized by specifying procedures that prevent or reduce the emissions. Atmospheric contact with these process fluids may occur at the point of discharge from process equipment or in the wastewater systems. Process fluids that are drained, purged or vented from process equipment can be collected for recycle, disposal, or pollutant destruction instead of allowing the process fluids to become atmospheric emissions. Work practices that identify emitting sources and apply emission reduction techniques are generally referred to as leak detection and repair programs. Fugitive emission tests have consistently shown that a large fraction of total emissions are contributed by a small fraction of the total number of sources. Therefore, periodic repair or replacement of all sources would be a very inefficient approach to fugitive emission control. Leak detection methods provide a way to identify which sources are contributing the bulk of emissions and therefore warrant emission reduction efforts. Leak detection and repair programs can be applied to these sources of process fluid leakage: valves, pumps, compressors, agitators, flanges, relief valves, and open-ended lines.

Leak detection methods include individual component surveys, area (walk-through) surveys, and fixed-point monitors. They are described in this order because the first method is also included as part of the other methods. In the individual component survey, every fugitive emission source (pump, valve, compressor , etc.) is checked for evidence of process fluid leakage at regular intervals (monthly, quarterly, yearly, etc.). The method used to detect leakage may involve sensory examination, soap bubbles spraying, or instrument techniques. Liquid leaks, especially pump seal failures, can be readily detected visually, but the liquid leak may be water or other unimportant compounds. High pressure leaks may be audible, and leakage of odorous compounds can sometimes be detected by smell. These sensory techniques are only useful for identifying very large leaks.

An individual component survey using soap bubbles involves spraying a soap solution on the area of potential leakage and observing any bubble formation caused by a gaseous leak. This technique is fairly rapid and inexpensive, but it is not applicable to moving shafts, hot sources (above

100°C), cold sources (below 0°C), or sources where leaks of compounds other than pollutants could give a false indication of leakage.

Instrument techniques require the use of some type of portable pollutant detector. The probe of the detector is traversed around the potential leak areas, and an increase in the detected pollutant concentration identifies the leak. Various types of detectors can be used for an instrument survey. An appropriate "action level" or leak definition is chosen, and all sources that exceed this level are repaired or replaced in order to reduce the leakage from the source. In the development of fugitive emission regulations, the most commonly selected "action level" has been 10,000 ppmv. In Table 6, the percent of sources that would be expected to exceed this action level and require repair is shown for several types of sources in different industries. The results of a leak detection survey show which types of sources have the most significant leaks.

A walk-through survey involves periodic leak detection by using a portable pollutant detector for measurement of ambient pollutant levels in the process unit. Areas that are found to have elevated pollutant concentrations are then subjected to individual component surveys in order to locate the leakage sources for repair. Fixed-point monitors have permanent pollutant detectors operating throughout the process unit. If elevated pollutant levels are detected, individual component checks are used to find the sources needing repair.

Once a source has been identified as a leak requiring repair, appropriate action is taken to reduce or eliminate the leakage. Repair methods vary, depending on the type of source, and source replacement is also a repair option. Most pumps have spares that can be operated while the pump is out of service for repair. Many compressors do not have spares, and if the seal repair required a shutdown of the process unit, temporary emissions due to the shutdown could exceed the emissions from the seal if it was not repaired until the next scheduled shutdown. Leaks from packed seals or pumps, compressors, agitators, and valves may be reduced by simple tightening of the packing. Mechanical seals require removal from the equipment for repair or replacement. Grease injection in some types of valves may reduce leakage. Leaks from open-ended lines can be reduced by closing the valve seat more completely.

Leak detection and repair for cooling towers would require the use of periodic or continuous monitoring of pollutant concentrations in the cooling water. Elevated concentrations would indicate leakage, but individual process equipment such as heat exchangers would be difficult to pinpoint as the source of the leak.

ENGINEERING CONTROLS

Engineering controls involve the use of equipment that can capture and control emissions, or that prevents emissions. Each type of source requires assessment of operating conditions and constraints in order to determine which types of engineering controls are applicable.

TABLE 6. COMPARISON OF PERCENT OF SOURCES LEAKING

Source Type Service	Percent of Sources Leaking* for Various Types of Industrial Processes				
	Kosovo Coal Gasification Plant**	Organic Chemical Manufacturing***	Refineries****	Natural Gas Plants*****	Coke By-product Plants******
Valves					
Hydrogen	4	-	20.8	-	-
Gas/Vapor		11.4	12.6	16.4	-
Light Liquid	1	6.5	11.4		3.23
Heavy Liquid		0.4	0.2	-	-
Pumps					
Light Liquid	2	8.8	24.0	29.7	20.5
Heavy Liquid		2.1	3.8	-	-
Compressors					
Hydrogen	-	-	44.6	-	-
Gas/Vapor	-	9.1	57.0	52.8	8.8*******
Flanges	0.5	2.1	0.54	3.1	0.0
Open-ended lines	4	3.9	7.7	11.9	-
Relief valves	-	3.2	8.6	17.5	-
Drains	-	3.8	4.7	17.0	-

* Leaking defined as a screening value $\geq$10,000 ppmv
** from Reference 4
*** from Reference 5
**** from Reference 6
***** from Reference 7
****** from References 8, 9, and 10
*******Exhausters

Engineering controls for pumps include sealless pumps, double mechanical seals, and closed vent systems. Sealless pumps such as diaphragm pumps or "canned" pumps do not have a shaft/case junction that is exposed to process fluid. Therefore the potential to emit is eliminated, although these pumps have operating limitations that prevent universal application. Double mechanical seals consist of two mechanical sealing elements with a barrier fluid in a chamber between the seals. This barrier fluid system can be operated to purge into the process fluid to prevent leaks or to dissolve any seal leakage in the barrier fluid. Leakage dissolved in barrier fluids can be emitted by degassing from the barrier fluid reservoir. Closed vent systems can be used to transport pump seal leakage to a control device such as a combustion source or vapor recovery system. Closed vents can be connected to the oil reservoir degassing vent or to an enclosure fitted to the pump case in order to contain seal leakage.

Engineering controls for compressors are similar to those for pumps. In addition to double mechanical seals, some types of compressor seals may also have oil reservoir degassing vents that can be connected to closed vent systems. Many reciprocating compressors have closed vent systems to transport seal leakage to a safe release point. These vents can also be connected to control devices. Engineering controls for agitators are similar to those for pumps and compressors.

Fugitive emissions from relief valves can be controlled with rupture discs, resilient seat relief valves, and closed vent systems. A rupture disc upstream of the relief valve will prevent leakage through the valve seat, but the disc must be replaced after each overpressure release. Resilient seat relief valves may have superior ability to re-seat after overpressure release, compared to rigid seat relief valves, but no test data are available to verify this advantage. Closed vent systems are frequently used to transport relief valve discharges to recovery or disposal systems. These closed vent systems would also convey any fugitive leakage to the control device.

Leaks from open-ended lines are the result of leakage through a valve seat to the atmosphere via the open-ended line. These leaks can be minimized by installing a cap, plug, blind flange or another valve to the open-ended line. These devices would be opened only when the lines were put into service for draining or purging.

Process fluids that are purged from sampling connections can be controlled by using closed loop sampling systems. The closed loop system is operated such that the process fluid purge is either returned to the process or is collected in a closed vessel for eventual recycle or disposal.

Engineering controls for valves provide an internal barrier to prevent contact of process fluid with the valve stem. Diaphragm valves and bellows sealed valves have a moveable internal seal to resist leakage. Operating constraints limit the applicability of these types of controls.

Engineering controls for wastewater systems are primarily aimed at isolating the contaminated wastewater from the atmosphere. Drains with liquid traps prevent atmospheric contact with the drain system vapor space. Covers for wastewater separators and transport systems also reduce atmospheric contact. A closed vent system connected to the wastewater system vapor space would provide the best control potential, but would be difficult to apply.

CONTROL EFFECTIVENESS

Control effectiveness for fugitive emission controls is dependent on many variables. Some of those variables cannot be estimated before actually applying the control method. It is possible to estimate the maximum achievable control effectiveness, although actual effectiveness will probably be lower. Table 7 shows the estimated control effectiveness for work practice and engineering controls.

Leak detection and repair programs are subject to many variables. The frequency of inspection, leak definition, interval between leak detection and repair, repair effectiveness, occurrence rate, and recurrence rate are all related to the overall effectiveness of leak detection and repair programs. The costs and benefits of changing these variables will determine the optimum control strategy for each process unit. Limited repair studies for valves in the organic chemicals industry indicate that a 70 percent emission reduction can be achieved by using "directed maintenance". Directed maintenance requires use of the pollutant detection instrument during repair in order to determine the success of repair immediately. This method has been shown to be much more effective compared with undirected maintenance, where the repair is completed and then the source is re-checked for evidence of leakage.

The effectiveness of double mechanical seals can approach 100 percent if the barrier fluid is at higher pressure than the process fluid. Closed vent systems are dependent on the control efficiency of the device to which emissions are transported.

Rupture discs provide 100 percent control, but must be replaced after overpressure release or deterioration of the disc. Closed vents are connected to control devices capable of handling overpressure relief discharges. Depending on the turn down capability of the control device, effectiveness can range from 60 to 90 percent.

Because the controls for open-ended lines, sampling connections, and valves essentially eliminate the source of emissions, control effectiveness approaches 100 percent. The achievable control effectiveness for wastewater systems is difficult to estimate because each system is different and all systems are complex with numerous potential emission points.

CONCLUSIONS AND RECOMMENDATIONS

Synfuels production facilities will have the same types of fugitive emission sources that are currently found in U.S. petroleum production and refining facilities, organic chemical plants, and coke by-product plants.

TABLE 7. MAXIMUM POTENTIAL EFFECTIVENESS OF FUGITIVE EMISSION CONTROLS

Source Type Control Method	Control Effectiveness (percent reduction)
Valves, pumps, compressors, agitators flanges, open-ended lines, relief valves	
Leak detection/directed maintenance	70*
Pumps, compressors, agitators	
Double mechanical seals	100
Sealless equipment	100
Closed vent systems	90
Relief valves	
Rupture discs	100
Resilient seat valves	-**
Closed vent systems	60-90
Open-ended lines	
Caps, plugs, blinds, valves	100
Sampling connections	
Closed loop sampling	100
Valves	
Diaphragm/bellows seal	100
Wastewater systems	
Trapped drains	-**
Covered systems	-**
Closed vent system	90-100

* Based on test data for valves in organic chemical industry, Reference 11.

**Effectiveness not estimated

The magnitude and severity of fugitive emissions from synfuels facilities will be dependent on various factors, some of them process- or site-specific. Fugitive emission testing in U.S. industries has provided a basis for developing test strategies and control techniques for synfuels facilities.

Because the sources of fugitive emissions are the same, emission control techniques identified for U.S. industies should also be applicable to synfuels facilities. The applicability and control effectiveness of these controls will also require a case-by-case analysis for each facility. The developing nature of this industry in the U.S. provides an excellent opportunity to develop and evaluate fugitive emission controls throughout the development of a process from design to commercialization.

The most significant recommendations that can be made regarding fugitive emissions in the U.S. synfuels industry are related to control strategy development. As each technology develops, the process of providing fugitive emission assessment and control can also develop.

In the design phase of a process, streams that will require fugitive emission control can be identified. Design changes to minimize the number of sources or to make the sources accessible for inspection and repair can be initiated. As the process moves into the pilot plant stage, fugitive emission testing can be applied to estimate the severity of the problem and to identify areas where special emission control efforts are needed. During pilot plant operation, different types of engineering controls can be evaluated, especially for sources in severe service due to temperature, abrasive fluids, hazardous compounds, etc. Pilot plant experience can be valuable for evaluating seal lifetimes, repairability of sources, and other factors that determine the most cost-effective fugitive emission control strategy.

Evaluation of fugitive emission controls throughout the development of synfuels process should result in a well-defined, effective control strategy that will be implemented upon start-up of full-scale facilities. Proper assessment of hazards and cost effectiveness of controls will prevent delays in obtaining approval of emission controls for operating permits.

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