

ELECTRICITY INDUSTRY ASSESSMENT OF LOW BTU

GAS FOR POWER GENERATION

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Introduction

Gasification of coal with air or oxygen to produce low Btu (80-180 Btu/SCF) or intermediate Btu (200-350 Btu/SCF) gas represents a technology that is being given close scrutiny by the electric power utility industry. Recent legislation has precluded the use of natural gas as fuel for baseload power generation. Fuel oil is following closely on the heels of natural gas and will not be available to the electric utility industry for baseload applications in the near future. Coal, therefore, represents the last remaining fossil option available to the utility industry for baseload power generation in the last decade of the twentieth century and on, into the twenty first century.

Coincident with the fuel crunch, the utility industry is being confronted by an equally serious and difficult to handle environmental crunch. Coal gasification offers the potential for controlling SO_x, NO_x and particulate emissions in a far more efficient and less costly manner than can be achieved in pulverized coal boilers.

There are a variety of different ways in which the utility industry can employ the concept of coal gasification for electric power generation. Some of the more obvious options are shown in Table 1. It is important to realize that most of the cost and performance figures presented in Table 1 represent estimates generated by the authors. Specific engineering studies addressing each option in detail are currently underway or are in the process of being initiated. It must be pointed out, however, that the Electric Power Research Institute (EPRI) has been funding engineering and economic studies of gasification and combined cycle systems with Fluor Engineers and Constructors, Inc., Stone and Webster Engineering Corporation, R. M. Parsons, the Bechtel Corporation and C. F. Braun for many years. Therefore, the estimates presented in Table 1 are based on a substantial body of cost and performance information (1) (2) (3) (4) (5) (6) (7).

A cursory glance at Table 1 indicates that option 7 (methanol production) is too expensive to be considered for baseload fuel production. Considering the other six alternatives presented in Table 1, EPRI has identified options 5 and 6 (integrated gasification-combined cycle plants and integrated gasification-gas turbine power systems) as the most attractive options for baseload power generation. Table 2 presents cost and performance estimates for a variety of gasification-combined cycle power plants(3). It can be seen from this table that, in general, integrated gasification based power systems have the potential for more efficient operation and lower cost of electricity than conventional coal fired power plants with flue gas desulfurization. Keeping in mind the fact that integrated gasification based power plants have the potential to meet more stringent environmental control

TABLE 1
UTILITY OPTIONS FOR COAL GASIFICATION

<u>Option</u>	<u>Time Frame for Initial Introduction</u>	<u>Capital Requirements (a)</u>	<u>Heat Rate Btu/kWh</u>
1. Retrofitting existing gas/oil fired boilers	1982-1990	0.70 - 1.0	13,000 - 17,000
2. Retrofitting existing combined cycle equipment	1982-1990	0.60 - 0.9	12,500 - 15,000
3. Centralized gas production including distribution to a number of utility plants	1982-2000	(\$3.50/MMBtu - \$5.00/MMBtu) (b)	
4. Integrated gasification-steam boiler power plants	1982-2000	0.90 - 1.2	9,600 - 11,000
5. Integrated gasification-combined cycle power plants	1990-2000	0.85 - 1.1	8,400 - 9,500
6. Integrated gasification-gas turbine power plants	1995-2010	0.75 - 1.1	7,500 - 8,500
7. Syngas generation for methanol production	1982-2000	(\$5.00/MMBtu - \$7.00/MMBtu) (b)	

(a) A pulverized coal boiler with stack gas scrubbers costs 1.0.

(b) These selling prices based on utility financing, instantaneous 1976 dollars with no escalation, and coal costing \$1.00/MMBtu.

TABLE 2
COST ESTIMATES FOR GASIFICATION-COMBINED CYCLE POWER PLANTS

Gasifier	BGC Slagger		Lurgi (a)		Foster (b) wheeler		Texaco (b)		PC Boilers with Stack Gas Scrubbers (b)
	O ₂	CC (c)	Air	CC (c)	Air	CC (c)	O ₂	gas turbine (f)	
Oxidant			Air		Air		O ₂		Air
Power System			CC (c)		CC (c)		CC (c)		steam turbine
Heat Rate, Btu/kWh	8,410		9,762		8,428		8,813		7,500 - 8,500
Make-up Water, gpm/1000MW	6,716		7,905		6,622		7,950		1,500 - 3,500
Total Capital Requirement, \$/kW (d)	711		906		705		816		650 - 900
Cost of Electricity, mills/kWh (e)	32.8		41.2		32.5		37.2		29 - 35

(a) Western coal

(b) Illinois #6 coal

(c) Combined cycles based on 2400°F gas turbine and 1450 p/900°F/1000°F steam turbine

(d) Mid-1976 dollars, no escalation, 1000MW, including construction loan interest, paid up royalties, initial catalyst and chemicals cost, preproduction costs, working capital, wet cooling towers, and emissions of < 1.2 lbs SO₂/MMBtu

(e) Coal costing \$1.00/MMBtu

(f) These estimates not included in Fluor report. Detailed performance and cost estimates for these systems are not yet available.

requirements as well as consuming substantially less water than conventional plants, it is evident why such systems represent a most attractive option for intermediate term baseload power generation.

It should be noted that gasification-combined cycle power systems have not yet been developed to the point where a utility company can order and install one with confidence. Such systems need to be demonstrated at sufficiently large scale (100MW - 200MW) such that the utility industry will have confidence that these plants can generate electricity reliably at the costs projected by the engineering studies.

Table 1 indicates that integrated baseload gasification-combined cycle power plants will only be available for utility use in the 1990's. A major question that must be addressed is: "Can coal gasification technology be utilized to alleviate utility needs for clean fuel prior to the 1990's?" The answer to this question has to be supplied in two parts i.e. a) an investigation of the development status of near term coal gasification technology and, b) identification of the technical possibilities and cost potential for rapid introduction of gasification systems for utility power generation.

Status of Near Term Gasifiers

Table 3 presents a summary of the development status of near term coal gasification options. It can be seen from this table that the suitability of the three commercially available gasifiers for combined cycle power generation is not good. Reasons for the lack of suitability range from low pressure operation to excessive by-product production - all of which result in an unacceptably high cost of electricity. It is the judgement of these authors that the gasifiers offering the greatest near term potential for combined cycle power generation at this time are the Texaco and Shell/Koppers partial oxidation units. This judgement is based on the extensive experience of the particular organizations in partial oxidation of oil, the simplicity of the gasifiers, their feedstock flexibility (ability to handle any coal as well as oil), absence of byproducts in the make gas, capability for high pressure operation, and the results of extensive engineering and economic studies. Information concerning the Shell/Koppers device is sparse. Texaco claims that based on successful operation of the 150 ton/day gasifier to be operated in Germany in 1978, they could scale-up to 1,000 tons coal/day capacity with confidence. Therefore, it appears that the Texaco gasification option could be available for utility use in the early 1980's.

Technical Possibilities for Near Term Introduction

It has already been mentioned that integrated gasification-combined cycle systems have not yet been demonstrated to the point where they would represent viable commercial options for the electric utility industry. Although all of the subsystems (i.e. gasifiers, gas clean-up modules, and combined cycles) have been operated at large scale independently, they have never been operated in an integrated mode for power production. Questions concerning the ability to control such integrated systems in a power plant environment can only be satisfactorily answered by building and operating an integrated test facility. One of the major control problems for these systems is posed by integrating the rapidly responding gas turbine and steam system with the more sluggish fuel production plant.

TABLE 3
DEVELOPMENT STATUS OF NEAR-TERM GASIFIERS

<u>Technology</u>	<u>Operational Mode</u>	<u>Suitability for Combined Cycle Operation</u>	<u>Current Status</u>	<u>Future</u>
Lurgi	Moving Bed	Intermediate	Commercial	---
Koppers Totzek	Entrained	Poor	Commercial	---
Winkler	Fluidized Bed	Poor	Commercial	---
Texaco	1 Stage Entrained	Good	15 ton/day running	150 ton/day 1978
Shell/Koppers	1 Stage Entrained	Good	5 ton/day running	160 ton/day 1978
BGC Slagger	Moving Bed	Intermediate - Good	360 ton/day running	1,000 ton/day 1983
Combustion Engineering	2 Stage Entrained	Intermediate	120 ton/day 1978	?

The influence of control problems on the operability of the system can be deemphasized by decoupling the fuel plant from the power equipment i.e. the gasification plant would operate independently of the power plant and would simply produce "over the fence" fuel gas to be consumed by the power system. The major penalty to be paid due to system decoupling is a significant decrease in power plant efficiency with a resultant increase in the cost of electricity (compare the heat rates of options 1 and 4 as well as options 2 and 5 from Table 1). The main advantage to be derived from decoupling the system is the fact that engineering for the first of such power plants could be started in 1978.

Non-integrated gasification based power systems of the type discussed above could most readily be achieved by retrofitting existing power plants which in the near future will have difficulty securing adequate fuel supplies i.e. gas and oil fired boilers as well as conventional combined cycle power plants. Such retrofitting can be accomplished in one of two different ways. Centralized gasification plants can be constructed to produce intermediate Btu fuel gas for limited distance pipeline distribution to one or more power plants. Alternatively, on-site retrofitting of individual power plants can be affected. The remainder of this paper will address the above two retrofit options and will attempt to highlight the advantages and disadvantages of each.

Centralized Gasification Plants

Large (10,000 tons/day coal - 30,000 tons/day coal) centralized gasification plants could be constructed to produce intermediate Btu gas for transmission to a number of power plants. Such gasification plants would have to produce 250 Btu/SCF to 300 Btu/SCF gas for two major reasons. First, the cost of pipeline distribution for low Btu gas is excessively high. Also, it has been shown by both Babcock and Wilcox (8) and Combustion Engineering (9) that retrofitting gas and oil fired boilers with fuel gas having a heating value much below 250 Btu/SCF will result in a rather serious derating of the existing boilers.

Some of the major advantages and disadvantages of large centralized gasification plants are shown in Table 4. Based on the high cost of fuel gas and the political and environmental problems associated with intermediate Btu gas transmission shown in Table 4, the option of large centralized gasification plants does not appear to offer sufficient economic incentive to be given major consideration by the electric utility industry at this time.

Gasification Plants For On-Site Retrofitting

There is an entire category of generic questions associated with on-site retrofitting of conventional steam electric power plants as well as combined cycle facilities with gasification systems that are site specific i.e. space availability, rail access, coal supply, environmental requirements (non degradation standards), etc. that need to be closely examined before any retrofit decision can be made. The purpose of this paper is to point out some of the technical opportunities and constraints associated with on-site retrofitting assuming that the answers to the above mentioned generic questions are all positive.

TABLE 4
ADVANTAGES AND DISADVANTAGES OF LARGE CENTRALIZED GASIFICATION PLANTS

ADVANTAGES

1. Fuel gas production decoupled from power plant operation.
2. Gasification plant can operate in steady state mode most of the time.
3. Transmission pipelines offer a minor form of fuel storage.
4. Ownership of the fuel production plant does not have to reside in the electric utility industry.
5. The gasification plant (and its emissions) can be remote from large population centers.

DISADVANTAGES

1. The cost of fuel will be high, i.e., \$3.50/MMBTU to \$5.00/MMBTU in 1976 dollars (see Table 1) and utility financing. If private financing is used, the gas cost will increase by approximately \$1.00/MMBTU.
2. Environmental and Right of Way problems associated with the installation of large underground pipelines.
3. Safety problems associated with the transmission of gases containing high concentrations of carbon monoxide.
4. Ownership If the electric utility industry does not own the gasification plant, the owner will require long term take-or-pay fuel contracts to insure the integrity of the large capital investment required.

A. Retrofitting Existing Gas and Oil Fired Boilers

In order to fire coal derived fuel gas in an existing boiler designed for natural gas or oil firing, Combustion Engineering (9) and Babcock and Wilcox (8) both claim that the heating value of the gas should be above 250 Btu/SCF in order not to derate the steaming capacity of the boiler. Summary results of the Combustion Engineering (9) study are shown in Table 5. The heating value requirement of the gas employed for this situation dictates that the gasifier be oxygen blown. As fuel gas for this application is not needed at high pressure, an atmospheric pressure gasifier could be utilized. Therefore, for boiler retrofitting, either an oxygen blown Texaco gasifier or an oxygen blown Combustion Engineering gasifier could be employed. EPRI has retained the Bechtel Power Corporation to study the cost of electricity from this type of retrofit.

It is the opinion of these authors that the electricity generated by this technique will be expensive due primarily to the excessively high heat rates anticipated for such systems (see Table 1, option 1). Such heat rates are unavoidable for decoupled systems as the efficiency of the conversion of coal to intermediate Btu gas ranges from 65% to 75%. These gasification efficiencies are somewhat lower than the much quoted cold gas efficiencies as they include the firing of up to 10% of the clean fuel gas produced to supplement superheated steam requirements for the air separation plant or to superheat steam generated in the gas coolers following the gasifier. Dividing the existing steam plant heat rates (ranging from 9,500 Btu/kWh to 11,000 Btu/kWh) by the fuel production efficiencies (65% to 75%) results in overall system heat rates in the range 13,000 Btu/kWh to 17,000 Btu/kWh. Not only are these high heat rates costly from a fuel consumption point of view, they will also require excessively high capital expenditures as the gasification plant needed to produce 1000 MW at a heat rate of 17,000 Btu/kWh will be twice the size of the same capacity system having a heat rate of 8,500 Btu/kWh (i.e. an integrated gasification-combined cycle power plant).

Notwithstanding the promise of substantial tax incentives by the current administration for this type of retrofit, the fuel and capital utilization efficiencies are sufficiently poor to render this option of low long term interest to the bulk of the electric utility industry.

B. Retrofitting Existing Oil Fired Combined Cycles

Most of the statements made concerning the retrofit of existing steam electric power plants apply to the decoupled retrofitting of oil fired combined cycle equipment with three differences:

- (i) For this application, a pressurized gasifier such as the Texaco unit would be preferred as fuel gas must be delivered to the gas turbine combustor inlet system at pressures ranging from 230 psia to 280 psia.
- (ii) Air or oxygen blowing of the gasifier would be acceptable as gas turbine combustors can be modified to fire either low Btu gas or intermediate Btu gas. This statement must be treated with extreme caution. If, for example, the gasifier is air blown and the air is not extracted from the gas turbine air compressor, the turbine would suffer a major derating due to the mismatch between compressor and expansion turbine sections resulting from the high mass flow rate of low Btu fuel gas. Modification of an existing gas turbine for air extraction is not simple and could result in a high capital cost.

TABLE 5

SUMMARY RESULTS OF COMBUSTION ENGINEERING BOILER RETROFIT STUDY (9)

With existing steam generating unit and auxiliary components, the approximate maximum rating that can be achieved firing low BTU gas with only minor modifications to the windbox and firing system equipment is:

Fuel Gas HHV	Original Design Fuel	
	Oil	Gas
396 BTU/SCF	100%	100%
292 BTU/SCF	100%	100%
179 BTU/SCF	70%	70%
128 BTU/SCF	65%	60%
105 BTU/SCF	50%	50%

(iii) The overall system heat rate would be approximately 10% better than that for the steam electric power plant due to the higher efficiency of the combined cycle system (see Table 1, Option 2).

Although the decoupled retrofit of existing combined cycle systems appears to be somewhat more attractive from a cost and heat rate point of view than the retrofit of existing steam electric power plants, the heat rates and capital requirement estimates shown in Table 1 are still too high to make this a high priority option for the electric utility industry.

To this point, the entire retrofiting discussion has been based on the premise that the power production plant (i.e. the steam boiler or the combined cycle system) has already been constructed and operated at a specific site. Based on the preceding discussions, none of the retrofit scenarios involving total decoupling of the gasification plant and the power system appears to offer an attractive baseload option to the electric utility industry.

There are, however, at least two additional possibilities for retrofiting combined cycle power plants with gasification systems that offer the potential for lower heat rates and lower costs than the decoupled retrofit discussed previously. These new situations will be termed integrated retrofits.

Potential for Integrated Retrofits

Two types of integrated retrofit possibilities will be discussed i.e.

- 1) Constructing the gasification plant first and firing the clean fuel gas in an existing boiler. When the gasification plant has been demonstrated to operate reliably and efficiently, it can be retrofit and integrated with a combined cycle power plant.
- 2) Constructing an oil fired combined cycle power plant initially to be retrofit and integrated with a gasification plant at some later date.

A) Integrated Retrofit - Gasification Plant Initially

The major attraction of this option is that it provides for the earliest possible introduction of coal gasification as a source of clean fuel for the utility industry without the disadvantage of having to suffer major thermal inefficiencies for the entire life of the gasification plant.

This could be achieved technically at an early time by constructing a self sufficient oxygen blown Texaco gasification plant at a utility site having the necessary space requirements as well as an oil or gas fired steam electric power plant. For the initial design, steam to power the air separation plant as well as the oxygen compressors would be generated in the gasifier gas coolers and could then be superheated in a furnace fired with clean fuel gas. The clean intermediate Btu fuel gas produced could be fired in the existing boiler for power production (at an overall system heat rate of 13,000 Btu/kWh to 17,000 Btu/kWh). The purpose of this phase of the project would be to demonstrate the operability of the gasification - gas clean-up system under utility operating conditions.

The second phase of the project would involve retrofitting and integrating the gasification plant with a combined cycle system. Major integration features would include:

- superheating steam produced in the gasification gas coolers in the new heat recovery steam generator (HRSG) for introduction into the new steam turbine.

- extraction of steam from the new steam turbine or HRSG to power the air separation plant, oxygen compressors and gas clean-up system.
- possibly reheating clean fuel gas in the new HRSG
- supplying hot boiler feed water from the new HRSG to the gasifier gas coolers.

The major purpose of this phase of the project would be to demonstrate the operability of an integrated gasification-combined cycle power plant (the major incentive for coal gasification) under utility operating conditions.

Some of the advantages and disadvantages associated with this option are shown in Table 6. In summary, this form of retrofit provides for the earliest low risk introduction of coal gasification for environmentally acceptable electric power generation. The penalties to be paid are high cost, limited capacity and a relatively short plant life.

B. Integrated Retrofit - Combined Cycle Plant First

The major attraction of this option is that it provides for extremely rapid introduction of new oil fired baseload capacity without any initial risk being taken concerning the integrability and operability of gasification-combined cycle power plants.

Initially, conventional oil fired combined cycle equipment would be installed. Salable electricity could be produced approximately three years after initiation of project engineering. At some later date, after demonstration of the viability of integrated gasification-combined cycle power plants, the existing combined cycle facility could be retrofit and integrated with a coal gasification plant. One of the major advantages of this scenario is based on the fact that knowing that the integrated retrofit is to take place some time in the future, the initially installed combined cycle plant could be designed to minimize the cost of the future retrofit. Some key technical questions concerning this type of retrofit are:

- can the gas turbine combustor cans be designed for dual fuel capability i.e. for firing oil initially and switching to low Btu or intermediate Btu gas at some later time? Such combustors are currently being designed by General Electric.
- If the gasification plant is to be air blown, can the gas turbine wrapper be designed to accommodate air extraction at some later date? If not, what would be the cost of changing the wrapper at the time of the retrofit?
- If the gasification plant is to be oxygen blown, will the compressor/turbine mismatch after retrofitting result in a significant derating of the gas turbine?
- A conventional combined cycle HRSG is balanced with respect to steam generation. For the integrated retrofit with a Texaco gasification plant, much interchange of boiler feed water and steam must take place between the gasification plant and the HRSG. Can the HRSG be designed initially to accommodate the retrofit? If not, what type of modifications will have to be made to the existing HRSG? Will it be cheaper to modify the existing HRSG than to scrap it and construct a new HRSG?

TABLE 6

ADVANTAGES AND DISADVANTAGES OF INTEGRATED RETROFIT - GASIFICATION PLANT FIRST

<u>Advantages</u>	<u>Disadvantages</u>
<p>1. Allows for the earliest possible introduction and demonstration of coal gasification technology for electric power production.</p> <p>2. The integrated retrofit provides an opportunity to dramatically improve the heat rate of the initially installed plant at an early date.</p> <p>3. Provides for the lowest risk demonstration of an integrated gasification-combined cycle power plant as the gasification plant will have been debugged prior to operation in an integrated mode.</p> <p>4. Project risk can be further minimized by designing the Texaco gasification plant to fire coal, coke and high sulfur heavy oil providing extreme fuel flexibility (risk is lowered as the Texaco gasifier has been commercially proven for oil firing).</p>	<p>1. Limited site availability as a site is required having an existing gas or oil fired boiler with sufficient space for the new project.</p> <p>2. Limited ultimate capacity of 100MW-150MW dictated by prudent engineering scale-up of gasification plant.</p> <p>3. Anticipated project cost will be higher than the cost of building an integrated system initially due to the two phase nature of the project.</p> <p>4. The resulting integrated plant will not be a commercial facility having a life of 20 years to 30 years due to the experimental nature of the project.</p>

- What is the incremental cost of initially sizing power plant auxiliaries (i.e. deaerator, water treatment, cooling towers, etc.) such that at the time of the retrofit only minor modifications would be required?

Answers to these and other technical questions should be developed as soon as possible if this form of retrofitting is to be given serious consideration by the electric utility industry.

Some of the advantages and disadvantages of this type of retrofit are shown in Table 7. In summary, this option provides the opportunity for rapid installation of new oil fired baseload capacity while awaiting the demonstration of the gasification-combined cycle power plant concept. The penalties to be paid are higher than normal costs associated with the original combined cycle equipment (which might be more than offset by the fact that the plant is being constructed at an early date, thereby eliminating inflation and escalation costs that would have been incurred if the entire plant had been constructed at some later date) as well as the possibility of owning a plant for which a guaranteed fuel supply cannot be assured if gasification-combined cycle power plants do not emerge as an economic option for electric power generation.

In conclusion, it can be stated that the information presented in Tables 6 and 7 indicates that the two forms of integrated retrofitting discussed in this paper have the potential for providing attractive options for the electric utility industry to replace oil and gas firing with coal gasification in a low risk and timely manner. A number of unanswered technical and economic questions have to be resolved before these options can be given serious consideration. During 1978, EPRI, in conjunction with a number of member utilities, will attempt to find answers to most of the major unresolved issues.

TABLE 7

ADVANTAGES AND DISADVANTAGES OF INTEGRATED RETROFIT - COMBINED CYCLE PLANT FIRST

<u>Advantages</u>	<u>Disadvantages</u>
1. Offers the opportunity to install new oil fired baseload capacity at an early date and an acceptable heat rate.	1. Higher than normal initial cost of combined cycle equipment due to the added flexibility required for the retrofit at a later time.
2. Provides maximum security for the initial investment as oil fired combined cycle plants can be considered to be minimum risk projects.	2. Possibility of having to make major modifications to or scrap the existing HRSG at the time of the retrofit.
3. Offers a low risk opportunity for the introduction of commercial scale coal gasification to the utility industry as the retrofit will only be attempted after large scale demonstration of the integrated concept has been achieved.	3. Space required for the ultimate retrofit of the gasification plant must be available at the beginning of the project i.e. eight to ten years before the retrofit is actually accomplished.
4. Provides the opportunity for rapid capacity expansion (500MW-1,000MW) as well as providing the potential for extending the time period in which oil is used for baseload generation.	4. If gasification-combined cycle power plants do not emerge as an economic option for electricity production the host utility company is stuck with a large investment in equipment for which a stable fuel supply cannot be guaranteed.
5. Project risk can be further minimized by designing the Texaco gasification plant to fire coal, coke and high sulfur heavy oil providing extreme fuel flexibility (risk is lowered, as the Texaco gasifier has been commercially proven for oil firing).	
6. The oil fired combined cycle plant can be operated over most of the construction period for the gasification plant. The down time required to accomplish the retrofit can be minimized.	

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Evaluation of Coal-Fired Fluid Bed Combined Cycle Power Plant

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ABSTRACT

Recent studies and research indicate that fluidized-bed combustion systems, operating at atmospheric or elevated pressure in a combined cycle power plant, offer the potential for producing electrical energy from coal within present environmental restraints for clean flue gas emissions and at a cost less than for conventional steam power plants utilizing low-sulfur coal or flue gas cleanup equipment. The team of Burns and Roe Industrial Services Corporation, United Technologies Corporation, and Babcock & Wilcox Company is under contract to the Department of Energy to prepare a conceptual design for such a plant. The major objectives of this program are to identify the technology required to develop a coal-fired pressurized fluid bed combustor to drive an industrial gas turbine and to define the technical and economic characteristics of a nominal 600 MW base- or intermediate-load combined cycle power plant.

Several cycle configurations with variations of cycle parameters were investigated during the course of this study. These include the consideration of different pressure ratios, the use of an unfired and fired steam bottoming cycle, and reheating the gas stream before the power turbine. Efficiency estimates for these variations range from about 38 percent for the unfired waste heat system to over 43 percent for the reheat system. As a result of various trade-off studies, a commercial plant cycle arrangement has been selected which incorporates a coal-fired pressurized fluid bed combustor, operating at 10 atm and 1650 F, and supplementary firing of the gas turbine exhaust in a coal-fired atmospheric pressure fluid bed boiler which produces 2400 psig/1000 F/1000 F steam. Preliminary estimates for coal pile to bus bar efficiency for the selected system are around 41 percent (gross, HHV).

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INTRODUCTION

Over the years, coal has become a major source of energy for power generation by electric utilities. However, it has become apparent that the use of coal requires control of the products of combustion to be compatible with the environment. This fact, coupled with the increased emphasis on coal usage has created an incentive to develop alternate methods of extracting energy from coal in an environmentally and economically acceptable way. In addition, it is highly desirable that these alternate methods result in more efficient coal utilization. Recent studies (1) indicate that the use of gas turbines in conjunction with fluidized bed combustion systems in a combined cycle power plant offer potential for satisfying these needs.

The feasibility of burning coal directly in an open cycle gas turbine was investigated by Bituminous Coal Research Inc., as early as 1944 when a coal-fired competitor to the diesel engine for railroad applications was being sought. In the intervening years, a number of organizations have attempted to design and test direct coal-fired gas turbines. However, problems with corrosion, erosion, and deposition on turbine blading due to the amount and nature of the ash passed through the high-temperature combustion zone have prevented the development of a commercially viable product. The low temperatures associated with fluidized bed combustion should alleviate the problems. Under Department of Energy (DOE) sponsorship (Contract EX-76-C-01-2371) the Burns and Roe Industrial Services Corporation, United Technologies Corporation, and the Babcock & Wilcox Company have formed a team to investigate the feasibility of a combined cycle plant utilizing a gas turbine with a pressurized fluid bed combustor. The purpose of this paper is to present important preliminary findings from the first year of effort on the DOE program. Because of the exploratory nature of this effort, some desired technical information is not yet available; indeed, more questions might be raised than are answered by this discussion. Nevertheless, it is deemed appropriate to present the preliminary findings to stimulate early discussion of this promising concept.

AIR-COOLED PRESSURIZED FLUID BED

Fluid bed combustion as currently discussed involves the combustion of coal in a fluid bed containing a crushed sulfur acceptor such as limestone or dolomite. Pressurized fluid bed (PFB) combustion is similar to atmospheric fluid bed (AFB) combustion except that the process takes place under a pressure of several atmospheres such as would exist at the exhaust of the compressor of a gas turbine unit. PFB combustion, therefore, offers the potential of serving as the gas turbine combustor (Figure 1). This use of a PFB as a gas turbine combustor has been studied by several investigators (2 through 7). Indeed, a 1-MW gas turbine has operated with a PFB combustor burning coal (8).

The temperature of the combustion process would be controlled by heat extraction from the bed and/or by controlling the fuel-air ratio in the bed. It would be necessary to maintain the PFB temperature at about 1650 F to minimize the release of

volatile alkaline metal compounds which would otherwise cause severe corrosion in the gas turbine and to assure an operating margin below the coal ash softening temperature to prevent agglomeration within the bed. The low combustion temperature also would result in NO_x emissions that are lower than the Federal EPA limits for coal fuel.

Higher PFB operating temperature would be beneficial to cycle performance and carbon utilization. It appears (9 through 13) that fluid beds could be satisfactorily operated up to 1750 F without incurring problems with sulfur retention or ash sintering, but deposits of elutriated material on the walls of the primary cyclone and in the turbine could be excessive. Considering the experience reported in the literature (9), a bed operating temperature of 1650 F was selected for the cycle analysis and PFB combustor design.

As the mechanical design of the PFB combustor developed it was determined that temperatures greater than 1650 F would not be practical. The heat exchange surface within the PFB must be designed for the bed temperature plus a margin for operating variations. Consequently, for the 1650 F bed temperature a 1700 F design temperature was used for the bed internals. At this temperature level the available materials exhibit little strength. The lower allowable stress levels that would result from using higher bed temperature would make such a design impractical, if not impossible. Also, while corrosion of the in-bed surface has not been quantified, it would be expected to be more severe at higher operating temperatures.

With the PFB process it should be possible to capture sufficient sulfur products to permit use of high-sulfur coals and still meet the current EPA limit of 1.2 lb SO₂/10⁶ Btu input. For a typical 3.4 percent sulfur, 12,000 Btu/lb HHV coal the required sulfur removal efficiency is about 80 percent. Dolomite appears to be an effective sulfur acceptor, and available data (9, 10) indicate that a calcium/sulfur ratio near 1.0 should be adequate to achieve the desired 80 percent sulfur retention at the selected bed operating conditions.

A low fluidizing (superficial) gas velocity is desirable to reduce elutriation from the bed, thereby reducing both the carbon loss and the required particulate cleanup duty. It should be noted that the size of both the coal and dolomite feed must be properly related to the fluidizing velocity, with increased velocity implying increased sizes. Low velocity also implies a larger bed area resulting in a shallower bed and, hence, lower bed pressure loss. A fluidizing velocity of 2.5 - 3.0 fps was selected for the PFB design reflecting previous work (9 through 11).

Even with low fluidizing velocity, a highly efficient particulate removal system would be required to prevent excessive turbine blade erosion. Since the cost of the particulate removal system is strongly influenced by the volume of gas passing through it, one method of reducing the system cost would be to limit the combustion air flow (and hence the dirty gas flow) to only as much as required for coal combustion within the PFB. This could be accomplished by splitting the compressor discharge flow with approximately 25 percent of the air being routed to the PFB combustion zone and the remainder of the air being routed through the bed cooling system consisting of tubes immersed within the fluid bed. The heat released during the combustion process would be transferred to the cooling air

less than one-quarter of the oxygen available in the air, the turbine exhaust gas could support considerable firing of additional coal. For this study, an AFB steam generator was considered as the means for capturing the SO_2 released during the final combustion process. The AFB could be steam cooled, as noted in Figure 4, or air cooled either by varying excess air to the bed or by using a split-flow arrangement similar to that described for the PFB in Figure 1. With either air-cooled approach, heat would be recovered from the air and combustion gases in a waste heat steam generator.

The performances of these various combined cycle configurations and of the simple cycle gas turbine are compared in Figure 5. Selected component efficiency, pressure loss, and temperature assumptions used in the calculations are summarized in Table I. As expected, the waste heat recovery system displays the lowest efficiency (about 38 percent, HHV) but, since it requires combustion at only one point in the cycle, it is a less complex configuration than the other cycles and has been utilized as a reference point in the economic analysis. The reheat system offers the highest potential efficiency (43 percent, HHV) but increases the complexity of the gas turbine design and requires a reheat fluid bed combustor with an associated particulate removal system. The PFB gas turbine topping of the AFB steam cycle has an attractive efficiency (approaching 41 percent, HHV) and shows promise for minimum equipment cost because of its relatively high specific work.

ECONOMIC ANALYSIS

The selection of the commercial plant configuration cannot be made on the basis of performance alone. The most important selection criterion is overall cost of electricity; therefore, an order of magnitude analysis was made to estimate the relative capital and operating costs of the alternative configurations. The operating cost differences due to fuel consumption were expressed in terms of equivalent capitalized costs where a one point difference in efficiency would give an equivalent fuel savings of \$10/kW.

The results of this economic screening analysis are given in Table II. All costs are given as incremental costs relative to the unfired waste heat recovery system which was taken as the base. The exhaust-fired, steam-cooled AFB with a gas turbine pressure ratio of 10 and the gas turbine system with reheat before the power turbine have the lowest evaluated net relative costs. The cost differential between these two systems is not statistically significant. The power turbine reheat cycle requires a more complex gas turbine design and additional hot particulate removal equipment. In addition, little data is available for design of a PFB combustor at the 2.5 atm pressure existing at the reheat point. Therefore, it was felt that the PFB cycle with an exhaust-fired steam-cooled AFB would offer less technical risk.

Capital costs were not estimated for all major pieces of equipment of systems required in the plant. Table III contains a list of those items which were considered. Obviously, some major systems (such as the coal and sorbent feed systems to the AFB and the low-pressure reheat PFB combustors) were omitted which would tend to decrease the advantage of the reheat and exhaust-fired cycles. However, it was

felt that the differences in the costs of these systems would not be large enough to offset the differences shown on Table II. Therefore, there is a strong probability that the trends shown in this study could be confirmed by more detailed design and cost estimates of the alternatives.

It should be recognized that the cost estimates did not consider some of the material, equipment, and other balance of plant costs normally associated with the items indicated on Table III. In addition, little more than conceptual outline drawings were available for many items that were considered. The basic intent of the effort was to provide a systematic approach for summarizing the relative pros and cons of each cycle on the basis of the preliminary design definition that was available. While each pro and con was, in effect, weighted on a cost basis, it would be misleading to consider the numbers shown as anything more than rough order of magnitude.

COMMERCIAL PLANT CONFIGURATION

On the basis of the preceding screening analysis, the PFB/AFB combined cycle power plant was selected for the commercial plant conceptual design study. During the course of the design study, further optimization of the selected configuration led to incorporation of three stages of regenerative feedwater heating and an adjustment in the relative power split between the gas and steam turbines. The resulting system, illustrated in Figure 6, utilizes two 63.5 MW gas turbines with two PFB combustors per gas turbine. The gas turbines would exhaust into a single exhaust-fired AFB steam generator and carbon burnup bed (CBB) which would generate steam at 2400 psig 1000 F/1000 F to drive a single 461.4 MW steam turbine. The resulting gross plant output would be 588.4 MW. Selected performance and cost data are summarized in the last column of Table II.

The gas turbine assumed for this study is a base load design which represents a modification of UTC's FT50 gas turbine or an engine of similar performance and physical characteristics. It would operate at 10:1 pressure ratio with 1600 F inlet temperature and have all necessary ducting to allow discharge of compressor air to the PFB combustor and return of hot gases to the turbine.

The PFB combustors, depicted in Figure 7, would heat the compressor discharge air from approximately 600 F to 1600 F. The compressor discharge air would enter the bottom of the refractory lined pressure vessel. The combustion air would flow through bubble caps in the distributor plate and into the fluidized bed. The cooling air would flow through supply pipes at the distributor plate to the inlet headers of the cooling circuits, through the tubes, and finally would be collected at the hot air outlet manifold. The flow split between cooling air and combustion air would be controlled by biasing valves in the hot air outlet piping and the hot gas outlet piping. The heat transfer from the bed to the cooling air would require a large surface area and a large bed volume. The desire to maintain a low bed superficial velocity (of the order of 3 ft/sec) is compatible with this large volume and would result in an expanded bed height of approximately 22 ft to submerge the cooling system within the bed.

Incoloy 800 alloy was selected for all material exposed to the fluid bed. This material has had greater usage than the other available high temperature alloys, and its physical properties (forming, welding, etc.) are better established. Also, currently available corrosion, creep, fatigue, and other data indicate that this alloy should give suitable life for the cooling system. However, ultimate material selection must eventually be based on the outcome of other more rigorous investigations of material characteristics within a PFB environment.

Operation at the elevated temperature of the PFB presents significant challenges in designing to accommodate the expected thermal expansion. The air in the bed cooling system would undergo nearly 1000 F temperature change from the inlet to the outlet in a total tube length of less than 26 ft. In addition, the cooling system from the distributor plate to the outlet header must be supported by the pressure vessel which operates at a temperature of 250 F. The design philosophy has been to support the outlet manifold and inlet and outlet headers of the cooling system from the same elevation on the vessel wall and to use U-shaped cooling tubes between the inlet and outlet headers. These U-shaped tubes would be designed with sufficient flexibility to accommodate the differential temperature along the length of the tube.

As previously noted, a particulate removal system would be required to limit the solid loading entering the turbine. Because of lack of actual operating experience with PFB exhaust gases in gas turbines, further testing is required to determine the acceptable level of particulate concentration in the gas entering the turbine. On the basis of limited data (14), an estimate of allowable gas turbine particulate loading was made showing that particles greater than 10 microns in size would give unsatisfactory turbine life, particles less than 2 microns in size would have negligible effect, and that some limited amount of particulate in the 2-10 micron size could be tolerated within the gas turbine. These estimates are compared in the top two lines of Table IV to the estimated particulate loading in the gas exiting from the PFB combustor.

Since the design requirements and characteristics of particulate removal systems are not fully known at this time, two different technologies were investigated in developing the overall plant design. The two concepts are a high-efficiency rotary flow cyclone and a granular bed filter, both of which are in the developmental stage at the temperature, pressure, and size required for the PFB combustion process. From a theoretical standpoint, both types of particulate collectors should meet the requirements of a commercial plant. The estimated effectiveness of the particle collectors is indicated in Table IV where the collector effluent is seen to satisfy the gas turbine requirement. Final dilution of the collector effluent with cooling air which bypassed the PFB combustion zone should reduce the particle concentration well below that required for the gas turbine. Only testing under actual operating conditions will ensure the suitability of these collectors.

The exhaust gases from the two gas turbines would be routed to the AFB steam generator system consisting of four AFB main beds in one structure (Figure 8) and a separate CBB. The main beds would combust coal using the exhaust of the gas turbines as combustion air. Unburned char elutriated from the AFB main beds would be captured and combusted in the CBB. The CBB would be in a separate enclosure, but the steam cooling system would be in parallel with that for the main beds. Most of

the superheater surface would be in three of the four beds, with the fourth containing only evaporator surface. The four main beds would each exhaust hot gas upward into a common convection section of the AFB steam generator. All of the reheater tubes and a portion of the primary superheater would be in the convection section. Gas from the convection section would flow into the economizer section. The CBB would consist of three beds, each with two compartments for load turn down control. All boiler surface would be above the beds in the convection zone.

The flue gas from the AFB boiler, after passing through high efficiency multi-clones, go through a high temperature electrostatic precipitator. The electrostatic precipitator would be designed for a maximum temperature of 750 F. The total volume of flue gas to be handled by the precipitator is 3.2×10^6 ACFM. The precipitator would have four electric fields in series. The total particulates emission would be less than 0.1 lb per million Btu of heat input. The gas stream from the precipitator would pass through the low level economizer to the induced draft fans and stack.

The hypothetical Middletown, USA site was selected for location of the PFB combined cycle power plant. An area site plan for the prospective power plant is shown in Figure 9. The plant island is centrally located with the cooling tower and switchyard to the east, coal and sorbent storage areas to the south, and wastewater treatment plant to the west.

CONCLUDING REMARKS

The air-cooled PFB offers the potential of using coal-fired gas turbines to top a more conventional coal-fired steam plant. The resulting combined cycle power plant has the capability of more efficient conversion of coal to electricity with the potential of yielding an overall lower cost of electricity than can be obtained with current technology. The PFB system requires development of high efficiency hot particulate removal systems and demonstration of material suitability. However, the technological challenges facing this type of system are less demanding than those for other advanced coal-fired conversion systems presently under study because of the lower temperatures and reduced degree of coal conversion and processing required. In closing, the prospective performance, economic, and environmental advantages of combined cycle power plants using PFB combustors suggest that development of this promising concept be energetically pursued.

ACKNOWLEDGMENT

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TABLE I
SYSTEM ASSUMPTIONS FOR PERFORMANCE ANALYSIS

Combustion Efficiency, %		
PFB, main and reheat		99.0
AFB		98.5
Pressure Loss, % of local gas pressure		
	<u>Bed</u>	<u>Cooling Tubes</u>
PFB, main and reheat	10.0	10.0 (air)
AFB	9.2	- (steam)
Temperature, °F		
	<u>Bed</u>	<u>Cooling Tubes</u>
PFB, main	1650	1575 (air)
PFB, reheat	1550	1475 (air)
AFB	1550	- (steam)
Component Efficiency, %		
Electric generator (steam turbine)		98.4
Electric generator (gas turbine)		98.7
Electric motors		95.0
Boiler feed pump		82.0
Boiler feed pump drive turbine		75.0
Condensate pump		82.0
ID fan		70.0

TABLE II

PFB COMBINED CYCLE POWER PLANT COST SUMMARY

Cycle Type	Screening Analysis										Selected Cycle					
	Waste Heat	Exhaust-Fired Air-Cooled AFB	Exhaust-Fired Steam-Cooled AFB	Exhaust-Fired Steam-Cooled AFB	Power Turbine Reheat	Exhaust-Fired Steam-Cooled AFB	Power Turbine Reheat	Exhaust-Fired Steam-Cooled AFB	Power Turbine Reheat	Exhaust-Fired Steam-Cooled AFB						
Gas Turbine Pressure Ratio	10	16	10	16	10	16	10	16	10	16	10	16	10	16	10	16
Number of Feedwater Heaters	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Output per Gas Turbine, MW																
Gas Turbine	66.7	62.0	60.0	55.0	63.5	58.4	63.5	58.4	77.0	63.5	77.0	63.5	63.5	77.0	63.5	77.0
Steam Turbine	32.0	19.0	86.0	87.0	134.0	118.0	134.0	118.0	88.0	118.0	88.0	118.0	230.7	88.0	230.7	88.0
Total	98.7	81.0	146.0	142.0	197.5	176.4	197.5	176.4	157.0	176.4	157.0	176.4	294.2	157.0	294.2	157.0
Specific Work, kW-sec/lb-air	121	100	179	174	241	216	241	216	192	216	192	216	350	192	350	192
Gross Efficiency, % (HHV)	38.4	37.2	41.0	40.3	40.9	40.4	40.9	40.4	43.1	40.4	43.1	40.4	41.1	43.1	40.4	43.1
Relative Equipment Cost, \$/kW																
Combustion System	Base	+33	-8	-26	-16	-12	-16	-12	-42	-12	-42	-12	-34	-42	-12	-42
Prime Movers & Electrical	Base	+55	-38	-17	-49	-32	-49	-32	-24	-32	-24	-32	-61	-24	-61	-24
Miscellaneous	Base	-5	+76	+79	-10	-2	-10	-2	+20	-2	+20	-2	-15	+20	-15	+20
Subtotal	Base	+83	+30	+36	-75	-46	-75	-46	-46	-46	-46	-46	-120	-46	-120	-46
Equivalent Fuel Savings, \$/kW	Base	+12	-26	-19	-25	-20	-25	-20	-47	-20	-47	-20	-25	-47	-25	-47
Net Relative Cost, \$/kW	Base	+95	+4	+17	-100	-66	-100	-66	-93	-66	-93	-66	-145	-93	-145	-93

TABLE III

MAJOR EQUIPMENT INCLUDED IN COST SUMMARY

- . Main PFB Coal/Sorbent Feed System
- . Gas Turbines/Generators
- . PFB Main Combustors
- . PFB Reheat Combustors
- . AFB Combustors
(Excluding: Flues, Duct, Cyclones,
Fans, Coal/Limestone Feed System)
- . Electrical Equipment
- . Steam Turbine/Generators
- . Waste Heat Boilers
- . Electrostatic Precipitators

TABLE IV

PARTICLE SIZE DISTRIBUTION AND LOADINGS

<u>Size Range</u>	<u>Predicted Particle Concentration, gr/scf</u>		
	<u>Under 2μ</u>	<u>2-10μ</u>	<u>Over 10μ</u>
Gas Turbine Limit	unlimited	0.01	nil
PFB Effluent	0.3	2.0	6.4
Collector Effluent	0.06	0.01	0.00
Entering Turbine	0.02	0.003	0.000

Fig. 1

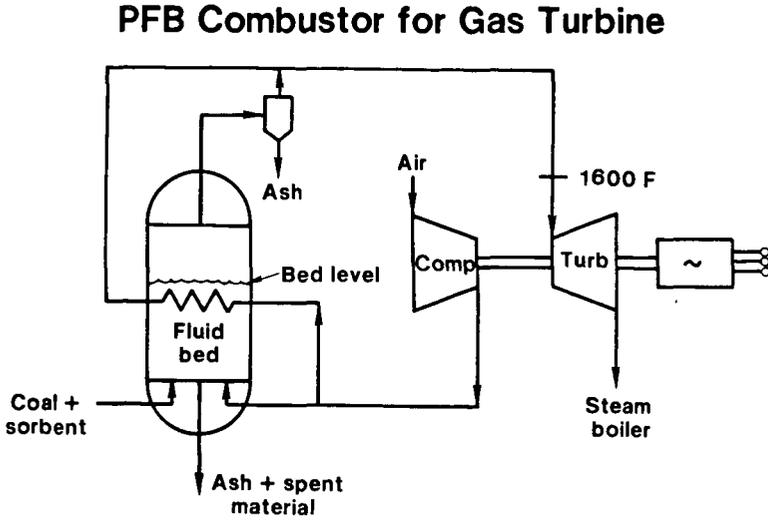


Fig. 2

Unfired Waste Heat Recovery Cycle

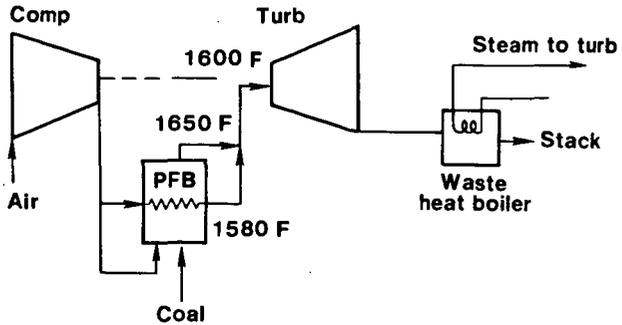


Fig. 3

Power Turbine Reheat Cycle

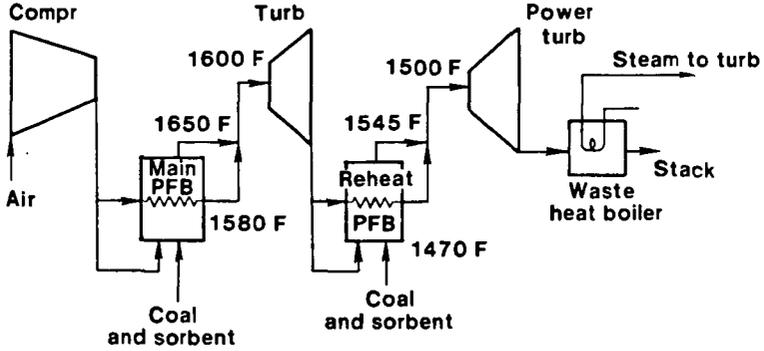


Fig. 4

Exhaust-Fired Steam-Cooled AFB Cycle

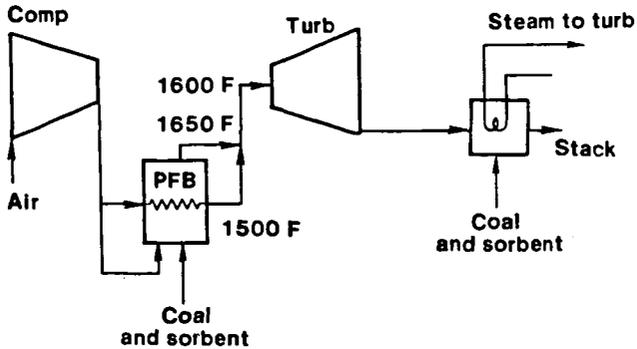
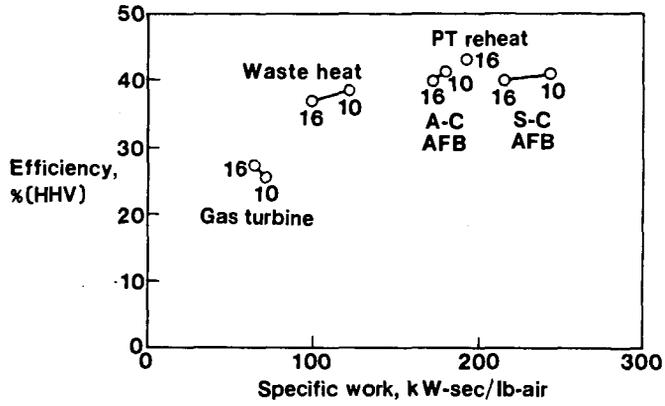


Fig. 5

PFB Cycle Performance Comparison



77-11-193-1

Fig. 6

PFB/AFB Combined Cycle Power Plant

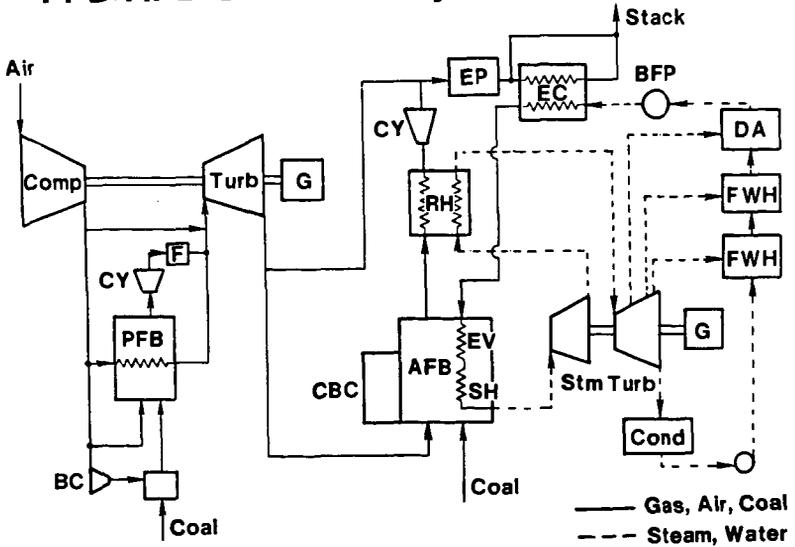


Fig. 7

Pressurized Fluid Bed Combustor

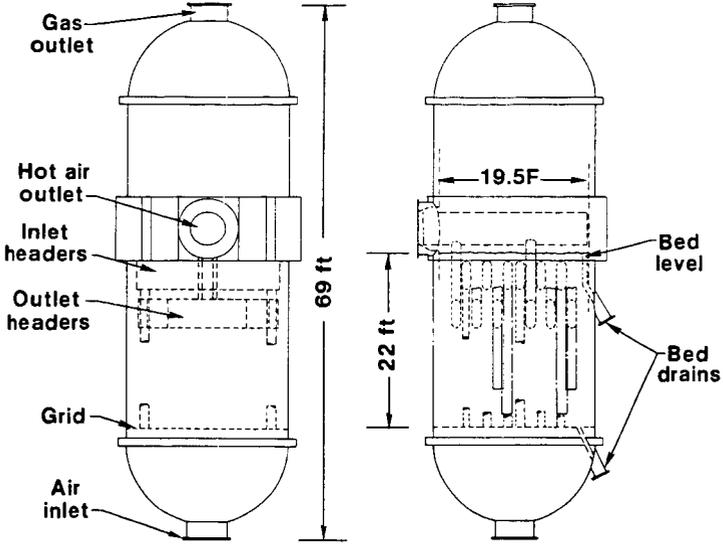


Fig. 8

Atmosphere Fluid Bed Boiler

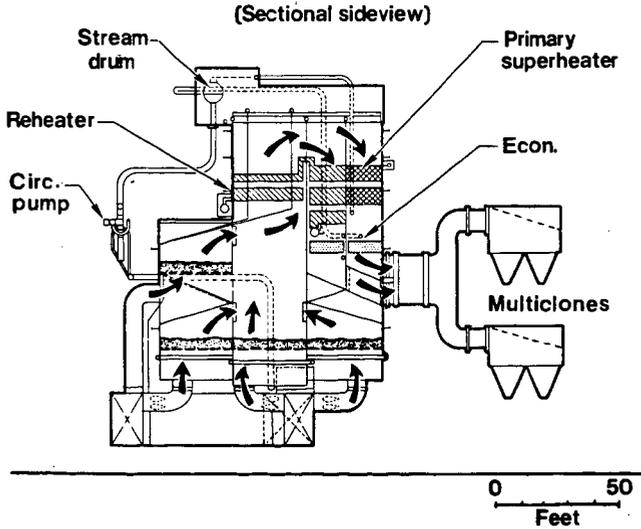
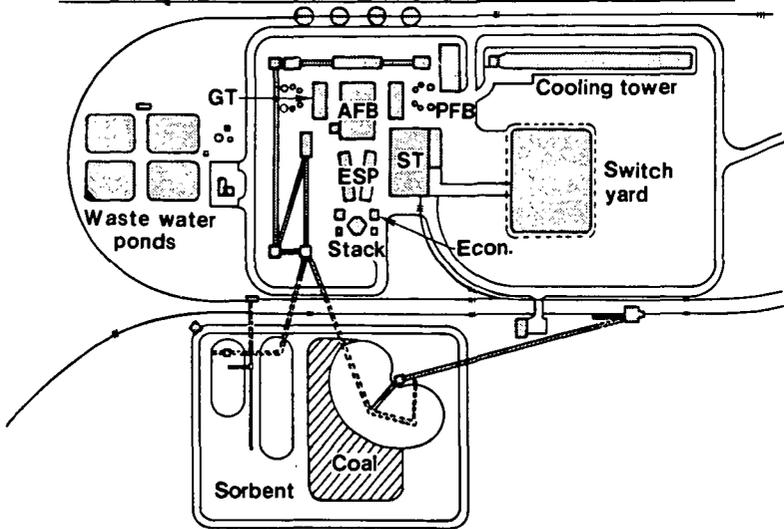


Fig. 9

Plot Plan for PFB Combined Cycle Power Plant



77-10-227-1

Assessment of Current and Advanced NOx Control Technology
for Coal-Fired Utility Boilers*

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INTRODUCTION

NOx is the remaining major air criteria pollutant that has not been effectively reduced to emission levels approaching 10% or less of those from an uncontrolled stationary combustion source. This is particularly true at the present in coal-fired utility boilers because of the conversion of fuel-bound nitrogen in the coal to NO during the combustion process. However, coal is our largest natural fossil fuel resource and DOE is responsible for developing methods of utilizing coal in an environmentally acceptable manner. An important factor in meeting future energy needs and achieving national energy independence is our ability to expand the use of coal in electrical power generation. Consistent with its responsibilities, EPA has established research goals for NOx emissions with coal of 200 ppm by 1980 and 100 ppm by 1985. If it is eventually shown that comparable levels are necessary to maintain air quality standards and cost-effective methods exist, then the likelihood of more stringent new source performance standards (NSPS) in the mid-1980's exists for coal-fired utility boilers.

For the reasons outlined above, a need existed to conduct a comprehensive state-of-the-art review of all potential combustion modification methods for NOx control on coal-fired units. Combustion modification has in the past been the most cost-effective approach to limiting NOx formation and emissions. With the emergence of selective gas-phase NOx decomposition methods, it was desirable to also conduct a review of the most recent developments in that field.

NOx FORMATION

Control of NOx formation during coal combustion is particularly difficult because nitrogen-bearing compounds in the coal are oxidized in the initial stages of the flame zone to produce "fuel nitrogen NOx". Important parameters in this process are local stoichiometry, temperature, and the residence time at these conditions plus the mixing conditions for supplemental air addition and carbon burnout.

Combustion modifications also influence the formation of "thermal NOx" at high combustion temperatures due to the thermal fixation of nitrogen and oxygen in the combustion air. Important parameters that affect peak flame temperature are local oxygen availability, fuel-air mixing patterns, the presence of heat absorbing inert combustion products, combustion air preheat, local heat transfer to adjacent cooled surfaces, etc. Both burner and furnace design are very important factors in total NOx emissions since they influence both thermal and fuel-related NOx.

*This study was conducted for Argonne National Laboratory under Contract 31-109-38-3726 as part of an ongoing program, Environmental Control Implications of Coal Utilization for Power Generation, being conducted in turn for DOE.

NOx CONTROL METHODS

One of the purposes of the study was to not only summarize the technical performance of various NOx control methods, but also to point out and quantify some of the more important operational constraints associated with these methods. The study was primarily concerned with the following control methods and operational concerns.

<u>Methods (or Factors)</u>	<u>Concerns</u>
Low excess air	Cost of combustion modifications
Staged combustion	Furnace wall corrosion
Flue gas recirculation	Tube wall erosion
Combination methods	Carbon carryover
Coal type - bituminous/ subbituminous	Combustion stability
Boiler design - wall fired, tangential, cyclone	Load restrictions
Burner design - conventional, low-NOx, advanced concepts	Secondary pollutants
	Energy penalties
	Retrofit applications
	Impact on auxiliary equipment
	Operation and maintenance

Available NOx emissions test program data was examined for the most prevalent boiler designs and the effectiveness of various combustion control measures is summarized in Table 1. The control method having the largest NOx reduction potential (short of reburnering with new low-NOx burners) was staged combustion, accomplished either by removing burners from service or by the use of overfire air (driving the remaining in-service burners fuel-rich). In the NOx Assessment Final Report (1) for Argonne National Laboratory, NOx reduction potential summary graphs were prepared for each of the various control methods. Although space limitations preclude showing all of this supporting data used in the preparation of Table 1, some examples for burner-out-of-service operation are shown in Figures 1, 2, and 3.

It should be emphasized that there are large unit-to-unit variations in coal-fired utility boiler NOx emissions, even within the same boiler design type. This is due to varied boiler geometry with size, age, and coal type. Boiler operating practice, maintenance, pulverizer settings, and coal characteristics often vary from plant to plant even within the same utility. Frequently a plant in the northeastern U.S. may obtain coal simultaneously from two or three sources. Therefore, it is not unusual to see baseline NOx emissions vary by as much as 500 ppm for a given boiler type (e.g., horizontally opposed fired). Because of this wide variation in baseline emissions, it frequently is more convenient to express the effectiveness of a given NOx control in terms of a potential percentage NOx reduction as in Table 1 and Figures 1 through 3. However, it is also recognized that many utility and government groups are interested in the lowest attainable "state-of-the-art" NOx emission levels as summarized in the table below.

STATUS OF COAL-FIRED UTILITY BOILER NOx CONTROL TECHNOLOGY
FOR NEW UNITS AND RETROFIT APPLICATIONS

	<u>Lowest Attainable NOx Emission Levels</u>			
	<u>New Units</u>		<u>Retrofit</u>	
	ppm at 3% O ₂	lb/MBtu	ppm at 3% O ₂	lb/MBtu
<u>Wall-Fired</u>				
Single Face Fired	300-350	0.45	400-500	0.6
Horizontally Opposed	300-350	0.45	400-600	0.6
<u>Tangential</u>	250-300	0.45	250-350	0.4

For new units, these emission levels are based on the most recent low-NOx burner designs (e.g., dual register configurations or overfire air on tangential units) frequently employed in combination with a compartmentalized windbox and liberal furnace volumes. Retrofit emission levels shown can be reached by reburnering or in some cases by carefully applied staged combustion firing modes. Although it is currently possible to attain these NOx levels with some consistency, this does not mean that all existing units can be modified to these levels regardless of boiler age, design, coal type, etc.

OPERATIONAL CONSIDERATIONS

Previous assessment studies have not properly evaluated the numerous operational factors that are of major importance to the user in selecting and implementing a combustion modification technique. Five major topic areas were examined as part of the current study:

1. Problems in design, installation, operation and maintenance of a NOx control technique
2. Applicability of a given technique for retrofit
3. Impact of low NOx modes on other pollutants
4. Effect of NOx control techniques on the performance of auxiliary equipment
5. Possible energy penalties associated with implementation of a given method

Some of the more important conclusions are outlined below by control method.

A. Operational Factors - Low Excess Air and Staged Combustion--

- . Low excess air operation is possible with NOx reductions of up to 15% and a boiler efficiency improvement if careful attention is paid to combustion uniformity in the burner region. Reductions of 35% are possible with staged combustion.
- . Close control of local and overall air/fuel ratio and rigorous combustion equipment maintenance is essential to the success of both methods.
- . Overfire air port configurations or burner patterns resulting in flame impingement and potential tube wall corrosion must be avoided.
- . New designs should incorporate adequate pulverizer and fan capacity to accommodate low NOx modes. Conservative windbox, furnace and convective section designs are recommended.
- . Carbon carryover and particulate loadings are no greater than normal operation if the excess air is properly established and maintained (as required) for all loads, fuel types, and boiler conditions.
- . No significant increase in secondary pollutants or impact on auxiliary equipment has been noted but more data is needed.

B. Operational Factors - Flue Gas Recirculation--

Flue gas recirculation was found to be a relatively unattractive NOx control method for some of the reasons listed below (2):

- . NOx reductions of 15% or less do not compare favorably with reductions of 25% to 35% with staged combustion (20% of the burners out of service).
- . A measurable efficiency penalty occurs (approximately 0.5%) with flue gas recirculation due to the auxiliary load of the fans.
- . Potential problem areas include tube erosion, flame stability, fan vibration, and increased maintenance.

C. Operational Factors - Corrosion, Slagging and Fouling--

Staged combustion and low excess air operation are the most attractive techniques for NOx control but the major unresolved issue concerns whether these operating modes with fuel-rich burner combustion zones tend to accelerate boiler tube wall corrosion. Because of the importance of this possible deterrent, a major subsection of the final report was devoted to this topic.

Since the more widespread application of low NOx operating modes tends to hinge on this issue, the "facts" concerning corrosion tend to be in a state of dispute but some of the more important observations and recent findings are outlined below:

- High temperature fire-side corrosion of water walls in the radiant section of pulverized coal-fired boilers is generally confined to areas of flame impingement and/or slag buildup.
- The slag deposit on a relatively cold tube wall is usually coupled to a locally reducing atmosphere caused by flame impingement.
- Two types of corrosive attack have been identified in boilers firing coals with appreciable sulfur content; alkali iron bisulfate and iron sulfide modes of attack. The sulfate-type attack predominates over the sulfide type.
- Deposits found on corroded tubes often possess high alkali content, high SO₃ content, and high water solubility. Deposits frequently are pale, bluish white with a glossy "enamel" appearance.
- Slagging, fouling, and corrosion problems have frequently been solved in the past with maintenance or adjustments to the pulverizer, coal distribution pipes, and enforced replacement schedules for the burner impellers.
- Numerous corrosion measurements in low NOx operating modes have been made in the past with air-cooled corrosion probes. These short term tests raise many questions concerning the validity of this technique. More extensive long-term tube-panel tests are necessary to resolve corrosion concerns.

COST OF COMBUSTION MODIFICATIONS

One of the most important factors in addition to NOx reduction effectiveness and operational limitations from the utility operator's standpoint is the cost of combustion modifications. Numerous cost analyses have been conducted under EPA sponsorship for new units and retrofit applications including those by Combustion Engineering (3) and A. D. Little (4). Total costs have been broken down by annual capital, operational, and fuel costs. The relative cost effectiveness of NOx emissions control on a 600 MW coal-fired unit is shown in Figure 4. With current technology, the cost effectiveness rapidly becomes unattractive at emission levels approaching 0.4 lb/MBtu.

ADVANCED NOx CONTROL CONCEPTS

The two most promising advanced NOx control concepts now undergoing research and development are the selective gas-phase NOx reduction flue gas treatment systems and new advanced burner/boiler designs.

Studies by Exxon and KVB have demonstrated NOx reductions up to 90% when ammonia is injected into flue gas streams in the vicinity of 1750 °F. Laboratory-scale feasibility tests with ammonia injection for coal applications has shown that 50% to 80% NOx reductions are possible for the coals tested. Full scale commercialization studies are currently underway and the possibility of a full scale utility boiler demonstration test in the next two or three years is very likely.

Advanced burner/boiler design concepts have concentrated on combustion methods that will minimize the conversion of fuel-bound nitrogen to NOx. Based on recent laboratory and subscale tests at EPA and EPRI contractor's facilities, the attainment of EPA's research goals of 200 ppm by 1980 and 100 ppm by 1985 are very likely.

This does not mean that all operational problems will be solved and production units will be available by that time. However, recent research programs at B&W, KVB, Aerotherm, and EER are establishing the proper stoichiometry, temperature, and residence times necessary to limit NOx formation to less than 200 ppm in these initial stages of direct coal combustion. Research is continuing into more complex problems of secondary air addition, carbon burnout, and containment of fuel-rich combustion conditions without extensive materials corrosion problems.

In conclusion, continued progress is being made to reduce NOx emissions from direct coal combustion through low NOx burner designs, currently capable of limiting emissions to 0.6 lb/MBtu and research designs expected to meet approximately 0.25 lb/MBtu emission goals by 1980.

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TABLE 1. COMBUSTION MODIFICATION ASSESSMENT SUMMARY

	Control Method					
	Low Excess Air	Biased Firing	Burners Out of Service	Overfire Air	Flue Gas Recirculation	New Burners
Basic Mechanism of Control	Increase fuel/air ratio at all burners	Increase fuel/air ratio to majority of burners	Increase fuel/air ratio to active burners	Increase fuel/air ratio to burners by diverting combustion air	Reduce peak flame temperature	Controlled diffusion flame
NOx Reduction Potential						
<u>Single Face Fired</u>						
Typical	0-15%	5%	30%	15%	--	--
Maximum	15%	7%	35%	30%	--	--
<u>Horizontally Opposed Fired</u>						
Typical	0-15%	5%	25%	30%	14%	30%
Maximum	15%	8%	35%	58%	17%	60%
<u>Tangentially Fired</u>						
Typical	0-10%	--	30%	30%	--	--
Maximum	10%	--	45%	35%	--	--
Modification Cost (\$/kW) New/Retrofit						
<u>Single Face Fired</u>	~ 0/0.64	--	--	0.2/0.75	--	--
<u>Horizontally Opposed Fired</u>	~ 0/0.64	--	--	0.2/0.75	--	--
<u>Tangentially Fired</u>	--	--	--	0.2/0.75	--	--
Primary Limitations	Slagging, smoke, flame instability	Degree of biasing, wall slagging and corrosion	Degree of staging, wall slagging and corrosion	Degree of staging, wall slagging and corrosion	Much less cost effective than staging	Cost
Limiting Factors in Effectiveness	Carbon carryover	Carbon carryover, flame stability, smoke	Carbon carryover, flame stability, smoke	Carbon carryover, flame stability, smoke	Flame stability	Windbox configurations, flame stability
Retrofit Limitations	Combustion controls and instrumentation	Pulverizer and fan capacity, flexibility in coal feed system	Pulverizer and fan capacity, flexibility of coal feed system	Furnace configuration, fan capacity	Unit layout, fan capacity	Furnace and windbox configuration, fan capacity
Energy Penalties	May increase slightly	None	None	None	0.5% due to auxiliary fan loadings	None
Secondary Pollutants	No effect*	No effect*	No effect*	No effect*	No effect*	No effect*
Operational and Maintenance Considerations	Additional combustion controls, increased maintenance	Additional combustion controls, increased maintenance	Additional combustion controls, increased maintenance	Additional combustion controls, increased maintenance	Tube erosion, fan vibration, increased maintenance	Minimal
Impact on Auxiliary Equipment	None	None	None	None	Increased fan loading	None reported

*Based on limited available data

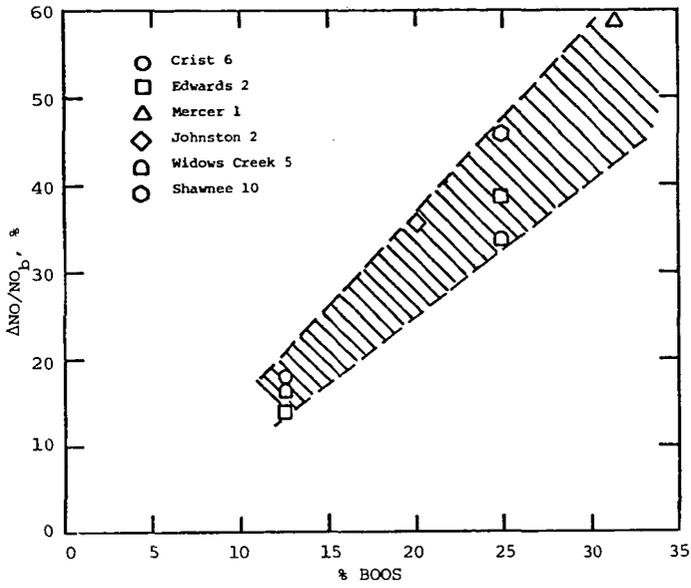


Figure 1. NOx reduction potential of BOOS for single face-fired units.

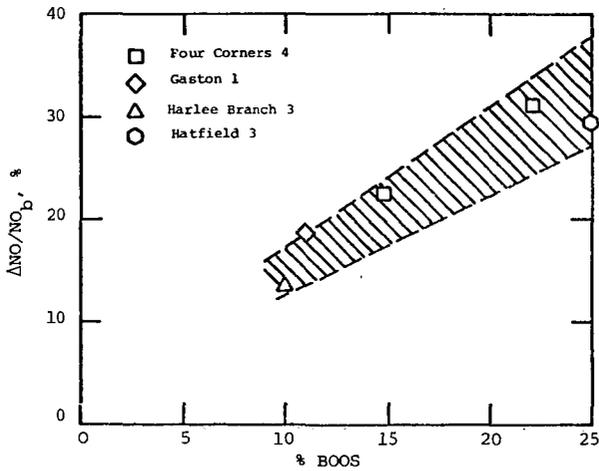


Figure 2. NOx reduction potential of BOOS for horizontally opposed units.

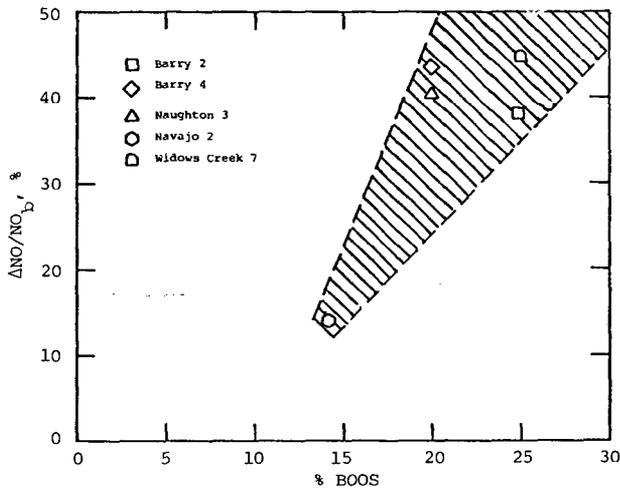


Figure 3. NOx reduction potential of BOOS for tangentially fired units.

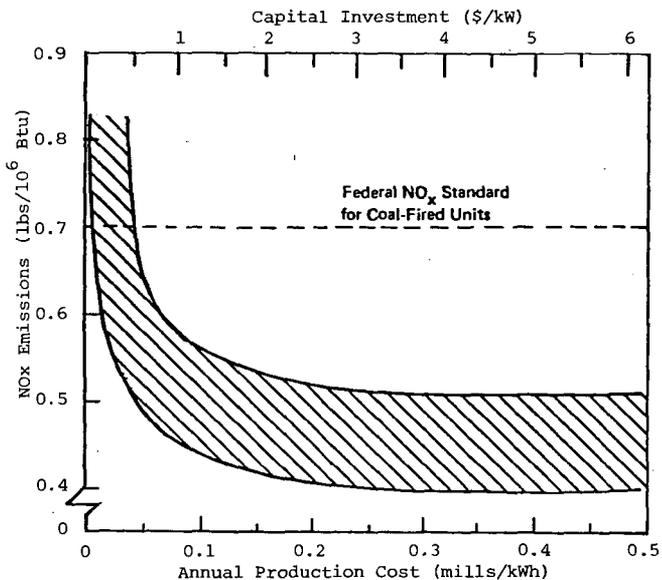


Figure 4. Cost effectiveness of NOx emissions control of a 600 MW steam electric generator (4).

MECHANISMS FOR TRACE ELEMENT ENRICHMENT
IN FLY ASH DURING COAL COMBUSTION

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INTRODUCTION

It is now well established that the smaller flyash particles formed during coal combustion show a significant enrichment of several volatile trace elements. The most widely accepted model for trace element enrichment in flyash formation involves the volatilization of these elements during combustion, followed by condensation or adsorption over the available matrix material (composed primarily of the nonvolatile oxides of Al, Mg, and Si) (1). The larger surface-to-volume ratio of the smaller particles leads to a trace element concentration in the free molecule regime(2) which is inversely related to the particle diameter. Indeed, flyash surfaces have been found to be enriched in several of the same trace elements showing enrichment in the smaller particles, supporting this mechanism(3-5). The smaller particles, which show the highest concentrations of several trace metals, are not efficiently collected by pollution control devices. These particles, enriched in potentially toxic trace metal, also have the highest atmospheric mobilities and are deposited preferentially in the pulmonary and bronchial regions of the respiratory system(1). A proper understanding of the trace element enrichment mechanism is a necessary prerequisite for the prediction of the environmental impact of coal-fired plants, as well as for improving the efficiency of pollution control devices.

Our goal is to determine the mechanism for flyash formation, the enrichment of certain elements in the smaller flyash particles, and the identity of the trace inorganic and organic products of coal combustion. In the initial phase of this study, our investigations have centered on the areas described below.

A. Surface Studies and Flyash Characterization

Studies of fly ash and flyash surfaces have been undertaken using photoelectron spectroscopy, proton induced X-ray emission, secondary ion mass spectrometry, Rutherford backscattering, and scanning electron microscopy. Several of these techniques were used in conjunction with sputtering to obtain concentration vs. sputtering depth profiles. Extensive studies have also examined the various types of flyash particles as a function of particle size and other characteristics. These studies have provided qualitative and semi-quantitative evidence showing the enrichment of several volatile trace elements on flyash surfaces.

B. Flyash Volatilization

On the assumption that species volatilized during combustion and condensed on flyash surfaces may be readily volatilized on heating, two experiments were designed to identify the volatile species. First, flyash samples were activated, and heated to temperatures up to 1400°C and the volatile components collected for neutron activation analysis. Volatilization vs. temperature profiles have been obtained for several elements including Se, Hg, Br, I and As. Second, flyash samples were heated up to 2000°C in a Knudsen cell and the volatile species analyzed by modulated molecular beam mass spectrometry; hence, obtaining information on the actual molecular species volatilized.

C. Extractions of Organic Matter

The organic fraction of the collected fly ash has been extracted from sized flyash fractions by both solvent extractions and a vacuum extraction of fly ash heated slowly to 400°C. These fractions have been analyzed by GC and GC/MS techniques.

D. Analysis of Sized Flyash Fractions

Flyash samples collected from the precipitators of two western coal-fired steam plants were separated into size fraction using a Bahco Microparticle Classifier. Separate aliquots of each size fraction were analyzed for 43 major, minor and trace elements by X-ray fluorescence (XRF), atomic absorption (AA), and instrumental neutron activation (INAA), to establish the concentration-particle size dependence for each element. Replicate analyzes of two separate size fractions have allowed us to assess the heterogeneity of the fly ash and sampling errors. Analytical results for the "best method" are collected in Tables 1 and 2; analytical results for the second coal-fired plant for a wider range of particle sizes ($<0.2\mu$ to $>150\mu$) have also been obtained. These results provide information on trace element enrichment in submicron flyash particles.

RESULTS AND DISCUSSION

The analysis of well-defined flyash size fractions offers the most promising method for determining the controlling mechanisms in the volatilization-condensation processes. Surface-depth profiles from sputtering are semi-quantitative (at best), are not usually sensitive to trace elements, and are often dependent on the simultaneous examination of a "field" of particles (or of individual particles, with added problems resulting from low sensitivity and the heterogenous nature of fly ash). These studies also carry the implicit assumption that diffusion will not significantly disturb the surface-depth profile after condensation. The observation of crystal growth on flyash particles(6) makes this assumption dubious. On the other hand, the major requirements for concentration vs. particle size measurements are much more readily fulfilled; the major assumption being that after condensation interparticle diffusion is negligible.

Elemental analyses of fly ash have often shown an inverse concentration dependence upon particle size for many trace elements. This relationship has been rationalized in terms of a Volatilization-Condensation Model (VCM)(1). According to this model, trace elements volatilized during the combustion process condense upon the (mostly) spherical particles of unvolatilized material in the cooler post-combustion region. The larger surface-to-mass ratio of smaller particles results in an enrichment of the volatilized trace elements, having an inverse or an inverse squared dependence upon particle diameter, depending upon the flow regime [i.e., free molecule or continuum](1,2).

The VCM, as proposed by Natusch and coworkers(1,7), predicts an inverse dependence of the total concentration (C) upon particle diameter,

$$C = C_m + \frac{6C_s}{\rho D} \quad 1)$$

where C_m is the concentration in the matrix upon which the volatiles condense, C_s is the surface concentration, ρ is the density, and D is the particle diameter. Flagan and Friedlander, however, have recently suggested that a direct dependence of C on D^{-1} should exist only in the free molecule regime where the Knudsen number, Kn , is greater than 1(2). At lower values of Kn , in the continuum regime, they suggest that the total concentration will be proportional to D^{-2} . This corresponds to a

surface layer thickness which is greater for smaller particles (proportional to D^{-1}) and predicts a much greater increase in the concentration of volatilized elements for the smaller particle sizes.

To compare models we have obtained least squares fits of our experimental results to the models of Natusch and coworkers(1) and Flagan and Friedlander(2). The model of Natusch and coworkers(1), with only a few exceptions, provides a significantly better fit than the Flagan and Friedlander model(2) to the data. In the following discussion we implicitly assume a concentration dependence similar to the VCM of Natusch and coworkers.

In order to increase the flexibility of the VCM it is advantageous to generalize the model by assuming a discrete surface layer of thickness L to be deposited over all particles. The relationship between the bulk concentration (C), the concentration in the matrix (C_m), and the concentration in the surface layer (C_s) of thickness L is:

$$C = \frac{C_m d_m (D - 2L)^3 + C_s d_s D^3 - C_s d_s (D - 2L)^3}{d_m (D - 2L)^3 + d_s D^3 - d_s (D - 2L)^3} \quad 2)$$

where

D = particle diameter

d_m = density of matrix material

d_s = density of surface layer

Results of analyses of fly ash as a function of particle size indicate that the elements, Mn, Ba, V, Cr, Co, Ni, Cu, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg and S, are mostly volatilized in the combustion process (Table 1). The elements, Ti, Al, Mg, Na, K, Mo, Ce, Rb, Cs and Nb, appear to have a smaller fraction volatilized during coal combustion. The remaining elements, Si, Fe, Ca, Sr, La, Sm, Eu, Tb, Dy, Yb, Y, Sc, Zr, Ta, Na, Th, Ag and In, are either not volatilized or show trends which are not readily rationalized in terms of the simple VCM (Table 2).

Figure 1 shows the concentration vs. particle size data plotted for As, Zn, Rb and Mn, which are typical of elements having behavior which may be attributed to volatilization during combustion. These data have been fitted to the VCM using Equation 2, indicated by the lines in Figure 1.

The elements listed in Table 2 show either very little enrichment in the smaller particles or unusual concentration profiles. The concentration of Si shows a definite direct dependence upon particle size, making it unique in this study (Figure 2). The VCM can be used to qualitatively rationalize the Si data; by assuming $L = 0.1\mu$, $C_m = 35.5\%$, and $C_s = 0$ (and $d_m = d_s$), one obtains the fit given by the line in Figure 2.

The most interesting trends with particle size are observed for a group of elements (Ca, Sr, La, Sm, Eu, Tb, Dy, Yb, Y, Sc and Th) which exhibit distinct maxima in concentration at an intermediate particle size (4-8 μ). These trends are most striking for Ca and Sr (Figure 3), where maxima at $\sim 4\mu$ are observed, confirmed by analysis of different samples by AA, XRF and INAA. The similarity of Ca, Sc, Sr and Y, and the rare earth elements is not surprising; these elements are known to be chemically similar. Barium might also be expected to behave in a similar fashion, but its lower oxide boiling point apparently results in sufficient volatility to obscure these trends. Concentration profiles for several of the rare earth elements

are shown in Figure 5. In Figure 6 we have plotted the rare earth element (REE) abundances normalized to chondritic values: The REE pattern observed for fly ash is similar to that observed in apatite, a mineral containing high concentrations of the rare earth elements and present as an accessory mineral in rocks and soils. (Similar REE patterns are also commonly observed for coal, plant and soil samples.) There are two plausible explanations for the observation of a maximum at $\sim 5\mu$, one involving geochemical fractionation, and the second, a combined geochemical-volatilization mechanism. The first involves an introduction of a geochemical fractionation mechanism to explain a maximum in the concentration vs. particle size profile at $\sim 4\mu$. The second couples a more reasonable geochemical fractionation process with the VCM. By assuming a decreasing value of C_m with particle size, setting $C_s = 0$ and choosing a finite surface layer thickness (L), one can obtain maxima in the concentration profiles; a condensed layer 0.1μ thick can rationalize a maximum at $\sim 5\mu$. Since the concentration profile resulting from any geochemical fractionation mechanism is unknown, a precise estimate of L is impossible. However, values of $L > 0.05\mu$ would be required to explain the results. To determine the relative importance of possible geochemical fractionation mechanisms, samples of the mineral matter obtained by solvent cleaning and low temperature ashing of coal have been sized and subjected to chemical analysis.

Analysis of the results in Table 1 (and Figure 1) shows that many elements are only partially volatilized during combustion, whereas others are essentially completely volatilized. Attempts to rationalize the volatility of elements in terms of simple parameters, such as the boiling points or melting points of the elements, their oxides, or sulfides are only partially successful, the best being the correlation with oxide boiling points. This is reasonable since oxides are known to account for the bulk of the fly ash and the "inorganic" elements in coal often exist as oxides, or form the oxide upon heating. While a rough correlation with oxide boiling points does exist, there are several elements with oxide boiling points above 1600°C which show appreciable enrichment in fly ash, including Cu, B, Tl, Zn, Ba, Ga, Cr, Mn, U and Be. A similar lack of correlation is observed for elements with oxide boiling points of less than 1500°C , with several elements showing only limited volatility (e.g., Cs, Li, Rb and Na).

The reasons for the enhanced volatility of specific elements may be either physical or chemical. The amount of trace element volatilization which will occur during coal combustion will be dependent upon a number of physical parameters, the most important being the residence time in the furnace and the concentrations and temperature vs. time profiles for both the gas and particulate phases.

The "inorganic" elements (defined here as all elements other than C, H, S and N) usually account for between 2% and 40% of the coal by weight, with a range of 5% to 15% being most common. While inclusions of mineral matter account for the bulk of the inorganic elements in coal, specific trace elements may be primarily associated with the organic fraction of coal.

The trace elements associated with the organic fraction of coal will be especially important in determining the gaseous and particulate emissions from coal combustion. During combustion, trace elements which are trapped in an organic matrix, or bonded in organic compounds (organometallic species), may be volatilized, or form an aerosol of minute particles. These elements may have a much higher probability of being transferred to the vapor state than a similar compound associated with the mineral fraction. It should be noted, however, that a volatilization of the organically associated elements is unnecessary for trace element enrichment; a similar inverse dependence of concentration upon particle size will result as the coal is consumed, and nonvolatilized inorganic elements associated with the organic fraction ultimately deposit on the remaining mineral inclusions which

finally form the fly ash. Organically associated elements which are not volatilized (or atomized) will be agglomerated with the mineral inclusions as the coal particles shrink during the pyrolysis and combustion processes. The precise concentration vs. particle size dependence predicted by this model depends on the relationship between the initial coal particle size and the size of the mineral inclusion.

Since insufficient information is available to determine a reasonable model, and the fraction of organically associated elements volatilized [or existing in the gas phase as fine particles, which will heterogeneously condense on larger particles (2)] is unknown, we cannot predict the precise concentration dependence of organically associated elements. However, the concentration of organically associated elements will be inversely dependent upon particle size, and may be qualitatively described by the VCM. Thus, the organically associated elements (which account for more than 50% of several elements) must play an extremely important role in the trace element enrichment observed in emitted flyash particles. To examine this theory we have begun sink-float separations of coal samples to determine the organic affinity of various elements in the feed coal at a coal-fired plant. These results will be compared with flyash enrichment data in our presentation.

The relationship between the percent of ash volatilized during coal combustion and the surface layer thickness in the VCM may be explored if the particle size distribution is known. As an approximation we have used the size distribution data obtained by Schulz et al. (8), and fit their results to a log-normal distribution (Figure 4). Assuming surface layer thicknesses of 0.01μ and 0.1μ (and $d_s = d_m$), one can integrate over the size distribution and determine that 5% and 28%, respectively, of the total ash was volatilized during combustion.

In Figure 4 we have also plotted the cumulative volume of the surface layer (V_s) over the total volume of all particles (V_t), as a function of particle size for a surface layer thickness of 100\AA . This analysis shows that for elements completely volatilized (assuming $d_s = d_m$), half of their total mass will be in particles of 0.33μ or smaller, and that more than 50% will be in particles between 0.1μ and 1.0μ in diameter. This result is especially important since there is a minimum in the collection efficiencies of most emission control devices in the same size regime.

In general, and despite its simplicity and crude approximations, the VCM appears to predict the concentration vs. particle size dependence remarkably well. While the agreement may be fortuitous, as a result of the complex gas-particle and particle-particle interactions during combustion which are only partially understood (2), the VCM does provide a good empirical fit to the data, using parameters which may be rationalized in terms of the chemical nature of coal. Our analysis has shown the organically associated elements, which are a major fraction of many trace elements in coal, play an important role in the enrichment of the smaller size particles and, hence, the emissions from coal-fired plants.

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TABLE 1
 Concentrations as a Function of Particle Size for Elements Showing Enrichment in the Smaller Size Fractions^a

Diameter ^b	Element															
	Ti ^c (%)	Al ^d (%)	Mg ^e (%)	Na ^d (%)	K ^d (%)	Mn ^c	Ba ^c (%)	V ^d	Cr ^d	Co ^d	Ni ^d	Cu ^c	Ga ^c	Nd ^d		
0.5	0.79	10.7	2.33	2.05	1.41	954	1.23	340	230	25.7	190	501	96	83		
2.0	0.78	10.0	2.29	1.85	1.24	701	0.78	300	220	22.4	130	396	77	80		
4	0.82	10.6		1.78	1.33	646	0.62	320	220	22.4	105	345	70	83		
5	0.75	9.56	2.15	1.79	1.20	505	0.45	240	140	19.0	67	275	52	50		
8.5	0.69	9.35	1.94	1.47	1.11	430	0.34	200	150	16.2	80	241	33	55		
12.5	0.34	8.80	1.10	1.20	0.89	262	0.21	110	75	10.0	36	156	14	45		
15.5	0.59	7.31	1.37	1.08	0.94	248	0.20	105	90	11.7	63	131		50		
25	0.54	6.95	0.82	0.76	0.72	190	0.31	74	60	7.6	35	105	5.4	32		
50	0.47		0.61			148						67	4.7			

Diameter ^b	Element															
	Mo ^c	Ce ^d	Rb ^d	Cs ^d	As ^c	Sb ^d	Sn ^c	Br ^c	Nb ^c	Zn ^c	Se ^d	Pb ^c	S ^c			
0.5	87	180	62.1	5.01	79	23.5	51	6.2	74	215	68	254	7920			
2.0	74	170	56.1	4.60	70	22.9	38	4.8	44	162	44	172	5060			
4	76	180	54.6	4.48	67	21.6	28	4.0	50	122	30	139	5120			
5	54	145	51.8	3.60	46	13.6	10	3.2	40	87	23	96	4160			
8.5	36	135	46.2	3.36	29	11.0	9	1.6	35	70	12	74	3100			
12.5	16	110	43.1	2.89	10.5	4.20		0.9	33	32	10	44	1440			
15.5	15	100	34.8	2.57	10.1	3.40	8	<0.7	30	30	8	21	<1500			
25	10	80	34.7	2.20	4.6	1.96		<0.6	27	20	5	42	<1500			
50	9				4.2			<0.6	16	10		17	<1500			

a. Concentrations given in PPM unless otherwise noted.
 b. Mass median diameter.
 c. By XRF.
 d. By INNA.
 e. By AA.

TABLE 2

Concentrations as a Function of Particle Size for Elements
Not Showing Enrichment in the Smaller Size Fractions^a

Diameter ^b	Element							
	Si ^c (%)	Fe ^e (%)	Ca ^d (%)	Sr ^e	La ^e	Sm ^e	Eu ^e	Tb ^e
0.5	21.9	3.47	5.14	1600	70.3	8.68	1.95	1.15
2	23.5	3.20	6.16	2080	73.7	10.9	2.14	1.5
4		3.22	6.71	2360	76.7	10.5	2.29	1.6
5	24.3	2.89	6.53	1720	72.8	10.1	2.17	1.4
8.5	26.7	2.66	5.99	1650	69.6	9.43	1.97	1.3
12.5	29.4	2.10	3.33	1270	53.4	5.92	1.49	1.1
15.5	29.4	2.20	3.16	1520	55.7	7.23	1.56	1.2
25	34.3	3.02	2.26	800	41.9	6.00	1.16	0.86
50	35.8		2.01	(600) ^d				

Diameter ^b	Dy ^e	Yb ^e	Y ^d	Sc ^e	Zr ^d	Ta ^e	Th ^e
0.5	7.3	4.26	48	24.6	280	3.2	32.6
2	8.7	4.69	54	26.8	290	3.0	35.2
4	9.6	4.79	61	28.7	306	2.9	37.6
5	8.8	4.96	55	26.9	330	2.7	58.2
8.5	7.8	5.00	49	24.7	320	2.8	32.8
12.5	6.6	3.47	37	17.7	350	2.1	25.6
15.5	7.1	3.49	36	18.5	440	2.1	28.4
25	4.7	3.33	32	13.7	624	1.8	22.8
50			28		374		

- a. Concentrations in PPM unless otherwise noted.
b. Mass median diameter (microns).
c. By AA.
d. By XRF.
e. By INAA.

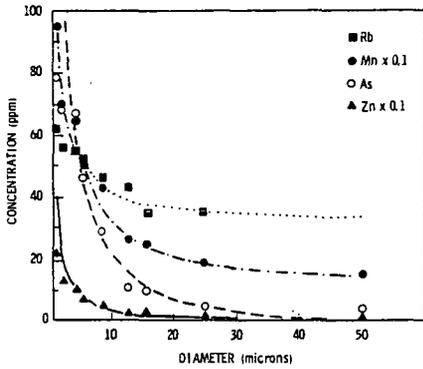


FIGURE 1. CONCENTRATION VERSUS PARTICLE SIZE DATA FOR Mn, Rb, As and Zn. ALSO GIVEN IS THE BEST FIT TO THE VOLATILIZATION-CONDENSATION MODEL

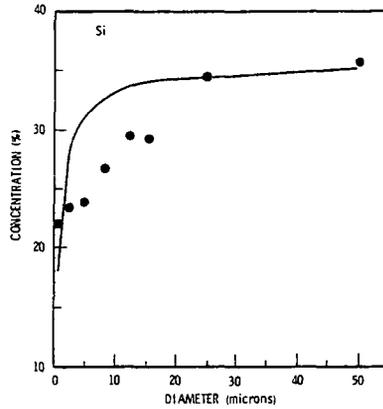


FIGURE 2. CONCENTRATION VERSUS PARTICLE SIZE DATA FOR SI WITH BEST FIT TO THE VCM ASSUMING A 0.1μ SURFACE LAYER THICKNESS

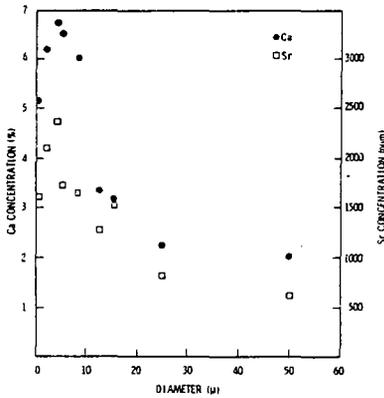


FIGURE 3. CONCENTRATION VERSUS PARTICLE SIZE DATA FOR Ca (●) AND Sr (□). A MAXIMUM WAS OBSERVED FOR BOTH ELEMENTS, AND MOST OF THE RARE EARTH ELEMENTS (TABLE 2), AT APPROXIMATELY 5μ . THE DATA FOR Ca AND Sr WERE CONFIRMED BY COMPARISONS OF ANALYSES BY AA, XRF, AND INAA TECHNIQUES

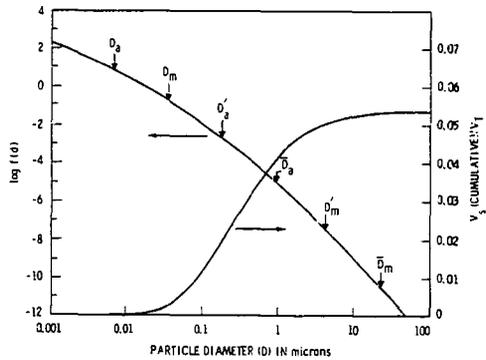


FIGURE 4. LOG-NORMAL DISTRIBUTION OF PARTICLE SIZES ASSUMED TO RESULT FROM COAL COMBUSTION (LEFT). D_a IS THE DIAMETER OF AVERAGE AREA, D_m IS THE DIAMETER OF AVERAGE MASS, D'_a IS THE AREA MEDIAN DIAMETER, D'_m IS THE AREA MEAN DIAMETER, D_a IS THE MASS MEDIAN DIAMETER, AND D'_m IS THE MASS MEAN DIAMETER. ALSO GIVEN IS THE CUMULATIVE FRACTION OF THE TOTAL VOLUME OF THE FLYASH PARTICLES DUE TO A SURFACE LAYER 0.01μ THICK (RIGHT) FOR THIS LOG-NORMAL DISTRIBUTION

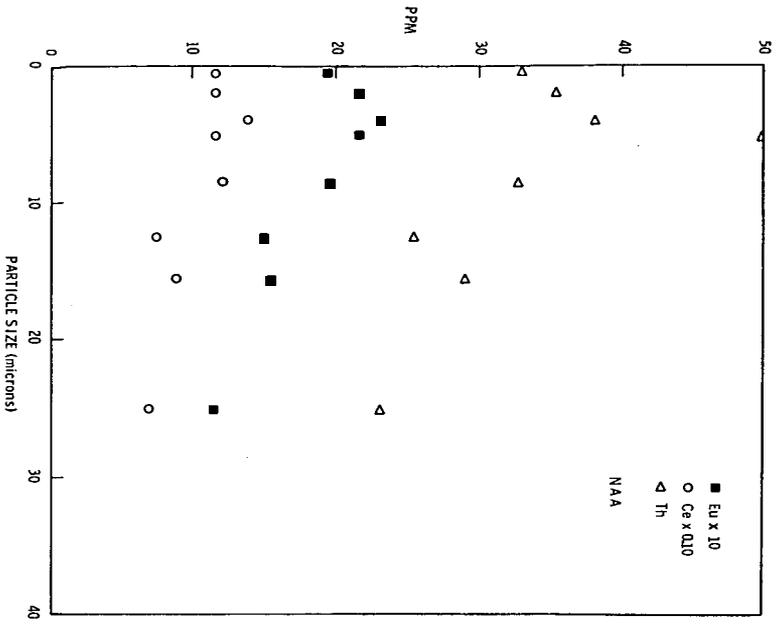
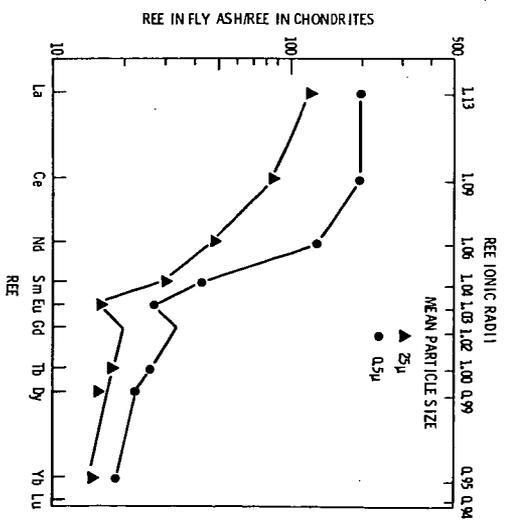


FIG. 5 (left) CONCENTRATION OF RARE EARTH ELEMENTS (REE) FROM NAA AS A FUNCTION OF PARTICLE SIZE
 FIG. 6 (above) RARE EARTH ELEMENT (REE) ABUNDANCES NORMALIZED TO CHONDRITES FOR TWO PARTICLE SIZES



Criteria for Selection of Coal Additives

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INTRODUCTION

Ash deposits are a major concern for coal users. They can reduce boiler availability, reliability, performance and efficiency.

The problems will become more acute in the near future. The energy crisis demands increased use of coal, and problems may be expected to grow at a faster rate than that of coal use. This is because disruption of normal coal supplies may be expected as increased demand puts a strain on the supply and transportation systems. Ash concentration will become less predictable. Cooperation will be needed among boiler manufacturers, coal users and coal suppliers.

Chemical treatment offers a means of alleviating the problems caused by coal ash deposits. Treatment of oil has been accepted for a number of years(1), but only occasional successes have been reported for coal (2-6).

This paper presents a rational approach to the choice of chemicals for treatment of ash from direct combustion of coal. It is hoped that application of the results of this study will advance the art, to the benefit of boiler owners and operators.

DEPOSIT PROBLEMS

There are two basic types of deposit problems, furnace slag and fouling of convection sections and superheaters. Corrosion of superheaters and supports is associated with the latter type of deposits. This study is addressed to alleviation of the fouling and corrosion of superheaters.

The key components in superheater corrosion by coal ash are the alkali iron sulfates. They are molten at superheater metal temperatures and participate in corrosive reactions, destroying the protective metal oxide coating and causing rapid corrosion. These compounds and their melting points are shown in Table 1.

TABLE 1. Alkali iron sulfates

<u>Compound</u>	<u>Melting points °F</u>
$\text{Na}_3\text{Fe}(\text{SO}_4)_3$	1155
$\text{NaFe}(\text{SO}_4)_2$	1274
$\text{K}_3\text{Fe}(\text{SO}_4)_3$	1145
$\text{KFe}(\text{SO}_4)_2$	1281

In addition to corrosion, the alkali iron sulfates may contribute significantly to the fouling of superheaters and the hotter parts of

convection sections. The molten sulfates can trap other ash particles and bond them.

CHEMICAL TREATMENT

There are two common mechanisms in direct chemical treatment of ash deposits. One is chemical reaction of the additive with the injurious deposit components or their precursors to form less harmful products. In the case of oil ash, for example, magnesium oxide reacts with vanadium pentoxide or sodium vanadyl vanadates to form magnesium vanadate, $3\text{MgO}\cdot\text{V}_2\text{O}_5$, which melts at 2179°F .

Treatment by chemical reaction has been suggested by Borio (7) and by Rahmel (8). Treatment with alkaline earth metal compounds was proposed to form compounds such as $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ and $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ at the expense of the alkali iron sulfates.

The second mechanism is physical. Dilution, formation of a barrier layer, or absorption of melts can prevent molten deposits from contacting tube surfaces, and hence prevent corrosion. All of these phenomena can also reduce the formation of bonded deposits. Certain types of successful oil additives are thought to work in this manner (1).

It appears from experience that the best method of application is to feed additives intermittently and to coordinate feed with the sootblower cycle. The treatment is fed immediately after the sootblowers have swept the target area, so as to allow maximum contact with inner deposit layers. Great care must be exercised in choosing the points and methods of addition to assure that the maximum amount of additive reaches the target surfaces. Success has been reported for intermittent feed (3, 6). To prevent corrosion and bonding, the alkali iron sulfates in the inner deposit layers must be affected. Attacking these compounds with additives is feasible, since they constitute a relatively small fraction of the total ash. Even with intermittent, directed feed, however, the major barrier to successful treatment is dilution or blocking of the additive by the bulk of the deposits. It is this effect of the matrix which chiefly distinguishes coal treatment from oil treatment.

Successful treatment with additives fed with the fuel is unlikely due to dilution by the bulk of the coal ash.

PRESENT INVESTIGATION

This paper reports a laboratory investigation of the effect of additives on synthetic superheater deposits which takes into account the effect of the matrix. The effect of additives on alkali iron sulfates was first determined. The experiments were then repeated with the addition of a third component: a matrix of bulk coal ash.

The criteria for success were the formation of solid, friable reaction products with the alkali iron trisulfates at 1100°F and maintenance of a solid, friable product with the addition of the ash matrix up to 1800°F , a representative gas temperature at superheater banks.

Friability of the mixture at the higher temperature was required since reaction of the additives with inner, sulfate-rich deposit layers will require periodic removal of outer layers by sootblowers. In

practice, if the additive and the outer parts of the deposit do not form friable products, attempts at treatment will simply powder the top of growing deposits.

EXPERIMENTAL

Additives were heated for two hours with alkali iron sulfates under a high-sulfur trioxide atmosphere to promote the stability of the sulfates. They were examined after heating at 1100°F and 1800°F. Appearance was noted visually and friability was tested with a spatula. It was noted whether the heated materials had wet the containers. Selected products were characterized by X-ray diffraction. The investigations were repeated with the addition of the ash matrix materials.

The equipment is shown in Figure 1. A commercial SO₂-air mixture was catalytically oxidized to SO₃ over a V₂O₅ catalyst.

ADDITIVES AND SYNTHETIC DEPOSITS

The alkali iron sulfates were prepared by the wet method of Corey and Sidhu (9). The synthesis and the stability of the materials at 1100°F under the experimental atmosphere were checked by X-ray diffraction. One simulated ash matrix had an elemental composition typical of Eastern coals. It was the following mixture: SiO₂ (40.1 weight %), Al₂O₃ (16.7), Fe₂O₃ (22.4), CaO (7.7), MgO (0.8), Na₂SO₄ (6.6), and K₂SO₄ (5.9). The other simulated Western coal ash and contained SiO₂ (25 weight %), Al₂O₃ (11), Fe₂O₃ (9), CaO (23), MgO (8) and Na₂SO₄ (25).

A mixture of K₃Fe(SO₄)₃ and Na₃Fe(SO₄)₃ by weight was used because the mixture melted below 1100°F. This allowed studies at 1100°F. Higher temperatures would have increased the instability of the sulfates and made the atmosphere more critical.

The additives in Table 2 are available in commercial grades. The rare earth oxide mixture contained 48% CeO₂ and 34% La₂O₃. The additives were applied at a ratio of 1:1 by weight to the alkali iron sulfate mixture. Matrix material was added as 1 part by weight to 1 part additive to 1 part sulfates.

RESULTS AND DISCUSSION

Without Matrix

Table 2 shows that effective deposit conditioning was achieved with a wide range of materials including both acidic and basic oxides. Mixtures contained the weight ratios shown.

TABLE 2. Additive evaluation, no matrix

Additive	Product at 1100°F	1800°F
Control	melt	melt
MgO	powder	melt
CaO	fusion, sticking	-
Rare earth oxide	powder	melt

TABLE 2. Additive evaluation, no matrix

Additive	Product at 1100°F	1800°F
TiO ₂	powder	melt
MnO	fusion, no sticking	fusion, melt
CuO	melt	
ZnO	melt	
Al ₂ O ₃	powder	fusion, slight melt
SiO ₂	powder	melt
MgO 66.7/Al ₂ O ₃ 33.3	powder	melt
MgO 28.3/Al ₂ O ₃ 71.7	powder	slight fusion
MgO 50.0/SiO ₂ 50.0	powder	melt
CaSiO ₃	slight fusion	melt

Of the transition and post-transition metals only titania, the rare earth oxides, and perhaps manganous oxide were satisfactory. Ti⁺⁴, La⁺³ and Ce⁺⁴ give a formal octet at the metal, as do the formal oxidation states in magnesia, alumina, and silica. The noble electronic configuration appears to be a favorable factor.

It is noteworthy that calcium and magnesium were not equivalent. A recent correlation of coal ash composition with melting behavior (10) distinguished elements on the basis of ionic radii and ionic potential. Magnesium fell with Si, Ti, and Al, while Ca fell with Na and K. The same trend appears to hold for reaction with alkali iron sulfates.

Another trend is that with the stability of the sulfate of the additive. Satisfactory additives with sulfates unstable at 1100°F were TiO₂, SiO₂ and Al₂O₃. Poor performers with stable sulfates at 1100°F included CuO, ZnO, CaO and MnO. MgSO₄ is stable, but less so than CaSO₄. Generally materials with unstable sulfates were more effective.

Since some of the heavier elements performed poorly, a study was conducted to assure that the results in Table 2 were not biased by unequal additive: sulfate mole ratios. It was determined that one mole of MgO per 0.23 moles of trisulfates was needed for a satisfactory product. All of the other oxides were then reacted with the sulfates at that mole ratio and their performance relative to MgO was not changed from that shown in Table 2.

The addition of a second component increased effectiveness in some cases. Calcium silicate performed better than CaO, and one MgO-Al₂O₃ mixture was superior to magnesia or alumina alone. The latter may have been due to spinel formation as shown in Table 3.

TABLE 3. Crystalline Reaction Products

<u>Additives</u>	<u>Temperature</u>	<u>Products</u>
MgO	1100°F	MgSO ₄ , K ₂ Mg ₂ (SO ₄) ₃ , (K, Na) ₃ Fe(SO ₄) ₃ *
MgO	1800°F	MgO, K ₂ Mg ₂ (SO ₄) ₃ , MgFe ₂ O ₄ *
Al ₂ O ₃	1100°F	Al ₂ O ₃ , (K, Na) ₃ Fe(SO ₄) ₃
Al ₂ O ₃	1800°F	Al ₂ O ₃ , Unidentified*
Al ₂ O ₃ 71.7 MgO 28.3	1100°F	K ₂ Mg ₂ (SO ₄) ₃ , Al ₂ O ₃ , Unidentified*
Al ₂ O ₃ 71.7 MgO 28.3	1800°F	MgAl ₂ O ₄ , K ₂ Mg ₂ (SO ₄) ₃ , Unidentified*

* Minor

The identification of the reaction products showed that magnesia reacted to form K₂Mg₂(SO₄)₃. No reaction was apparent for alumina. Its beneficial effects were due to dilution and absorption. At 1800°F magnesia and alumina reacted to form the spinel MgAl₂O₄. Alumina has been shown to be an effective adjunct to magnesia for conditioning oil ash deposits (11), and spinel has been identified in those deposits. The same beneficial effect is apparent here.

With Matrix

The results in Table 4 are cautionary and provide no simple trend to allow one to predict the relative performance of the additives.

TABLE 4. Additive Evaluation with Matrix

<u>Additive</u>	<u>Matrix</u>	<u>Product at 1800°F</u>
Control	Eastern or Western	melt
MgO	Eastern or Western	sl. fusion, sticking
Al ₂ O ₃	Eastern or Western	sl. fusion, sticking
SiO ₂	Eastern or Western	melt
MgO 28.3 Al ₂ O ₃ 71.7	Eastern or Western	powder, some sticking
MgO 50 SiO ₂ 50	Eastern or Western	powder, some sticking
CaSiO ₃	Eastern Western	melt powder, some sticking

Magnesia, alumina, their combination and the magnesia-silica combination showed satisfactory performance. Beneficial effects of mixtures were again seen for these materials, as the combinations were superior to MgO or Al₂O₃ alone.

However, silica, which performed well in the absence of the matrix, was unsatisfactory. The formation of the melt with the Eastern matrix was not predictable by standard composition-behavior correlations (12). The extreme difference for the two matrices with CaSiO_3 was also surprising. This unpredictability is a reflection of the complex chemical system involved. The complexity may be seen in mechanistic studies which have been reported (13). An empirical approach is suggested.

CONCLUSIONS

The corrosive components of superheater deposits may be chemically treated by a wide range of materials, both acidic and basic. They include magnesia, alumina, titania, silica and rare earth oxides and their combinations.

Only those additives which form high-melting friable products with the alkali iron sulfates in the presence of a matrix of bulk ash should be used. It is not possible to predict suitability from composition at this time.

Suitable additives may be selected empirically by studies such as the present one using samples of the appropriate deposits. The studies may be conducted by reputable chemical treatment suppliers.

Suppliers and boiler operators must then work in close cooperation to apply the additives in such a way that maximum benefits may be achieved. Only with such cooperation may the difficulties inherent in a high-ash fuel be overcome.

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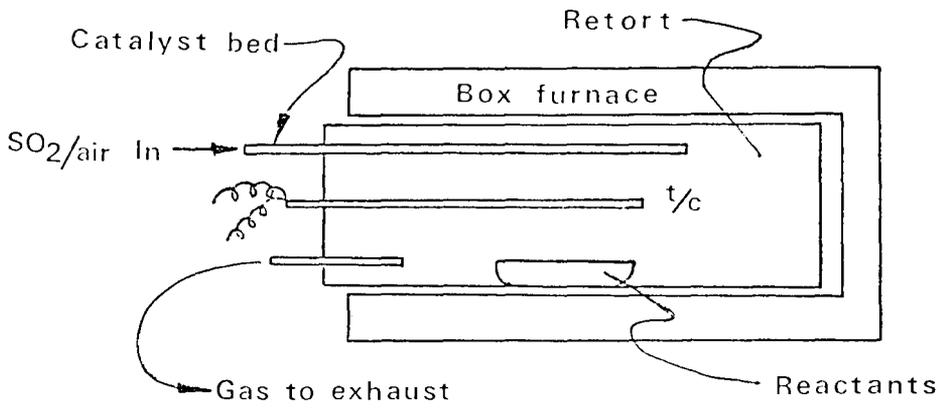


Figure 1 Furnace & Retort