13. Project Environmental Aspects

The basic premise of the test facility is to operate it in such a way that it does not increase criteria pollutants over what would normally be emitted from the Fort Martin Station if the GPIF were not operating.

The test gasifier will potentially prove to be an air pollution control system for SO2, NOx, particulate and CO2 mitigation, followed by a hot cyclone for additional particulate removal. An internal PyGas™ gasifier limestone based hot gas cleanup system to remove sulfur will be tested. Emissions are expected to be maintained well within limits of the new Clean Air Act for both 1995 and the year 2000 requirements with this potential second generation IGCC system which the project sponsor considers will likely become "Best Available Control Technology" (BACT).

14. Emission Reduction of NOx

NOx reduction during testing is anticipated to be achieved via a two pronged approach:

1. It has been shown that ammonia generation from fixed-bed gasifiers can be reduced by operation at low moisture (steam injection) levels in the gasifier where the coal's fuel bound nitrogen is released. The PyGas™ coal gasification process provides for coal devolatilization within the pyrolyzer section of the gasifier which is logically where fuel bound nitrogen will be released. The significant modelling effort using both the METC-MGAS and the KRW kinetic rate limiting mathematical expressions produced excellent results when less steam injection is introduced into the pyrolyzer or the top gas region of the PyGas™ gasifier. This is very significant in that it can be logically concluded that the PyGas™ gasifier can be controlled to produce the least amounts of ammonia when compared with other gasifiers by admitting less steam into the reaction where devolatilization and fuel nitrogen is released.

2. Acurex Corporation (DE-AC21-86MC23275) demonstrated 95% to 98% ammonia destruction through the use of staged combustion of low Btu coal gas. They concluded that ammonia is cracked in the first rich-burning stage, and higher pressure accelerates kinetics which favor more rapid ammonia destruction. They also concluded that fuel nitrogen can be controlled effectively.

It is the intention of this project to test rich/lean combustion of the low Btu coal gas produced from the PyGas™ gasifier, which we expect will demonstrate effective control of NOx generation from the minimized ammonia produced from the PyGas™ gasifier.

Relative to current Fort Martin Unit #2 NOx emissions, the GPIF will generate considerably less NOx per unit of heat input because of the longer flame development and lower peak flame temperatures associated with low Btu/cu ft coal gas combustion. It is reasonable to expect at least a 25% NOx reduction, however, since the firing rate is only approximately 1.5% of the Fort Martin Generating Station firing rate, an overall insignificant NOx reduction is expected.

15. Greenhouse Gases and Air Toxics

There will be a slight theoretical, but likely unmeasurable increase in carbon dioxide and air toxic emissions during GPIF operations. This is due to minor anticipated GPIF thermal losses and heat losses through the insulation of the steam piping between the GPIF and Fort Martin Generating Station. The increase is expected to be on the order of 0.07%.

Although no direct reductions in carbon dioxide and air toxic emissions are anticipated from the GPIF during testing, successful testing will lead to coal fired power generating systems which will directly result in the reduction of greenhouse gases and air toxics.

Socioeconomically, eventual retrofitting any existing pulverized coal fired furnaces with coal gas burners, and repowering with the PyGas™ coal gasification process utilizes most of an existing coal fired power plant, and increases its output by 15% while reducing the coal input by 13%. Therefore, all emissions are proportionally reduced. The following calculated expected effluent quantities were produced for a CCT IV 300 MWe Fig. 2A Ref. Plt.:

Table 8
Effect of Repowering on Effluents

Effluent	Reference Plant	PyGas™ Gasifier R/R Plant
(Ref. Plt.)	lb/MMBtu	lb/MMBtu
117.6 tons coal/hr 12,360 BTU/lb		
SO_2	3.8	0.01
NO_x	1.2	0.03
CO_2	200	174
Particulates	.1	.03
SO_3	0.050	0.003
H_2S	unk	13% less
HCl	0.080	0.013
	tons/ton coal	tons/ton coal
Spent Sorbent	-	0.39
Coal Ash	0.16	0.16
Wastewater Suspended Solids	unk	13% less
Sulfur Byproducts	unk	0.05 liquid SO_2
Water Consumption	unk	13% less

Future fully implemented coal gas burner retrofits to the existing furnaces with the GPIF PyGas™ gasifier in a combined repowering cycle are expected to reduce CO_2 (greenhouse gases) by 13% compared to the 300 MW Reference Plant. This is because the cycle heat rate is 8,281 BTU/kw vs. 9,493 BTU/kw for the Reference Plant. Construction of the GPIF and its subsequent test program are essential to meeting these future reduction potentials of full sized plants.

16. Production and Handling of Other Effluents

It has been reported by PSI Technology Company (DE-AC21-89MC26291) that aluminosilicates which occur naturally in coal ash are capable of tieing up previously volatilized alkali species upon their condensation, a phenominon which occurs within the PyGas™ coal gasifier during the endothermic char gasification reactions.

In like manner, it is likely that other volatilized trace metals can be effectively controlled within the PyGas™ coal gasification vessel, such that they become part of and are removed with the bottom ash from the PyGas™ gasifier. Since the final gasification process prior to the removal of gasifier ash is that of combustion of remaining ash carbon, the ash is subjected to an oxidizing atmosphere where such metals can become chemically stabilized and rendered non-leaching.

Coal ash is an unavoidable by-product of any coal conversion process, and must be discharged as a solid from the gasification system. Other solid wastes include desulfurization system by-products, and a small amount of sorbent material from zinc ferrite pellet decomposition from decrepitation. The quantities of such materials can only be determined by testing which is the objective of the GPIF project.

Liquid wastes include storm water runoff, submerged combustor blowdown and boiler water blowdown. These streams will be collected in a waste water holding tank and returned to the existing Fort Martin Station waste water system.

Acids and bases from the waste water holding tank will be neutralized before discharge back to the Fort Martin wastewater treatment system. Sanitary waste streams will be collected, removed from the premises by permitted sanitation trucks and treated in the conventional manner for such systems.

A distinct advantage of hot gas cleanup systems is that they do not produce process condensates which could contain dissolved and suspended hydrocarbons, ammonia, and other contributors to chemical oxygen demand (COD), and biological oxygen demand (BOD), and toxicity, because the coal gas is maintained well above the dew point of condensible species.

17. EHSS Compliance

Emissions regulations with which the GPIF will comply are:

- Existing Source Performance Standards (ESPS) as defined for coal fired utility boilers under the new Clean Air Act.

- National Pollution Discharge Elimination Standards (NPDES), state and local regulations for cooling water discharge.

- RCRA, state and local solid waste disposal regulations.

It is expected that testing will confirm that the GPIF will comply with the criteria emission limits of the Clean Air Act, and the ultimate result of this R&D facility will be the development of combined cycle systems which will achieve stack emissions levels well below those required by the new Clean Air Act. The new Clean Air Act required levels are interpreted to be as follows:

SO2:	50% SO2 reduction by 1995, and 1.2 lb/million Btu by the year 2000 for high and medium sulfur coal
NOx:	0.6 lb/million Btu
Particulates:	0.03 lb/million Btu

Compliance with OSHA regulations for personnel protection will be ensured during construction and initial subsystem test operation of the GPIF.

18. Plan For EHSS Risks and Impacts

Due to the flamable and toxic nature of coal gas, monitoring and alarm systems as well as a flare dump stack are planned. Carbon monoxide and hydrogen sulfide monitors are expected to be placed at several strategic locations within the coal gasification and hot gas cleanup systems. Self contained breathing apparatus will also be located throughout the facilities.

Continuous in situ emission monitoring is expected in the flue gas ductwork and at the exit of the hot gas cleanup system to assure emission levels are within compliance levels. Provisions for alarming and fail safe plant operation are anticipated in the event of a major system failure resulting in a master fuel trip. As with all fixed-bed coal gasifiers, it is anticipated that the PyGas™ gasifier will be capable of being "banked" by subtending coal, steam, and air flow.

Monitoring:

A summary of monitoring categories is as follows:

- Process Monitoring
- Stack
- Ambient Air
- Solid Waste
- Waste Water
- Industrial Hygiene

Detailed monitoring plans will be prepared during the permitting process.

Toxic elements are present in trace levels in coal ash. Emission of these trace elements to the atmosphere, although not currently regulated, are being given considerable scrutiny by regulators and technologists. Following is a listing of average values of trace element in 101 coal analyzed by the Illinois State Geological Survey. The potential concentrations and tonnages of these trace elements released to the atmosphere are:

Table 9
Trace Elements Present in Coal Ash

Element	Amount in Coal, ppm	Amount Emitted, Tons/Year
Lead	34.8	24,673
Arsenic	14.02	9,940
Cadmium	2.52	1,787
Selenium	2.08	1,475
Beryllium	1.3	922
Mercury	0.2	142

The emissions of trace metals may be controlled to an as yet undeterminable extent within the PyGas™ gasifier vessel by virtue of its endothermic cooling zones where coal ash is exposed and available to chemically tie up those trace metals which condense at the operating temperature of the gasifier (1200°F to 1500°F).

Since typical fixed-bed gasifiers including the PyGas™ gasifier are designed to operate below the coal ash melting temperature, less metal volatilization can be expected than from the pulverized coal fired burners which the PyGas™ gasifier is replacing. Therefore, less emissions of trace metals can be expected from the PyGas™ gasifier than from pulverized coal burners and entrained bed gasifiers which operate at very high temperatures.

There exists the potential for the CaSO4 "blinding" of CaS crystals formed through the reaction of calcined lime and H2S within the gasifier vessel. Since the potential of CaS existence in the solid waste product from the gasifier could eventually lead to the release of H2S to the atmosphere, consideration of several hydration options is being planned for this GPIF project. This approach involves the quenching of hot gasifier solid waste directly in an oxygenated aqueous tank either under gasifier or atmospheric pressure. This process is being designed to release and react trapped CaS by submerged combustion forming hydrated CaSO4.

19. Viability of the PyGas™ Gasification Concept:

There exists significant data to suggest the viability of the two major components which comprise the PyGas™ gasifier, and the use of limestone as a sulfur capture agent.

C. Lowell (Wormser Engineering) et al demonstrated as high as 95% sulfur retention by the use of limestone injection with the coal into a "slug flow" pyrolyzer operated at 1600°F and of the same geometry as the one used within the PyGas™ gasifier vessel. Since the PyGas™ coal gasifier operates at from 1300°F to 1600°F in its rapid devolatilization pyrolyzer section, it is expected that the limestone will calcine as it does at these temperatures in any fluidized bed process, and will subsequently form calcium sulfide while in the pyrolyzer section of the PyGas™ gasifier. In this manner, it is expected that the limestone will not "deadburn" at these temperatures as it might be expected to in conventional fixed-bed gasifiers operating at 2300°F. Once CaS is formed along with char in the pyrolyzer, it is further expected that increasing the gasifier operating temperature to 2300°F at the top of the gasifier by combusting pyrolysis gases will not adversely affect the CaS solids since both the METC MGas and the KRW kinetic rate models predict very rapid endothermic gasification and temperature drop to the vicinity of 1500°F within a very short distance within the upper solids bed. Similarly, it is believed that the lower PyGas™ gasifier solids bed region will allow the CaS to oxidize to CaSO4 since the grate area operates in an oxidizing atmosphere.

J.M. Eakman (Exxon Research) et al identified that alkali metal gasification catalysts increase the rate of steam gasification, promote gas phase methanation, and minimize agglomeration of caking coals in a slugging pilot scale unit whose geometry was very similar to that of the Offeror's proprietary gasifier pyrolysis section.

C.Y. Wen (West Virginia University) et al concluded from their entrained-bed coal gasification modeling that the effect of total pressure increased carbon conversion at any steam to fuel ratio. They also concluded that increasing oxygen to fuel ratios increased carbon conversion at any operating pressure and at an optimum steam to coal ratio. The existence of an optimum steam to fuel ratio is important, because one can obtain the same carbon conversion at a lower oxygen feed by maintaining optimal steam to fuel ratios in the 0.4 to 0.5 range. Moreover, their carbon conversion efficiencies considerably exceeded that required by the pyrolyzer section of the PyGas™ gasifier indicating that acceptably high carbon utilization may be expected thereby minimizing conventional fixed bed gasification air and steam requirements.

H.S. Muralidhara (West Virginia University) et al concluded from their study that after initial pyrolysis kinetic reaction rate increases in direct proportion to calcium content of the coal. This may prove valuable to the Offeror's proprietary gasification process and may serve to explain in part why C. Lowell et al achieved greater than 50% carbon utilization during carbonization.

D.E. Woodmansee et al (General Electric) found that the efficiency of converting coal enthalpy to cold gas fuel value increased by 4% when the steam/air mass ratio was reduced. This is consistent with the Offeror's concept of pyrolysis and cracking control by air flow with minimization of steam flow, and water spray for gasifier combustion zone temperature control in lieu of steam injection.

E. J. Nemeth et al (U.S. Steel Corporation) pilot scale results showed that the desulfurization of coal-derived gas at 1500 to 1770 °F is feasible. They found that desulfurization of the hot reducing gas initially exceeded 97% removal of H2S with dolomite.

C.Y. Wen et al (West Virginia University) stated that the understanding of coal pyrolysis is very important in view of the potential of the process to take advantage of (1) the phenomena of rapid pyrolysis and (2) obtaining higher yields of gaseous hydrocarbons by the application of pressure and hydrogen atmosphere. It was also stated that pilot plant studies of Union Carbide showed that of gaseous hydrocarbons is improved significantly under high partial pressure of hydrogen. The char-gas reactions that take place during the second stage following the pyrolysis reaction may be classified into two distinct categories, namely volumetric reactions and surface reactions. Thus, diffusion is an important step in heterogenious char-gas reactions. Higher hydrogen partial pressure improves the carbon conversion in the first stage of fast pyrolysis. For this reason, the Offeror intends to provide for the introduction of steam into the pyrolysis section of the gasifier along with the coal, limestone, and air.

Squires et al experiments showed that there is practically no liquid tar in the volatiles at temperatures above 1650°F when the gasification was done in a hydrogen partial pressure of 100 atm. and at a rapid rate.

If in the char-oxygen reaction (burning of char), the temperature and/or the particle size decrease substantially, the reaction may proceed toward the chemical; reaction control regime, and it may take place uniformly throughout the internal pore surfaces of the particles. This observation may allow the Offeror's gasifier to operate at lower steam to coal ratios in the gasifier combustion zone without experiencing the ash melting problems of conventional fixed bed gasifiers.

Wen observed that very little study has been done on the relative reactivities of different coal-chars in char-steam reactions. Jenson, Klei et al, and Kayembe et al each demonstrated that carbon-steam or char-steam reaction is chemical reaction controlled for smaller carbon/char particles (roughly <500 micron) and at temperatures up to 1800°F. At these conditions, the reaction occurs uniformly throughout the interior of the pore surfaces of the solid particles.
Wen concluded that the phenomena of pyrolysis, particularly those of rapid and flash pyrolysis are yet to be understood well. The GPIF will be an excellent way to correct this deficiency.

Since the PyGas™ gasification process also is intended to crack gaseous tars, it is expected to result in significantly less tar sulfur related sulfur bypass of the hot gas cleanup system, and far less concern for operational constraints relating to tar and carbon-black thermophoresis pluggage potential downstream of the gasifier than currently exists for current fixed-bed gasifiers.

The anticipated condensation of volatilized alkali onto the coal ash within the gasifier where it can be stabilized by the aluminosilicates in the ash represents yet another very substantial technological advantage of the PyGas™ coal gasification process.

Another technical advance of PyGas™ type of coal gasification process was demonstrated by Acurex under DOE contract. Less ammonia conversion to NOx was reported for low Btu gas combustion than for medium Btu gas. When combusted in a rich/lean mode, as much as 95% NOx reduction resulted. Additionally, when low Btu PyGas™ gasifier coal gas is also combusted in the burners of an existing retrofit/repowered boiler with turbine exhaust gas, a significant amount of NOx reduction by "reburning" can also take place. West Texas Utilities San Angelo plant demonstrated a 50% reduction in the NOx that had been produced by the gas turbine when operated in the fired gas turbine and fired boiler combined cycle mode.

Yet another technical advance which the PyGas™ gasifier enjoys over other fixed-bed gasifiers is its consistently relatively high raw gas exit temperature (1200°F to 1500° F). Typical coal gasifiers cannot control their raw gas exiting temperatures due to the evaporative process of the entering coal's moisture which can vary daily with coal moisture content.

Particulate carryover from the PyGas™ coal gasifier is expected to be very low since none of the coal feed fines can bypass the gasification process as with most fixed-bed coal gasifiers.

Existing boilers fired with high gas mass flows as is the case for a fired combined cycle retrofit/repowered boilers with low Btu PyGas™ gasifier coal gas produce more burner turbulence, better mixing and low CO emissions.

The final technical advance is the ability of the PyGas™ gasifier to produce exit gas temperatures very near the optimum for hot gas cleanup systems. This is in deference to the very hot slagging gasifiers which must either quench their gas (very inefficient), or indirectly cool their gas which shifts more heat to the less efficient Rankine thermodynamic cycle and away from the more efficient Brayton thermodynamic cycle.

Therefore, the the PyGas™ gasifier coal gasification process claims the following TECHNICAL ADVANCES:

1. Operates even on eastern high caking bituminous coals.
2. Cracks tars, promotes high temperature thermophoresis avoidance
3. Liberates tar related sulfur promoting higher hot gas cleanup system sulfur capture.
4. Condenses and captures volatilized alkali with in-bed ash-aluminosilicate bonding.
5. When low Btu PyGas™ gasifier coal gas is fired in a gas turbine, then fired in a retrofit/repowered existing boiler on turbine exhaust gas, the an emission of rate less than 0.1 lb/MMBtu of NOx is anticipated even without an SCR.
6. High raw gas exit temperatures consistent with the needs of hot gas cleanup systems.
7. Low particulate carryover since coal feed fines cannot bypass the gasification process.
8. Low Btu coal gas combustion increases turbulence and mixing in existing burners producing low CO emissions.
9. Not requiring significant raw gas cooling (with associated Btus going to the Rankine cycle) keeps more Btus in the more efficient Brayton cycle.

All the above result in the following emission expectations for SO2, NOx, CO, and particulates:

- 99.5+% sulfur removal capability with hot gas cleanup (zinc ferrite type) due to the release of tar bound sulfur by cracking within the PyGas™ gasifier vessel.

- 97.5+% reduction of oxides of nitrogen due to low Btu gas firing in an auxiliary steam generator with exhaust gas ducted back to the existing precipitator.

- While CO per cent reduction expectations vary with each individual application, existing boilers fired with high gas mass flows as is the case for a fired combined cycle retrofit/repowered boiler produce more burner turbulence, better mixing and low CO emissions.

- 99.9+% particulate removal mostly within the PyGas™ gasifier vessel since coal feed fines do not bypass the gasification process as with most fixed-bed coal gasifiers.

The following test data illustrates the flexibility of the PyGas™ coal gasification process. The operating temperature of the pyrolyzer section is controlled by the quantity of air flow to it. The anticipated operating temperature range is from 1300°F to 1600°F which requires from approximately 14% to 27% of stoichiometric air for pyrolysis.

In 1973, Menster, et al illustrated "rapid pyrolysis" as a method of carbonizing many different U.S. coals. In 1982, Lowell, et al showed strikingly similar results when operating their pyrolyzer on caking bituminous coal with air as shown in the devolitization versus operating temperature figure.

The pyrolyzer turndown tests showed that very high rates of organics being driven into gaseous state (approximately 50% by weight) was possible over a very wide operating range while holding operating temperature constant by simply varying air flow to the pyrolyzer.

These most significant developments show conclusively that adding a pyrolyzer such as contemplated by the PyGas™ gasifier increases the gasifier yield by avoiding liquid phase tars, as well as by quickly consuming 50% of the coal in a relatively small fluidized bed vessel operated in the "slug flow" regime.

If all that the PyGas™ gasifier ever did was to condition caking coal to avoid agglomeration, it would no doubt be considered very successful. However, the PyGas™ gasifier actually performs several additional process benefits in the gasification of coal. These include cracking tar, condensing volatilized alkali, preventing coal fines carryover from the gasifier, producing raw gas at temperatures ideal for hot gas cleanup systems, and handling coal of any expected moisture content with no adverse affect on gasifier exit temperature.

Additional air is specifically introduced at the top of the gasifier to raise its operating temperature sufficiently to crack the tars driven to gaseous form during pyrolysis. To do this requires only to add air until the gasses at the top of the PyGas™ gasifier reach approximately 2300 F. The specific coal inorganic fraction fusion characteristics will dictate more precisely the top gas operating temperature just as it does for conventional fixed-bed gasifiers.

As both char and coal gas pas co-currently downward through the PyGas™ gasifier, endothermic reactions predominate thus cooling both from 2300°F to approximately 1500°F by producing hydrogen and carbon monoxide. In so doing, any volatilized alkali have the opportunity to condense onto the coal ash and become tied up by naturally occurring aluminosilicates in the ash, and subsequently are removed from the PyGas™ gasifier along with the ash in the conventional fixed-bed coal gasifier way. This process provides for volatilized alkali condensation and removal on the coal ash while within the PyGas™ gasifier vessel rather than on combustion turbine blades at 1800°F where significant damage can occur.

The PyGas™ gasifier forces all of the incoming coal to pass entirely through the entire pyrolyzer and gasifier sections before it can leave the gasifier. This virtually assures that no coal fines can bypass the gasifier as is commonly the case for any counter-current fixed-bed gasifier with gasifier top coal feed and raw gas removal. This then eliminates concern that coal fines might plug downstream piping due to thermophoresis and tar condensation both well known conventional fixed-bed gasifier realities. It also allows much more flexibility to the hot gas cleanup system mechanical hardware design which up to now has been limited by coal fines and condensible tar carryover concerns.

Since the last stage of the PyGas™ coal gasification process is that of carbon gasification, the raw gas exit temperature will always be very close to the optimum for zinc ferrite types of hot gas cleanup systems, in the 1200°F to 1500°F range. This is a decided advantage as opposed to either the molten slag bottom entrained bed gasifier types which produce raw gas too hot for hot gas cleanup systems, and conventional fixed-bed gasifiers whose raw gas product is often too cold depending on how much coal moisture had to be evaporated hence cooling down its exiting temperatures.

Irrespective of coal moisture content, the PyGas™ gasifier's raw gas exit temperatures remain nearly constant at near optimum hot gas cleanup temperatures. Conventional fixed-bed gasifiers which have little control over raw gas exit temperatures affected by incoming coal moisture will create significant difficulty for hot gas cleanup system control.

Based upon the significant past success of pyrolyzers (sometimes called "carbonizers") built and operated by several U.S. Government agencies as well as independent private organizations, and owing to the simplicity of merely placing such a device within the confines of a fixed-bed air-blown coal gasifier vessel in such a manner that gravity alone is necessary to move the products of pyrolysis into the conventional gasifier, the decision by the DOE to accept the PyGas™ gasifier as "ready for testing" is quite reasonable.

20. OVERVIEW OF THE PyGas™ PROCESS

Crushed coal (1/4 x 0) is pneumatically conveyed to the pyrolyzer. Upon entry into the preheated pyrolysis cone, the oxygen in the air reacts with the coal to provide the necessary heat to rapidly drive off the volatile content of the coal. The rapid devolatilization of the coal results in gaseous "bubbles" that pass upward through the bed and exit the top of the pyrolyzer tube. This action, along with the continuous feed of air and coal, moves the char/ash granules, at a slower rate than the gases, toward the top of the pyrolyzer. The solids flow over the edge of the pyrolyzer tube, falling by gravity onto the upper fixed bed while the gases disperse into the upper zone of the gasifier and subsequently down through the upper solids bed. Injection of air and steam into the top of the gasifier partially oxidizes the exiting pyrolyzer gases. This raises the mean bulk gas temperature of the upper gasifier zone. The resulting high temperatures crack hydrocarbon compounds that have resulted from pyrolysis. The hot gases in the upper zone of the gasifier then flow co-currently with and through the carbon/ash (char) bed. Gasification of the carbon in the upper bed occurs until the bed temperature (cooling off due to the endothermic gasification reaction) reaches approximately 1300° F to 1500° F.

While the upper gasifier zone gases endothermically cool in the presence of carbon/ash (char) from approximately 2300° F, any previously volatilized alkali is expected to condense onto the char. There it can become chemically bonded to and hence stabilized by alumionsilicates present in the ash as the gases cool to 1300° F to 1500° F.

At this point, gases evolved through the upper bed flow out of the gasifier. The remaining carbon in the char is consumed in the typical fixed-bed gasification manner through the lower bed. Air and steam are introduced through the gasifier grate. Entering oxygen consumes carbon in the lower bed to raise bed temperatures to approximately the ash fusion temperature. As the gases pass counter-current to the char/ash particles, carbon is consumed by endothermic gasification reactions. Gases evolved from the lower and upper beds then combine and exit the gasifier. Air and steam requirements to the grate are controlled to ensure that the ash exiting the gasifier contains less than 5% carbon by weight.

21. THE PYROLYZER

Pyrolysis is the chemical change created by the addition of heat in a reducing atmosphere. Gasification is the phase change from solid to gas also produced by the addition of heat also in a reducing atmosphere. As coal enters any gasifier, it must be heated to gasification reaction temperatures. During heating, volatiles-the light gases (ie CO, CO2, H2, H2S, & NH3) and condensable hydrocarbons (referred to as tars)-are released. The release of the volatile products is directly affected by the heating conditions. As coal is heated, its volatiles form bubble-cell structures throughout the coal. Under rapid heating conditions (10^4 °F/sec), the expansion of the volatiles within the bubbles quickly reach high enough pressures to "break" the bubbles and escape before the coal particle expands. However, as the heating conditions decrease to under 10^3 °F/sec, the coal particles swell before the pressure within the "volatile bubbles" is high enough to rupture the "bubbles" [2]. The phenomenon of tars forming a sticky surface coating on coal results in adjacent particles "sticking" together and forming an incipient clinker. This phenomenon is known as agglomeration. Air and steam pass around such agglomerated lumps following a path of least resistance. This bypassing results in a diminished gasification reaction since the air and steam cannot reach the unreacted coal contained within the agglomerated lump. When this happens, channeling occurs within a gasifier and its productivity and efficiency quickly diminish.

Rapid devolatilization occurs in the PyGas™ pyrolyzer section. The rapid heating liberates the tars in gaseous form rather than tacky liquid form. Thus, the agglomeration characteristics of highly caking coals from most eastern American bituminous seams becomes irrelevant.

The PyGas™ pyrolyzer resembles the pyrolyzers used by the United States Bureau of Mines to devolatilize, a process sometimes called "carbonization" various coals. In addition to reviewing their empirical relationships, reports produced by Wormser Engineering, Inc. and West Virginia University were reviewed to model the pyrolyzer performance. A major objective of PyGas™ is the rapid devolatilization and maximization of carbon conversion in the pyrolyzer. This, in turn, minimizes air and steam requirements needed to gasify the remaining carbon (char) in the fixed bed gasifier section. Volatiles released, and thus carbon conversion, can be higher than ASTM predictions. The US Bureau of Mines notes that bituminous coal volatile yield peaks at approximately 1300° F if rapid heating is applied. On the other hand, if the heat rate is slowed down, the volatile yield becomes proportional to pyrolysis temperature [3].

Reviewing material from US Bureau of Mines reports and other experimental work has shown that pyrolysis done by rapid heating has a distinct temperature in which maximum carbon conversion is achieved. Therefore, the PyGas™ pyrolyzer will be operated under controlled conditions at the temperature that achieves the greatest carbon conversion.

Once the temperature has been chosen to ensure maximum volatile release, the amount of air needed to provide the pyrolysis temperature and to ensure rapid heating is determined. A study conducted for the Department of Energy under contract No. DE-AC21-78MC-10484 by Wormser Engineering, Inc. found that pyrolyzer temperature is a function of air fed to the pyrolyzer [4]. Hence, an equation to relate pyrolyzer temperature to air feed was derived and incorporated into the math model. Once the air feed rate per unit of coal to the pyrolyzer and carbon conversion is calculated, the composition of the product gases must then be determined. The following reactions occur in the pyrolyzer:

Reaction 1 and 2 : (oxidation of carbon)

(1) $C(s) + O_2(g) \longrightarrow CO_2(g)$ Heat Released = 169,293 Btu/mol

(2) $C(s) + 0.5\, O_2(g) \rightarrow CO(g)$ Heat Released = 47,550 Btu/mol

Reaction 3 : (reduction of carbon dioxide)

(3) $CO_2(g) + C(s) \longrightarrow 2CO(g)$ Heat Absorbed = 74,196 Btu/mol

Reaction 4 : (oxidation of hydrogen)

(4) $H_2(g) + 0.5O_2(g) \rightarrow H_2O(g)$ Heat Released = 104,036 Btu/mol

Reaction 5 : (formation of methane)

(5) $C(s) + 2H_2(g) \longrightarrow CH_4(g)$ Heat Released = 32,200 Btu/mol

Reaction 6 : (formation of hydrogen sulfide)

(6) $H_2(g) + S(s) \longrightarrow H_2S(g)$ Heat Released = 8,586 Btu/mol

Reaction 7 : (formation of ammonia)

(7) $0.5N_2(g)+1.5H_2(g) \rightarrow NH_3(g)$ Heat Released = 19,728 Btu/mol

The following assumptions with the above chemical reactions are used to calculate the gas composition at the exit of the pyrolyzer:

1. 90% of nitrogen bound in the coal forms ammonia, (although a link between steam to gasifier and ammonia generation exists, we currently have insufficient data to better correlate this conversion)
2. all of the sulfur forms hydrogen sulfide (even though a small amount of COS is formed, then partially cracked by the PyGas™ gasifier), and
3. methane formation is based on a study conducted by Lurgi under elevated pressure conditions [5].

Mass and heat are balanced using the above reactions to consume all the oxygen in the feed air and produce the desired pyrolysis temperature. The gas composition is then compared against predicted pyrolysis gas composition by the late Dr. C.Y. Wen, formerly of the Chemical Engineering Department at West Virginia University [6].

Pyrolysis Predicted Gas Composition
(volumetric percentages)

	WVU	PyGas™
CO	27.15	23.38
H2O	3.50	2.03
H2	18.55	19.50
CH4	3.74	4.75
CO2	4.71	4.16
N2	40.92	43.73
H2S	0.66	1.02

By virtue of agreement, assumptions and equations within the math model were believed to be reasonably accurate. In all cases developed with the math model and subsequently presented in technical papers, the results shown above were held constant since the pyrolysis performance shown above is believed to be maximized.

22. UPPER ZONE OF THE GASIFIER

Gases and solids exiting from the pyrolyzer are approximately 1300° F - 1600° F. These temperatures are too low for the gasification reactions to rapidly proceed and for exiting tars produced in the pyrolyzer to "crack." Temperatures are therefore raised in the upper zone of the gasifier by the simple introduction of air and steam. Maximum temperatures within this zone are set by the ash fusion characteristics of the coal. Exceeding this upper temperature limit causes an unwanted slagging environment within the gasifier. In the case of gasifying Pittsburgh #8 coal, the maximum temperature is approximately 2300° F. To achieve this temperature, the oxygen within the air combines with the combustible gases exiting the pyrolyzer. Steam is used as an inert medium to control peak temperatures or enhance hydrogen production. Since gases are more reactive than solids, the char and ash particles exiting the pyrolyzer are merely heated and fall unreacted to the upper gasification bed.

The combustible gases exiting the pyrolyzer consist of carbon monoxide, hydrogen, methane and a small quantity of condensable tars. The resulting high temperatures from the addition of air "crack" the condensable tars and methane. Any oxygen not consumed by the methane and tars is consumed by hydrogen and carbon monoxide to form water vapor and carbon dioxide, respectively. The following reactions are incorporated into the math model to predict gas composition after partial oxidation:

Reaction 8 : (oxidation of methane)

(8) $CH_4(g) + 2O_2(g) \text{---->} CO_2(g) + 2H_2O(g)$ Heat Released = 345,166 Btu/mol

Reaction 9 : (oxidation of carbon monoxide)

(9) $CO(g) + 0.5\ O_2 \text{-->} CO_2(g)$ Heat Released = 121,745 Btu/mol

Reaction 10 : (oxidation of hydrogen)

(10) $H_2(g) + 0.5O_2 \text{--->} H_2O(g)$ Heat Released = 104,036 Btu/mol

The first reaction is controlled by the formation rate of methane in the pyrolyzer. However, reactions (9) and (10) are a function of temperature and partial pressures of the gaseous constituents in the upper zone.

23. UPPER BED GASIFICATION

The upper zone oxidation results in peak temperatures of 2300° F when gasifying Pittsburgh #8 coal. This is high enough for the following endothermic gasification reactions to rapidly proceed:

Reaction 11 and 12 : (gasification of char)

(11) $C(s)+H_2O(g) \text{->} CO(g)+H_2(g)$ Heat Absorbed = 56,490 Btu/mol

(12) $CO2(g) + C(s) \rightarrow 2CO(g)$ Heat Absorbed = 74,196 Btu/mol

The following rate equations by METC [7] and KRW [8] were compared to determine which set would be used in the mass and energy balance to predict the gases evolved in the upper gasification bed.

Rate equation for reaction 11:

Used by KRW:
(1) rate = $k_2[C](K_2P_{H2O}/(K_2P_{H2O} + P_{H2}))$

Used by METC:
(2) rate = $930e^{-45000/RT}[C](P_{H2O} - P^*_{H2O})$

where:
$k_2 = 0.18*f_{RR}e^{48,200/R*(1/1255-1/T)}(1+0.5/K_2)$ hr^{-1}
f_{RR} - relative reactivity for coal compared to coke breeze at 1800° F - 3.2 for Pittsburgh #8 coal
R - universal gas constant
T - absolute temperature (K)
[C] - concentration of carbon
$K_2 = 2.25x10^6e^{-42,600/RT}$
P_{H2O} - partial pressure of water vapor
$P^*_{H2O} = P_{H2}*P_{CO}/e^{(17.29-16330/T)}$
P_{H2} - partial pressure of hydrogen
P_{CO} - partial pressure of carbon monoxide

Rate equation for reaction 12:

Used by KRW
(3) rate = $k_1[C](K_1P_{CO2}/(K_1P_{CO2} + P_{CO})$

Used by METC
(4) rate = $930e^{-45000/RT}[C](P_{CO2} - P^*_{CO2})$

where:
$k_1 = 0.06*f_{RR}e^{48,200/R*(1/1255-1/T)}(1+0.5/K_1)$ hr^{-1}
f_{RR} - relative reactivity for coal compared to coke breeze at 1800° F - 3.2 for Pittsburgh #8 coal
R - universal gas constant
T - absolute temperature (K)
[C] - concentration of carbon
$K_1 = 5.86x10^3e^{-27,000/RT}$
P_{CO2} - partial pressure of carbon dioxide
P_{CO} - partial pressure of carbon monoxide
$P^*_{CO2} = P^2_{CO}/e^{(20.92-20280/T)}$
P^2_{CO} - partial pressure of carbon monoxide squared

Partial pressures of the gases were varied to show that general agreement in the two equations can be obtained for a variety of conditions. At higher temperatures, the KRW rate equation predicts faster carbon conversion in reaction (11) than the METC (MGAS) equation. Also, the KRW equation predicts that the carbon-steam reaction will proceed below 1200° K (approx. 1700° F), while the METC (MGAS) equations show that this gasification reaction essentially quits below 1200° K (approx. 1700° F). While usage of the KRW equations results in a more efficient gasifier because of the higher conversion of carbon to gases at higher temperatures, only actual operation of the PyGas™ gasifier will demonstrate such potential rate limits.

Again, comparison of these two equations were checked over a range of gas partial pressures. Similarly as in the case of the carbon-steam reaction, the METC (MGAS) rate equation shows that gasification reactions substantially diminish below 1200° K
(approx.1700° F).

Both sets of equations were incorporated in a mass and energy balance to compare the results of the KRW rate equations versus the METC (MGAS) rate equations. Assuming enough air is added into the top of the gasifier to raise the gases and solids at the top of the upper gasification bed to 2300° F, and the gasification reactions proceed until the upper bed cools to 1500° F. The gases exiting the gasifier from the upper bed have a higher heating value of 152.6 Btu/scf using the KRW rate equations and 145.5 Btu/scf using the METC (MGAS) rate equations.

24. LOWER BED GASIFICATION

The gasification reactions that occurred in the upper bed resulted from the gas flowing co-currently with the bed. However, all of the available carbon is unable to be gasified in the upper bed due to the requirement to adhere to peak operating temperature limitations specific to each particular coal ash characteristic. This then results in the need for a lower bed to gasify the balance of the carbon. In the lower bed, the gasification reactions occur with the gases flowing counter-currently to the bed as is the case with most conventional fixed-bed gasifiers. Air and steam are introduced into the ash grate of the gasifier. The air/steam mixture comes in contact with the exiting ash to cool the ash down. Upon reacting with available char, all of the oxygen is consumed to form carbon dioxide and raise bed temperatures to allow the gasification reactions to begin. Once again, peak bed temperatures are controlled by the injection of steam with the air. Once the bed temperatures rise, the gasification reactions (11) and (12) proceed until heat absorbed during these reactions cools the lower bed to 1500° F. The resulting gas combines with gases evolved from the upper bed and both subsequently exit the gasifier. Air and steam requirements for the lower bed are based on the amount of carbon conversion in the pyrolyzer and upper bed and on the need to keep carbon in the exiting ash to less than 5% by weight.

25. MATH MODEL PREDICTIONS

A math model was developed to predict PyGas™ performance as the amount of air and steam injected into the top of the gasifier is varied. As mentioned above, the pyrolysis section was held constant over the cases to provide maximum carbon conversion in the pyrolyzer. The following assumptions were used to obtain the results

1. The ash contains 5% carbon.
2. Peak combustion zone temperature in the gasifier is 2300° F.
3. Gasification reactions continue until bed temperature reaches 1500° F.

4. Temperature and gas composition are uniform along the radial direction.

5. Gas and solid temperatures are equal at every point in the gasifier.

6. The process as modeled is adiabatic.

7. Pressure throughout the gasifier has been held constant.

8. The ash composition is simplified as SiO2.

9. Minimum Steam-to-Air ratio to grate of 0.4.

The amount of air added in case 1 resulted in the ability to reach upper zone temperatures of 2300° F without the addition of steam to the top of the gasifier. As more air is added to the top of the gasifier, additional steam must be added to keep temperatures from exceeding 2300° F. As the air-to-coal ratio at the top of the gasifier increases, total steam-to-coal ratio to the gasifier increases. As the air-to-coal ratio to the top of the gasifier increases, the amount of air needed for lower bed gasification decreases. The total amount of air for pyrolysis and gasification remains relatively constant over the range of upper area air-to-coal ratios. Carbon conversion can be optimized. As would be expected, as the amount of top air increases, the carbon conversion in the upper bed increases and the lower bed decreases. The amount of moisture in the product gas and the higher heating value of the product gas, respectively, are a function of top air-to-coal ratio. As the amount of air to the top of the gasifier increases, steam needed to maintain gasifier peak temperatures increases. The result is a gas with a large amount of moisture and a low heating value. Additionally, peak performance should be gained by operating the PyGas™ gasifier with minimal amount of steam to gasify the coal. Table 10 illustrates the gas constituents exiting the pyrolyzer, exiting the upper gasifier bed, exiting the lower gasifier bed, and finally the combined raw product gas.

Table 10
Predicted Gas Compositions at Various Stages in the PyGas™ Gasifier
Using DOE - CCT4 Reference Coal Analysis
(volumetric percentages)

COAL GAS CONSTITUENT	PYROLYZER EXIT	UPPER GASIFIER EXIT	LOWER GASIFIER EXIT	COMBINED RAW PRODUCT GAS
CO	23.8	27.39	23.51	26.34
H2	19.77	17.59	15.33	16.98
CO2	3.94	1.8	6.08	2.95
H2O	2.14	2.35	17.49	6.43
CH4	4.70	0.00	0.00	0.00
H2S	0.91	0.57	0.00	0.42
N2	43.31	49.13	37.14	45.90
Tars	<1.0	<0.1	<0.1	<0.1
Alkali (ppmv)	<.1	<.1	<0.01	<0.01
Temp (°F)	1300	1500	1500	1500
HHV (Btu/scf)	198	151	134	144

26. CONCLUSIONS

The PyGas™ coal gasification process promises to alleviate previous limitations in the type of coals that can be effectively gasified in an air-blown, fixed-bed gasification system.

1. Caking coals can be gasified without the adverse effects of sticky tars which have historically resulted in agglomeration in fixed-bed gasifiers.
2. It incorporates features to eliminate (by cracking) tar formations from exiting the gasifier and plugging downstream piping and equipment.
3. It provides a bed of ash on which volatilized alkali can condense and become retained by aluminosilicates either contained within or added to the coal ash.
4. By cracking sulfur containing tar formations, a previous concern of hot gas cleanup system sulfur bypass is eliminated.
5. High moisture containing coals can be gasified without lowering the gasifier exit temperature which would otherwise adversely affect the hot gas cleanup system, and without excessive exit gas moisture which can otherwise exceed turbine compressor surge margin limitations.
6. In contrast to slagging gasifiers, coals with high or low ash fusion characteristics can be gasified in this air-blown gasifier.
7. The exit temperature allows for optimum performance of the hot gas cleanup unit to remove sulfur compounds.
8. Utilized in concert with hot gas cleanup and a combination of auxiliary steam generator combustion followed by flue gas ducting back to the existing boiler precipitator breeching, emissions of SO2, NOx, and CO2 are expected to be the lowest ever achieved by an IGCC system.

The result is expected to be a clean, low-Btu gaseous fuel of approximately 150 Btu/scf at 1500° F, suitable for firing gas turbines, power boilers, and other combustion processes.

27. Description of the PyGas™ Gasifier

Coal is crushed and pneumatically conveyed with air and steam into the bottom of the pyrolysis reactor tube located in the center of the gasifier. Once in the pyrolyzer, the coal becomes rapidly heated to approximately 1600F, where its volatile content and some of its fixed carbon is converted into gaseous fuel (hydrogen, carbon monoxide, and methane).

Within the pyrolyzer tube, the gaseous fuel forms bubbles which rise to the top of the pyrolyzer tube in slug flow fashion gradually moving the remaining carbon and ash char granules upward until they too exit the top in fountain fashion where they fall due to gravity onto a fixed bed of carbon and ash char solids.

More air and steam is introduced into the top of the gasifier to further increase the temperature to approximately 2300F. This increases the kinetic rates of endothermic reactions to consume more of the fixed carbon in the fixed bed of char. As the gaseous products of hot pyrolysis gas and char solids pass co-currently downward through the gasifier, more carbon in the char converts to gaseous carbon monoxide endothermically cooling the products to approximately 1300F to 1500F.

The remainder of air and steam is introduced through the rotating ash removal grate to both cool the grate and consume any remaining carbon in the ash prior to ash disposal out the bottom of the gasifier.

The resulting hot raw coal gas exiting the gasifier is rich in hydrogen and carbon monoxide.

28. Unique Features of the PyGas™ Gasifier

The aforementioned proprietary pyrolysis-gasification process and device (although comprised of two previously singularly well proven concepts) is a genuine technological breakthrough in the coal gasification industry. Its unique configuration and process (unlike any other gasifier) allows all coal types and characteristics to be utilized in a very simple inexpensive gasification device. Following are several of its unique features:

28.1 Run of Mine Coal

All previous fixed bed gasifiers were confined to the use of carefully graded lump coal sizes (examples include Lurgi and Wellman Galusha). This meant that much of the coal is either wasted, or must be separated (at considerable expense) and briquetted in order to be utilized.

The PyGas™ gasifier uses crushed coal. It therefore uses all of the cheapest run of mine coals available without any costly coal sizing and briquetting equipment.

28.2 Air Blown

Most coal gasifiers currently under serious industry consideration require very expensive air separation plants to provide pure oxygen to their gasifier (examples include Texaco, Shell, & Dow).

The PyGas™ gasifier is designed to use air directly without the added expense of an oxygen production facility. Virtually all of the gas turbine manufacturers have agreed that the hot raw gas produced by the PyGas™ gasifier is acceptable for combustion in their equipment.

28.3 Caking Coals

Previous fixed bed gasifiers have a long history of operational difficulties when attempting to utilize highly (or even mildly caking) coals. Unfortunately, most eastern bituminous coals are of this caking type.

The PyGas™ gasifier avoids the agglomeration problems initiated by sticky tar and asphaltine formations by completely changing the process by which coal tar is vaporized and subsequently cracked to hydrogen and carbon monoxide within the gasifier. This is considered by some to be the single greatest the PyGas™ gasifier advancement to fixed bed gasification.

28.4 Tar Cracking

Previous fixed bed gasifiers produced nasty tar condensibles which historically plugged many downstream coal gas handling equipment. In addition, it has been found that the sulfur in such tar is not removed by hot gas cleanup systems. This phenominon has been a great setback to fuel cell advocates who require extremely high sulfur removal efficiencies for successful adaptation to future electrochemical power production concepts.

The PyGas™ gasifier assures complete cracking of coal tar at the high temperature transition from pyrolysis to gasification. This means that tar free gas exits the gasifier. In turn, this also opens the door to the PyGas™ gasifier applications to fuel cell combined cycles which potentially can double the efficiency of coal fired utility power plants (cutting global warming greenhouse carbon dioxide gas by one half).

28.5 Volatilized Alkali Control

Sodium and potassium sulfates have been known to condense on gas turbine blades creating unwanted corrosion and deposits which adversely affect blade life and operating availability. It is known that fluidized and slagging gasifiers produce from one to three orders of magnitude more volatilized alkali than fixed bed gasifiers. To date, the removal method of choice has been to spray cool the coal gas to condense out such harmful products. This significantly adversely affects efficiency and creates a water pollution concern.

The PyGas™ gasifier operates like a fixed bed gasifier in its final gasification stage, so it will not emit significant volatilized alkali. In addition, the PyGas™ gasifier enhances catalytic alkali condensation and reformation due to the presence of coal ash containing significant quantities of catalyzing aluminosilicate mineral species where condensation occurs.

28.6 Minimized Ammonia Production

Ammonia yield in gasification processes is maximized by the use of large amounts of steam. The configuration of previous fixed bed gasifiers exacerbates this problem since coal moisture is evaporated in the final stages of coal gas generation resulting in relatively high coal gas moisture and ammonia concentrations and subsequent fuel nitrogen related NOx emissions.

The PyGas™ gasifier promotes the consumption of moisture via endothermic reactions due to its process configuration in contrast to previous fixed bed gasifiers. This minimizes unreacted moisture and ammonia in its exit gas.

29. Emissions Characteristics

Low Btu coal gasification technology has already demonstrated emission levels which are considerably lower than NSPS for targeted source categories. All gasification combined cycle projects to date have demonstrated very low emission levels superior to either fluidized bed or scrubber technologies.

Now that "greenhouse gasses" and "global warming" concerns abound, it is time to demonstrate integrated gasification combined cycles (IGCC) because these more efficient power cycles can markedly reduce carbon dioxide emissions by some 20% to 25%. Since the PyGas™ coal gasification process produces low (150 Btu/scf) raw gas at approximately 1500°F, when combined with a hot gas cleanup system, it can produce the very highest efficiency of any coal gasification process to date. The reason for this is that the molten slagging entrained bed gasifiers produce such a high raw gas exit temperature that cooling it to hot gas cleanup system operating temperatures means transferring that sensible heat into the Rankine thermodynamic cycle (most tout steam generation types of hot raw gas cooling).

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Prepared by:
M.E. Morgan, J.J. Helble, and S. A. Johnson
PSI Technology Company
20 New England Business Center
Andover, MA 01810

Prepared for:
CRS Sirrine Engineers Inc.
1041 East Butler Road
Greenvile, SC 29606-5456

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1. ANTICIPATED TRACE EMISSIONS FROM GPIF FACILITY

This portion of the NEPA report is concerned with the emission of toxic metal compounds by the gasification process improvement facility (GPIF). The toxic metal emissions and all emissions of the GPIF facility must be put in context of its location. The GPIF facility will be located on site at the Fort Martin facility of Allegheny Power Company, and the energy produced (steam) will be directly used by Fort Martin to produce electricity. The coal used at the GPIF facility will be the same coal used by the utility. Therefore, the emissions of the GPIF will be put in context of the entire facility.

The GPIF assessment will be divided into four section:

- Estimation of the toxic metals content of the raw coal
- Calculation of the emissions from Fort Martin normally
- An estimate of the emission from the GPIF
- A comparison of the two flows

The Fort Martin facility average coal consumption rate is 622,000 lb/h. The GPIF facility will consume about 12,000 lb/h. Additionally, the GPIF facility will produce steam, which will be used to displace some of the steam from the Fort Martin facility, making the overall change in coal consumption, due to GPIF, negligible. However, the partitioning of the metals may change among the various streams, either favorably or unfavorably. The estimate of the partitioning of the metals is the main subject of the comparison.

1.1 Trace Elements in Coal

As the starting point in an analysis of trace element behavior at Fort Martin, the range of possible concentrations in the parent coal must be considered. This is because the behavior of trace elements in combustion systems is strongly dependent on both the concentration of the element and its form in the parent coal. The association of a trace element with a particular mineral can determine its combustion behavior (Boni et al., 1990); for example, elements associated with clays will likely be retained by the clays during combustion, whereas elements associated with pyrite will likely oxidize independently, and may therefore associate with the finer, more difficult to capture fly ash particles. In general, most of the trace elements are associated with the mineral constituents in bituminous coals, while a significant fraction may be associated with the organic matrix in subbituminous and lignitic coals (Raask, 1985).

The ultimate, proximate, and ash chemical analyses of the current coal used at Fort Martin is presented in Table 1. An analysis of the trace metals content of the Fort Martin coal was not available, therefore literature values were used. The results of a number of studies of the trace metal contents of coals and their forms are presented in Tables 2 and 3. The values of Finkleman (1992) were used for the assessment. The Finkleman values were calculated from an average of 6000 to 8000 coals contained in the National Coal Resources Data System (NCRDS) for the U.S. Geological Survey. The NCRDS values represent the most comprehensive and up-to-date summary of trace elements data on U.S. coals.

Table 1. Fort Martin Coal Analyses (As-Fired Basis)

		%
Proximate		
	Moisture	1.6
	Ash	15.1
	Volatile	28.9
Ultimate		
	Carbon	70.11
	Hydrogen	4.43
	Nitrogen	1.24
	Sulfur	0.93
	Oxygen	8.19
	Ash	15.1
Ash Composition (as the oxide)		
	SiO_2	55.7
	Al_2O_3	31.8
	Fe_2O_3	4.6
	TiO_2	1.6
	MgO	0.98
	MnO	0.03
	P_2O_5	0.23
	K_2O	2.5
	CaO	0.9

Table 2. Trace Element Concentrations in Pulverized Coals

Element	(A)	(B)	(C)	(D)	(E)
Sb*	**1.2**	-	1.3	1.1	2
As*	**24**	20	14	15	10
Ba	**170**	-	-	150	250
Be*	**2.2**	2.2	1.6	2	1
B	**49**	-	102	50	50
Cd*	**0.47**	0.9	2.5	1.3	1
Cr*	**15**	20.5	14	15	20
Co*	**6.1**	-	9.6	7	10
Cu	**16**	17.8	15	19	20
Pb*	**11**	-	35	16	20
Mn*	**43**	100	49	100	40
Hg*	**0.17**	0.21	0.2	0.18	0.1
Mo	**3.3**	-	7.5	3	3
Ni*	**14**	16.9	21	15	20
Se*	**2.8**	-	2.1	4.1	3
V	**22**	-	33	20	40
Uranium (238)	**2.1**	-	-	-	-
Thorium (232)	**3.2**	-	-	-	2

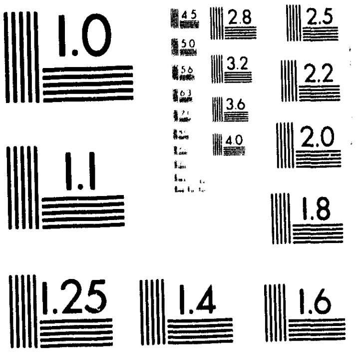
(A) - Finkelman (1992), mean of at least 7100 coals (except Cd = 6150) from

Bold indicates values used in mass balance calculations.
(B) - Brooks (1989), mean of 3572 bituminous coals in NCRDS as of 1982.
(C) - Ruch et al. (1974) mean of 101 samples Ill. bituminous; as reported in

(D) - Swanson et al. (1976) mean of 799 samples bituminous and

(E) - Smith (1980), mean value for a "typical" bituminous coal.

*Hazardous Air Pollutants identified in Title III/Section 112 of 1990 Clean Air Act Amendments


1.0
4.5
5.0
5.6
6.3
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

2 of 2

Table 3. Common Forms of Trace Elements in Coal

Element	Forms in Coal	Ref.
Sb	uncertain - sulfides, organic association, pyrite all possible	1,2
As	pyrite (solid solution), small amount organic association	1,2
Ba	50% organic in bituminous coals; 90%+ in low rank coals	2
Be	predominantly organic association; clays also possible	1,3,5
B	organic association; incorporation in illite also possible	1,3
Cd	replacement for zinc in sphalerite (ZnS)	1,3
Cr	uncertain - clays or chromite?	1,2
Co	sulfides, also incorporated in pyrite	1,2
Cu	chalcopyrite ($CuFeS_2$)	1,3
Pb	galena (PbS) in high sulfur coals; PbSe also possible	1,3
Mn	incorporation in siderite and calcite minerals	1
Hg	solid solution in pyrite; generally w/fine minerals	1,3,4
Mo	uncertain - sulfides? (correlates w/S in Hungarian coals)	1,3
Ni	uncertain - (sulfides, organic association, clays)	1
Se	70-80% organic - low rank coals; fine pyrite, PbSe also	1,2,3,4
V	clays; some organic association possible; uranium mineral?	1,3
Uranium (238)	some organic, some silicates	1,2
Thorium (232)	rare earth phosphate	1
(1) Finkelman (1992) (2) Finkelman et al. (1990) (3) Raask (1985) (4) Akers (1991) (5) Smith (1980)		

1.2 Emission from Fort Martin Plant Under Normal Operation

Now that the concentration of the trace metals in coal has been estimated, the flow of these metals at Fort Martin can be evaluated. In order to discuss the flow of toxics at Fort Martin, the plant has been divided into five units:

- Coal pile
- Boiler
- Economizer and air heater hoppers
- Electrostatic precipitator
- Stack

Fort Martin is comprised of two pulverized coal-fired boilers with a total generating capacity of 1,107 MW. A block diagram of the facility is contained in Figure 1. At Fort Martin there are two separate pulverized-coal-fired boilers (one CE boiler and one B&W boiler), but they share a common coal source and a common stack. Because of this configuration, we will consider the two units as a combined unit operation.

A NEPA assessment of the Fort Martin facility is not the main goal of this report. This analysis is a basis for evaluation of the GPIF facility. Therefore, the analysis of the Fort Martin facility will be based on an "average" emission level.

1.2.1 Coal Pile

The first unit for the balance is the coal pile. The pile is the first place that the inorganics enter, and there are modifications and losses occurring in this region. For example, all coal constituents begin to oxidize in the coal pile. The oxidation process is a very slow, low temperature combustion process. Among the mineral components that oxidize are sulfides (e.g., pyrite), which react with water and oxygen to form sulfuric acid and iron sulfate. Trace toxic elements associated with sulfides (e.g., lead, nickel, arsenic among others) may, therefore, leach out of the coal and contaminate the runoff water. The degree of leaching will be influenced by the pH of the runoff (i.e., the acidity of the rainfall and the amount of pyrite oxidation occurring.)

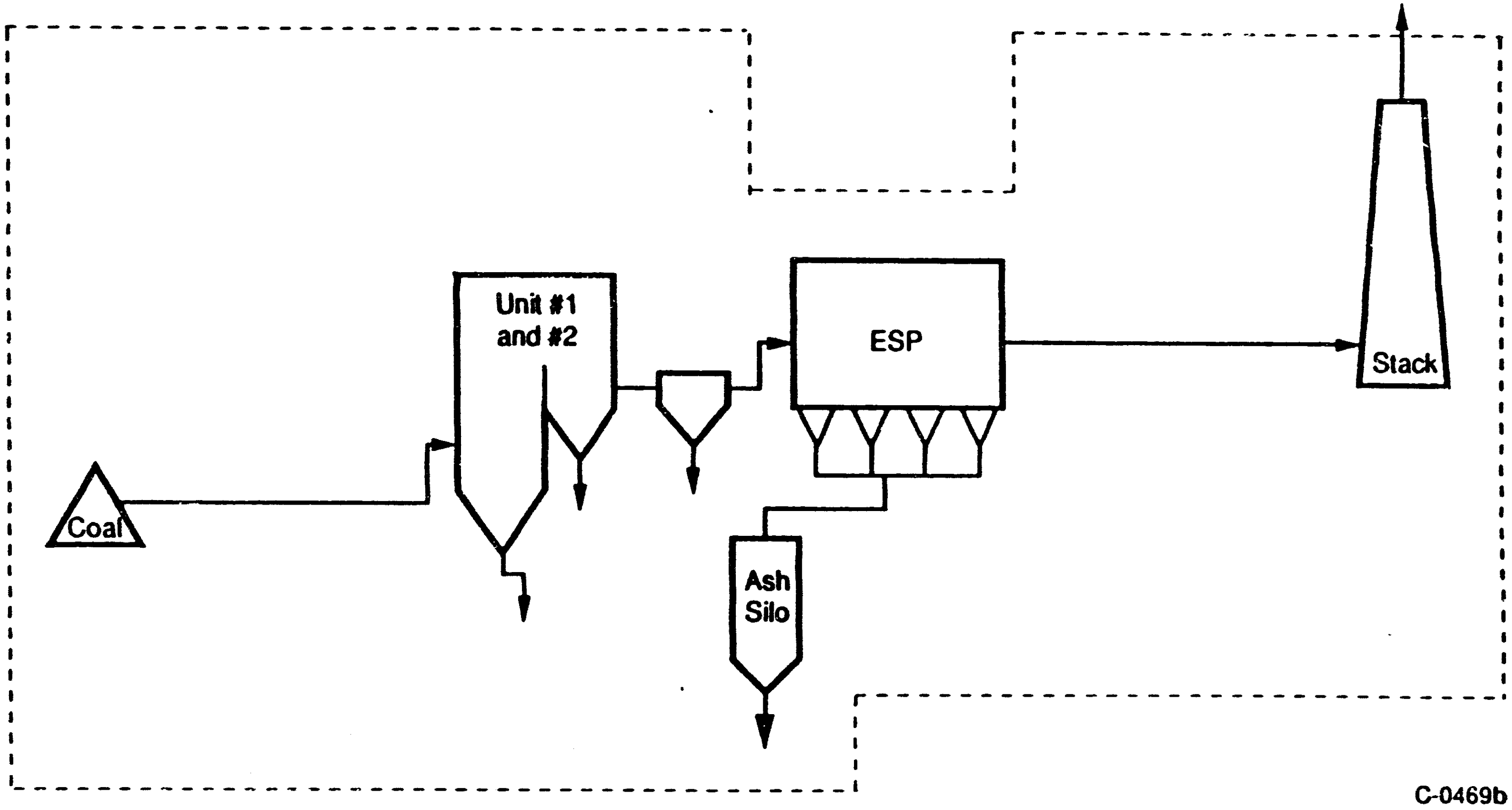


Figure 1. Process flow diagram for Fort Martin.

The most important factors affecting the rate of ambient oxidation of the coal and coal minerals are coal rank, surface area, duration of exposure to air, and temperature. Low rank (subbituminous) coals are more reactive than high rank coals (e.g., bituminous). Small coal particle size, long storage times, and a high ambient temperature contribute to increased degree of oxidation (and potentially increased mobilization of trace elements into the runoff).

There is insufficient data to accurately assess the magnitude of this waste stream. Besides the scarcity of data, the sporadic nature of this stream complicates measurements. For example, the monthly precipitation controls both the flow rate and concentration of trace metals. The lack of data makes estimation of this stream difficult. In addition, the GPIF will not affect the size or composition of the coal pile. Therefore, no significant change will occur due to the addition of the GPIF facility.

1.2.2 Boiler

Coal from the coal pile is first pulverized and then fed to the individual burners of the boiler. Injected with preheated air, the pulverized coal particles devolatilize, ignite, and burn as they travel upward through the furnace. As the coal particles react, the associated mineral matter begins to react as well. Some of the resulting ash particles will attach to boiler walls and eventually fall to the bottom due to excessive mass, load shedding, or sootblowing, eventually becoming bottom ash. Other ash particles - denoted fly ash - are carried out of the furnace with the stack gases and downstream where they can collect on convective heat transfer surfaces, hoppers, or pollution control equipment.

Against this backdrop of coal combustion and major inorganic species transformations, the trace metals contained within the coal will also transform. Some may vaporize, some may concentrate in the fly ash, and still others may be found in the bottom ash. To properly assess the partitioning of trace elements to the effluent streams in coal-fired power plants, the transformations undergone in the boiler must be carefully addressed. For example, an element which vaporizes extensively at the high temperatures of combustion may either condense on small fly ash particles or remain in the vapor phase. In either case, it may be difficult to collect with downstream particulate capture devices. Elements which are relatively non-reactive, on the other hand, may concentrate in larger fly ash particles or the bottom ash, making their removal from the boiler more straightforward.

Because fundamental data are lacking, previous field measurements can be used to provide guidance in assessing trace element partitioning in boilers. Table 4 summarizes the results of several studies conducted during the past two decades. Each column in the table presents results from a specific study. Columns with headings 1, 2, and 3 report the ratio of the concentration of an element in the fly ash to that in the bottom ash. Columns with headings 4, 5, 6, and 7 report the stream with the highest concentration of the element - Fly ash, Fly ash (slightly enriched), Vapor, or Bottom ash.

From the table, it is clearly evident that a range of behavior has been observed for several of the trace elements. For example, although antimony and arsenic are concentrated in the fly ash in all of the studies cited, a range of concentration levels is reported. Sampling differences, differences in power plant operation, and differences in the form of these elements in the parent coal could all account for the observed behavior. The two low values reported for selenium are surprising, as it is expected to vaporize during combustion and subsequently recondense on small ash particles (Finkelman et al., 1990; Meserole and Chow, 1991). Consistent with this, Smith (1980) and Davison both report Se concentrations in the small fly ash particles 4 to 5 x greater than in the large (>20 micron) ash particles for bituminous and subbituminous coal fired boilers.

Based upon this review and Table 4, the partitioning of trace elements in coal fired boilers can be summarized as follows, using the classification scheme employed by Brooks (1989) and Tumati and Devito (1991):

- Class 1 - Equally partitioned: Mn, Ba, U_{238}, Th_{232}
- Class 2 - Concentrated in the fly ash: Sb, As, Cd, Pb, Mo, B, Se
- Class 3 - Intermediate: Be, Cr, Co, Cu, Ni, V
- Class 4 - Vapor: Hg.

Table 4. Field Measurements of Trace Element Partitioning in Coal-Fired Combustion Boilers

Element	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Sb	2	4	19	F	F	F	-
As	4-5	8	6	F	-	F	F
Ba	-	-	0.9	equal	F	-	-
Be	1.5	1.5	-	-	F	-	F (s)
B	-	-	-	-	V	F	-
Cd	1	6	7	F	-	F	F
Cr	5-6	2	2	F (s)	F(s)	-	F(s)
Co	1	-	1.9	equal	F	-	-
Cu	1	1.5	7	F	F	-	F(s)
Pb	2.5	4	13	F	F	F	-
Mn	< 1	1.3	1	equal	B	-	F(s)
Hg	-	-	2	V	V	-	V
Mo	-	-	-	F	F	F	-
Ni	2	1.5	2.5	F(s)	F	-	F(s)
Se	1	0.9	310	F	V	F	-
V	1	-	1.7	F(s)	-	F	-

Numbers signify ratio of fly ash to bottom ash concentration
F and F(s) signify fly ash and sly ash (slightly enriched)
V signifies an element concentrated in the vapor phase
B signifies an element concentrated in the bottom ash

(1) Davison et al. (1974) - pulverized coal power plant; probably

(2) Tumati and Devito (1991) - 1.5 MW pilot scale, washed

(3) Barrett et al. (1983) - literature survey
(4) Klein et al. (1975) - cyclone fired power plant, Ill. basin

(5) Clarke (1991) - Netherlands power plant
(6) Akers et al. (1989) - literature survey
(7) Brooks (1989) - literature survey

For class 2 elements and Ni, Cu, and Cr, increasing concentrations with decreasing fly ash particle size have been observed (Smith, 1980; Barrett et al., 1983; Davison et al., 1974; Meserole and Chow, 1991). Note that despite differences in partitioning, most of the trace metals *on a mass basis* will be found in the fly ash. This is because the fly ash is generally 80 to 85% of the total ash formed in a dry bottom pulverized coal boiler (Brooks, 1989; Akers et al., 1989). Elements such as Mn which are slightly enriched in the bottom ash will therefore principally exist (on a total mass basis) in the fly ash.

After the combustion process, the ash is collected in several areas. Hoppers are used to collect the bottom ash material falling from the furnace walls. The bottom ash is removed from the hopper by drag or screw conveyors and sent to the ash pond for storage and ultimate disposal.

A mass balance around the Fort Martin boilers is shown in Figure 2. For this figure, both boilers are addressed as one unit operation. The flow of the coal (as received), ash, air, and flue gases is shown. A value of 20% is used as an estimate of the fraction of ash which reports to the bottom hopper.

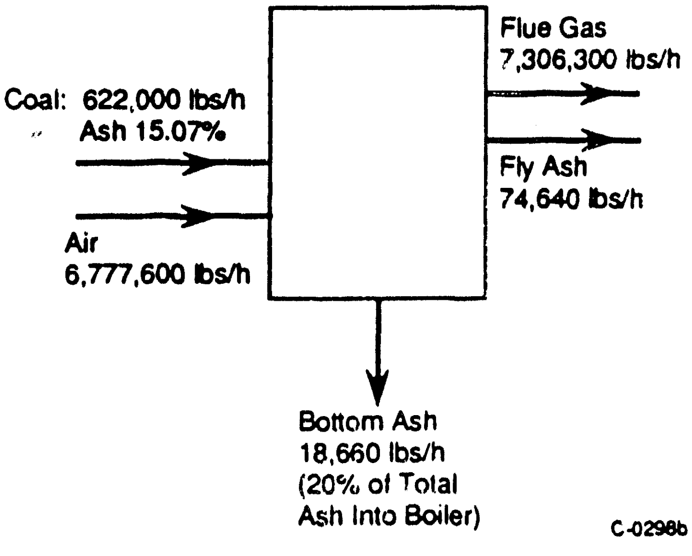


Figure 2. Boiler mass balance calculation results.

Table 5 contains a mass balance of the trace metal flows indicating both the concentration and flow rates in the various streams. In the first column, the concentration of the element in the coal is given. The second column contains the ratio of the element concentration in the fly ash to the bottom ash, derived from Table 4. The third and fourth columns list the concentration of the various elements in the fly ash and bottom ash streams, respectively. The last two columns list the absolute flow rate in each of the steams.

Table 5. Balance of Trace Element Concentrations Around the Boilers

Element	Coal (ppm)	Conc. Ratio FA/Bottom	Fly Ash (ppm)	Bottom Ash (ppm)	Fly Ash (lb/h)	Bottom Ash (lb/h)
Antimony	1.2	2	8.9	4.4	0.66	0.083
Arsenic	24	5	190	38	14	0.71
Barium	170	1	1133	1133	85	21
Beryllium	2.2	1.5	16	10.5	1.2	0.2
Boron	49	5	388*	78	29*	1.5
Cadmium	0.5	2.5	3.6	1.4	0.27	0.027
Chromium	15	2	111	56	8.3	1.04
Cobalt	6.1	1	41	41	3	0.76
Copper	16	1	107	107	8	1.99
Lead	11	2.5	83	33	6.2	0.62
Manganese	43	1	287	287	21	5.3
Mercury	0.2	20	1.4*	0.07	0.1	0.001
Molybdenum	3.3	1.25	23	18	1.7	0.34
Nickel	14	2	104	52	7.7	0.97
Selenium	3.1	5	25	4.9	1.8	0.09
Vanadium	22	1.5	157	105	11.7	1.95
Uranium (238)	2.1	1	14	14	1.0	0.3
Thorium (232)	3.2	1	21	21	1.6	0.4

*Including vaporized fraction

1.2.3 Economizer and Air Heater Hopper

After exiting the boiler and the superheater region, the dust-laden flue gas enters the convective heat recovery section of the power plant, where the gas passes through the secondary superheater, vertical and horizontal reheater, primary superheater economizer and air heater. As the hot gases pass the cooler heat transfer surfaces, ash vapor and ash particles may condense and deposit on the tube surfaces. Eventually these ash particles are shed, or removed via sootblowing of the tube surfaces. Hoppers are located in both the economizer and the air heater to collect the resulting ash and fallen deposits.

Figure 3 contains a mass balance around the convective section. A value of 10% is taken for the flow of ash into the air heater and reheater hoppers. Since the temperatures are much lower than in the furnace, it is expected that condensation of vaporized inorganics will occur in this region. However, it is reasonable to assume that the ash in these hoppers will be identical to the ash entering the ESP, because the reduction in temperature between the air heater and the ESP will not affect the condensation reactions. Mercury was the only exception, and all of the mercury was assumed to reamin in the flue gas.

Table 6 gives the details of the overall balance for the convective section hoppers. Ash was distributed according to the overall mass flow with no change in concentrations of the trace elements.

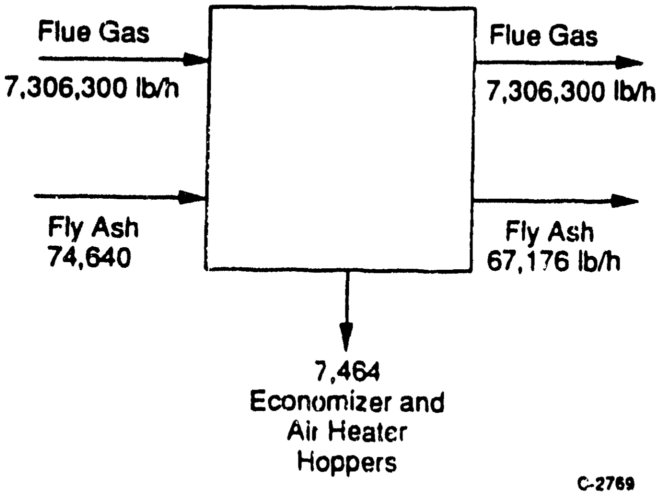


Figure 3. Balance around convective section.

Table 6. Balance Around Air Heater and Economizer Hoppers

Element	Fly Ash In (lb/h)	Fly Ash Out (lb/h)	Fly Ash Out (lb/h)	Fly Ash Out (ppm)	Hopper Ash (lb/h)	Hopper Ash (ppm)
Antimony	0.7	8.9	0.6	8.9	0.07	8.9
Arsenic	14.2	190.5	12.8	190.5	1.42	190
Barium	84.6	1133.3	76.1	1133.3	8.46	1133
Beryllium	1.2	15.7	1.1	15.7	0.12	16
Boron	29.0	388.9	26.3	388.9	2.50	388
Cadmium	0.3	3.6	0.2	3.6	0.03	3.6
Chromium	8.3	111.1	7.5	111.1	0.83	111
Cobolt	3.0	40.7	2.7	40.7	0.30	41
Copper	8.0	106.7	7.2	106.7	0.80	107
Lead	6.2	83.3	5.6	83.3	0.62	83
Manganese	21.4	286.7	19.3	286.7	2.14	287
Mercury	0.1	1.4	0.1	1.4	0.001	1.4
Molybdenum	1.7	22.9	1.5	22.9	0.17	23
Nickel	7.7	103.7	7.0	103.7	0.77	104
Selenium	1.8	24.6	1.7	24.6	0.15	25
Vanadium	11.7	157.1	10.6	157.1	1.17	157
Uranium (238)	1.05	14.0	0.9	14.0	0.10	14
Thorium (232)	1.6	21.3	1.4	21.3	0.16	2.1
Total Ash Flow	74640		67176		7464	

1.2.4 Electrostatic Precipitator

ESPs are used to remove virtually all the remaining ash in the flue gas. The Fort Martin ESPs achieve 99.5% removal of ash entering the ESPs. The mass balance used to evaluate the trace metal flow in this area is shown in Figure 4. While the overall efficiency is assumed to be 99.5%, it is assumed that the efficiency for all the particles less than 3 microns is 95% (5% of the total particles), and the efficiency for particles greater than 3 microns is 99.74% (95% of the fly ash particles) (Smith, 1980). This partitioning is performed because of the known effect of particle size on ESP efficiency.

A trace metal balance around the ESPs was performed to show the flow of the various metals. Literature estimates were used to give values for a number of factors (Smith, 1980, Tumati and DeVito, 1991). The results of this balance are shown in Table 7. In the first column is the assumed ratio of the concentration of each element in the small to large particles. As seen, many of the elements concentrate in the smaller, more difficult to remove, particles. The flow rates were taken from Table 6 with assumptions that 5% of the boron, 90% of the mercury, and 10% of the selenium is in the gas phase. The rest of the table is calculated given the previous mentioned values about the distribution of small and large (greater than 3 microns) particle, and the removal efficiency for these particles.

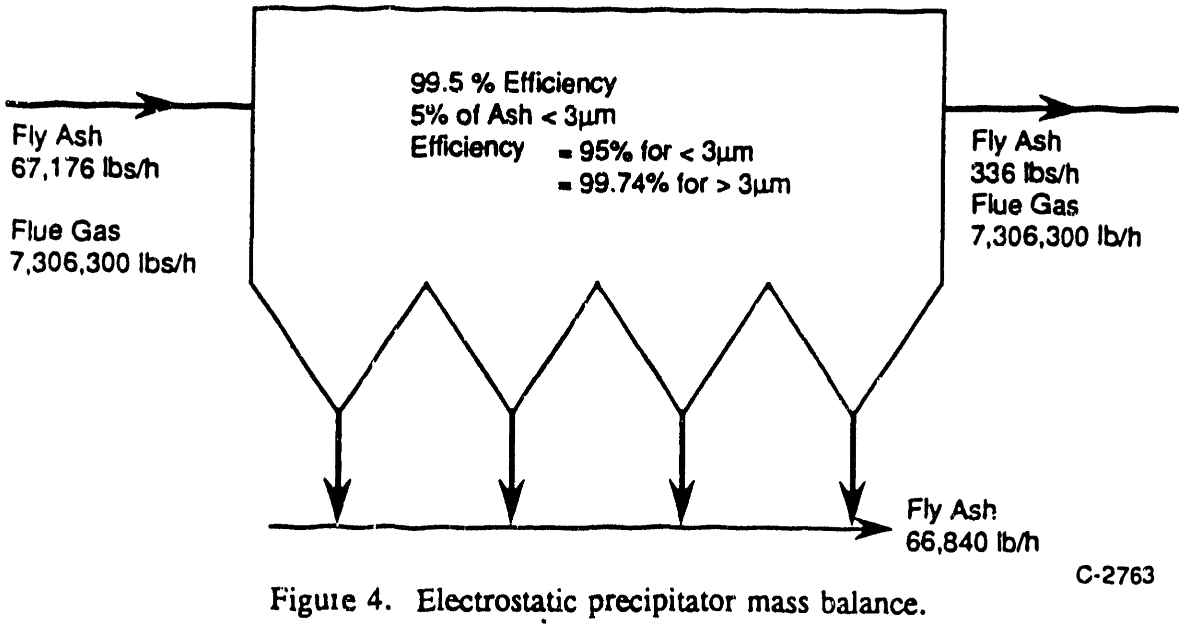


Figure 4. Electrostatic precipitator mass balance.

Table 7. Trace Metal Balance Around the ESP

Element	Concentration Ratio Small/Large	Total Mass Flow (lb/h)	Gas Mass Flow In (lb/h)	ESP Hopper Solid (lb/h)	ESP out Gas (lb/h)	ESP Out Total (lb/h)	Removal Efficiency (%)
Antimony	2	0.597	0	0.593	0	0.004	99.3
Arsenic	11	12.8	0	12.5	0	0.26	98.0
Barium	1	76.1	0	75.8	0	0.38	99.5
Beryllium	1.5	1.05	0	1.04	0	0.006	99.4
Boron	5	25.0	1.4	23.3	1.38	3.05	93.3
Cadmium	2.5	0.239	0	0.237	0	0.002	99.2
Chromium	4.7	7.5	0	7.4	0	0.09	98.8
Cobalt	1	2.73	0	2.71	0	0.014	99.5
Copper	2.5	7.17	0	7.11	0	0.06	99.2
Lead	6.6	5.6	0	5.5	0	0.083	98.5
Manganese	1.6	19.3	0	19.1	0	0.12	99.4
Mercury	5	0.1	0.1	0.01	0.09	0.02	09.8
Molybdenum	4.9	1.54	0	1.52	0	0.019	98.8
Nickel	2.5	7.0	0	6.9	0	0.057	99.2
Selenium	5	1.5	0.2	1.3	0.17	0.35	87.9
Vanadium	2.6	10.6	0	10.5	0	0.088	99.2
Uranium (238)	1	0.941	0	0.936	0	0.005	99.5
Thorium (232)	1	1.433	0	1.426	0	0.007	99.5

1.2.5 Stack

The concentrations of the trace elements in the stack are those exiting the ESP, as defined previously in Table 7.

1.3 Trace Element Behavior in GPIF System

To assess the environmental impact of the GPIF facility, it is necessary to identify the concentrations and mass flows of trace metals in all of the relevant input and effluent streams. These values must then be compared with flows associated with the Fort Martin Power Station to determine the relative impact of GPIF.

There are four major streams associated with the GPIF facility. Two are input streams of coal and limestone, one is the bottom ash effluent, and one is the product gas effluent. The bottom ash, containing spent sulfur sorbent, is subsequently treated in an oxidation unit that produces a moist solid effluent stream. Trace metal concentrations and mass flows for each of these streams are described below.

1.3.1 Mass Balance Around Gasifier

Overall - Overall mass flow balances around the gasifier portion of the GPIF facility were performed as the first step in this analysis. Results of these calculations are shown in the block flow diagram of Figure 5. Values for most total mass flows were taken directly from the CRS Sirrine proposal to DoE/METC for this program. The limestone mass flow was calculated from the coal sulfur content of 0.93% (Table 1) and the assumption that a calcium to sulfur molar ratio of 2.5/1 would be used. The fly ash concentration in the product gas stream was calculated with the assumption that 5% of the total ash flow is entrained as fly ash, based upon operating experience of pilot scale fixed bed gasifiers.

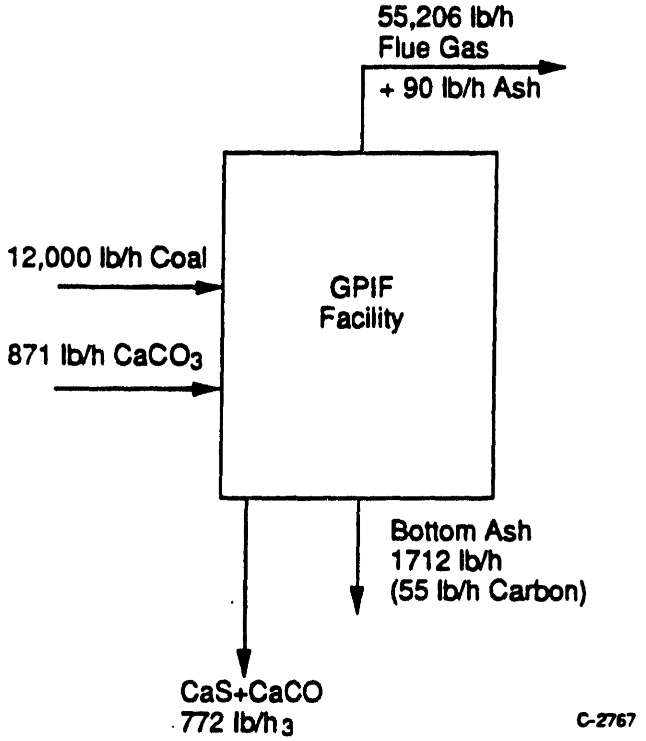


Figure 5. Overall balance at GPIF facility.

Because measurements are lacking, we will assume that the size distribution of the fly ash is equivalent to the size distribution of fly ash produced during combustion of pulverized coal, i.e. 50% < 10 μm and 5% < 3 μm. Note that this is an extremely conservative or worst-case analysis - the actual size distribution of ash produced in the PyGas unit should be larger because of the large coal particle size distribution .

Trace Elements - Our analysis of trace metals behavior in the PyGas gasifier is broken down into three sections: 1) the 11 trace metals identified on the Hazardous Air Pollutants list in Section 112 of the 1990 Amendments to the Clean Air Act; 2) the two primary radionuclides contained in coal, uranium, and thorium; and 3) five other trace metals in coal. Thus, each table presented in this sub-section has the metals grouped accordingly.

Using the total mass flows into the gasifier shown in Figure 5 and the trace metal concentrations shown in Table 8, trace metal flows into the gasifier can be calculated.

These results are shown in the final column of Table 8. For all elements except antimony, the contribution of the limestone to the total trace metal input flow is negligible. For antimony, slightly less than half of the inlet flow is provided by the limestone. Coal trace metal concentrations shown in the table were taken from data provided by Finkelman (1992) and are the same values used in the power plant trace metals balance described previously. Trace metal concentrations in limestone are from data provided by Huber (1992) for a typical Mississippi River sedimentary limestone.

Partitioning of Trace Elements in Gasifier - Because of the high maximum temperature encountered in the PyGas™ unit (2300°F), it is reasonable to assume that trace element partitioning will be similar to that observed in a pulverized coal boiler. Thus, three literature studies of trace element partitioning in boilers were combined with two studies of trace element partitioning in fluidized bed gasifiers to provide a broad range of possible values for the PyGas™ gasifier. Although trace elements in coal may partition differently than trace elements in limestone, for the purposes of this analysis it was assumed that they behaved identically.

Partitioning coefficients are presented in Table 9. "Low" represents the lowest value from the combined five studies, "average" represents the median value (or an average value if four of the five values were in close agreement), and "high" represents the maximum observed in the data set. In any given column, a value close to one indicates that there was no enrichment of the metal in the fly ash. Values significantly greater than one reflect enrichment. Note that certain metals in one paper in the set - Tamhankar and Wen (1981) - were considerably skewed toward higher concentrations in the fly ash. Nevertheless, these values were retained as a representation of "worst case" behavior.

Using this partitioning data (Table 9) and the mass flux of trace metals into the gasifier as specified in Table 8, the mass flux out of the gasifier in two streams - fly ash and bottom ash - was calculated for average and maximum partitioning levels. The results of

Table 8. Trace Element Concentrations - GPIF Inlet Streams

Element	Coal Conc. (ppm)[a]	Limestone Conc. (ppm)[b]	Total Inlet Flow (lb/h)[c]
Sb	1.2	14.	0.026
As	24	<4	0.291
Be	2.2	<0.5	0.027
Cd	0.47	<0.5	0.006
Cr	15	<1	0.181
Co	6.1	<0.5	0.074
Pb	11	<2	0.134
Mn	43	-	0.553
Hg	0.17	<0.5	0.002
Ni	14	<0.5	0.168
Se	2.8	<0.5	0.034
Th	3	-	0.039
U	2.1[d]	-	0.027
Ba	170	2	2.042
B	49	-	0.631
Cu	16	<0.6	0.193
Mo	3.3	<6	0.045
V	22	10	0.273

[a] Finkelman (1992), values for typical coal

[b] Huber (1992), values for typical sedimentary limestone

[c] Based upon inlet flow of each stream and concentrations in this table. If no data available for limestone concentration, coal concentration assumed. If upper limit specified (i.e., <x ppm), value of "x" used in calculations

[d] Brooks (1989), value for typical bituminous coal

Table 9. Trace Element Partitioning in Gasifier
- Ratio of Elemental Concentrations in Fly Ash to Bottom Ash

Element	Low	Average	High
Sb	2	6	19
As	1.5	5	35
Be	1.5	1.5	5
Cd	1	2.5	7
Cr	1.2	2	6
Co	0	1	1
Pb	1.2	2.5	33
Mn	1	1	1
Hg	2	20	*
Ni	1.25	2	6
Se	1	5	310
Th	1	1	1
U	1	1	1
Ba	1	1	1
B	5	5	5
Cu	1	1.5	7
Mo	1.25	1.25	1.25
V	1	1.5	1.7

*100% vaporization is upper limit.

these calculations are shown in Table 10 for average partitioning coefficients and in Table 11 for maximum partitioning coefficients. In these tables, "c" represents concentration; the subscript "b" represents bottom ash or slag; and the subscript "f" represents fly ash. Using the average partitioning values (Table 10), over 90% of all trace elements except mercury are contained in the gasifier bottom ash. Under "maximum" partitioning conditions, corresponding to the maximum concentration of trace elements in the fly ash, 84% of the metals are still collected with the gasifier bottom ash.

Because the gasifier product gas stream is to be fed to an HRSG at Fort Martin, all trace metals associated with the fly ash will also pass to the boiler. It is assumed that all of the fly ash fed to the HRSG with the gasifier product gas is emitted from the HRSG as fly ash. Thus, the fly ash and trace metals content of the gasifier product gas is assumed to be identical to the fly ash and trace metals content of the HRSG flue gas. Because this product stream is sent to the Fort Martin station ESP, the concentrations and mass flows must be compared to those produced by the pc-boilers for the impact of GPIF to be determined.

1.3.2. Treatment of Bottom Ash

As ash is produced in the PyGas™ gasifier, it is dropped through the bottom and into a quench tank. From this quench tank, the ash stream passes to a reactor vessel where CaS sorbent is oxidized under wet conditions. Inlet and outlet streams to the CaS oxidation unit are shown in Figure 6. Mass flows were calculated by assuming that the ash/sorbent effluent stream contains 15% moisture.

To analyze the environmental impacts of this system, the trace metals concentration in the effluent stream must be determined. this is broken into three sections below.

Air Effluent Stream - Upon exiting the reactor, this stream should consist only of moist or saturated air. Provided that a water mist is not generated, this stream should not contain any detectable levels of trace metals. Additionally, this stream will be fired into the HRSG so that all trace metals will report to the ESP units.

Table 10. Trace Element Partitioning in the Gasifier - Average Partitioning Values Used

Element	Inlet (lb/h)	c_f/c_b	c_b (ppm)	c_f (ppm)	Bottom Ash (lb/h)	Fly Ash (lb/h)
Sb	0.026	6	11.5	69.3	0.020	0.006
As	0.291	5	134.6	673.0	0.230	0.061
Be	0.027	1.5	14.6	21.9	0.025	0.002
Cd	0.006	2.5	3.1	7.7	0.005	0.001
Cr	0.181	2	95.7	191.3	0.164	0.017
Co	0.074	1	41.1	41.1	0.070	0.004
Pb	0.134	2.5	69.2	172.9	0.118	0.016
Mn	0.553	1	306.8	306.8	0.525	0.028
Hg	0.002	20	0.6	11.4	0.001	0.001
Ni	0.168	2	88.8	177.6	0.152	0.016
Se	0.034	5	15.7	78.6	0.027	0.007
Th	0.039	1	21.6	21.6	0.037	0.002
U	0.027	1	15.0	15.0	0.026	0.001
Ba	2.042	1	1133.2	1133.2	1.940	0.102
B	0.631	5	291.9	1459.3	0.500	0.131
Cu	0.193	1.5	104.5	156.7	0.179	0.014
Mo	0.045	1.25	24.7	30.8	0.042	0.003
V	0.273	1.5	147.8	221.7	0.253	0.020

Table 11. Trace Element Partitioning in the Gasifier - Maximum Partitioning Values Used

Element	Inlet (lb/h	c_f/c_b	c_b (ppm	c_f (ppm)	Bottom Ash (lb/h	Fly Ash (lb/h)
Sb	0.026	19	7.6	144.4	0.013	0.013
As	0.291	35	59.9	2094.8	0.102	0.189
Be	0.027	5	12.5	62.4	0.021	0.006
Cd	0.006	7	2.6	17.9	0.004	0.002
Cr	0.181	6	80.4	482.2	0.138	0.043
Co	0.074	1	41.1	41.1	0.070	0.004
Pb	0.134	33	28.6	944.5	0.049	0.085
Mn	0.553	1	306.9	306.9	0.525	0.028
Hg	0.002	9999	0	22.2	0.000	0.002
Ni	0.168	6	74.6	447.6	0.128	0.040
Se	0.034	310	1	355.9	0.002	0.032
Th	0.039	1	21.6	21.6	0.037	0.002
U	0.027	1	15	15	0.026	0.001
Ba	2.042	1	1133.2	1133.2	1.940	0.102
B	0.631	5	291.9	1459.3	0.500	0.131
Cu	0.193	7	82.4	576.9	0.141	0.052
Mo	0.045	1.25	24.7	30.8	0.042	0.003
V	0.273	1.7	146.4	248.8	0.251	0.022

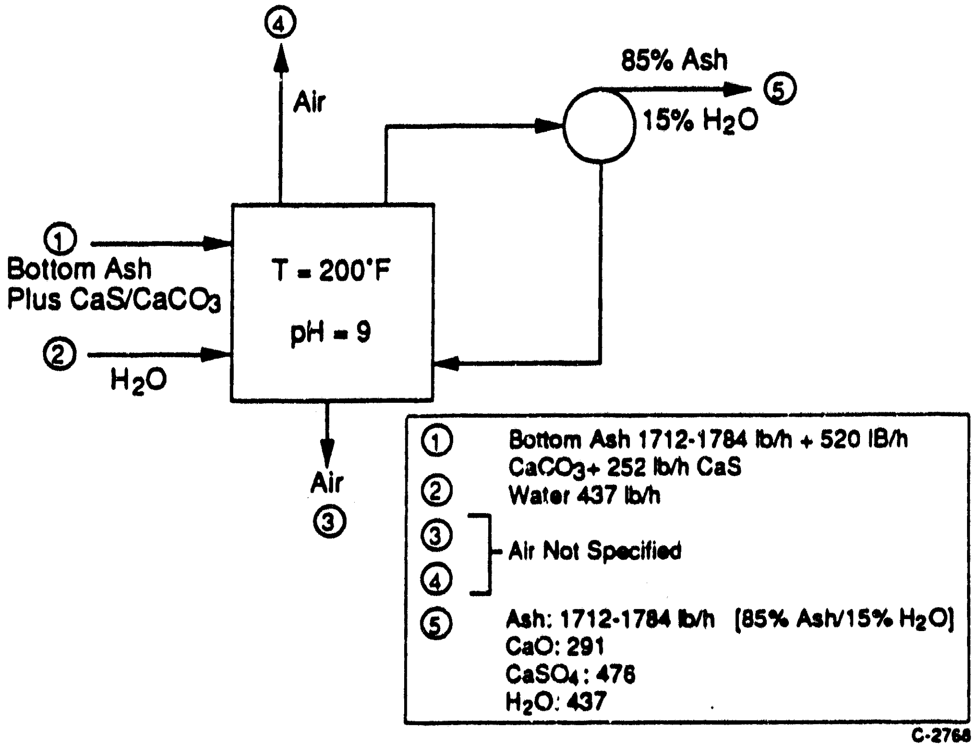


Figure 6. Balance around CaS oxidation unit.

Solid Ash Effluent Stream - The ash contained in this stream shall be representative of the gasifier bottom ash stream. Thus, trace element concentrations are those provided in the penultimate column of Tables 10 and 11. This ash, along with the hopper ash from the ESP and the boilers at Fort Martin, is next sent to a settling lagoon, so the appropriate environmental impact question concerns the concentrations in this stream relative to the hopper streams.

Water Associated with Ash Effluent - Consider the moisture that constitutes 15% of the ash exit stream. The only issue of concern here is the solubility of the trace metals in the reactor moisture. This is a strong function of water pH, as shown in Table 12. Solubility of all of these metals (except Cr) decreases significantly with increasing pH. As long as the pH of the CaS reactor is greater than that of the ash settling lagoon water, therefore, there will be no adverse metal leaching associated with this additional water stream. Based upon discussion at the program kickoff meeting, the pH of this reactor will be approximately 9. As the values in Table 12 indicate, much less than 1% of the trace metals will be leached.

Table 12. Trace Element Leachability as f(pH)

	% of Metal Leached			
	6	7	9	10
Cd	50	30	0.2	
Pb	0.3	0.1	0.01	
Cu	0.8	0.08	0.01	
Zn	20	3	0.005	
As	0.3	0.04	0.1	
Sb	0.8	0.6	0.5	
Cr	0.015	0.03	1	
Mo	3	3	3	
Mn		x		0.0005x
Ni		x		0.04x
Data from Van der Sloot et al. (1989); DePietro et al. (1989).				

1.3.3. Fate of Trace Elements in Fly Ash

The gas from the GPIF will be combusted in a separate boiler to generate steam for the Ft. Martin facility. The gas will contains one particulate which will be combined with the flue gas form the Ft. Martin plant and put through the ESP.

Table 13 contains an analysis of the trace element partitioning in the flue gas and the ESP hoppers. The analysis was performed exactly the same as for the Ft. martin facility flue gas, substituting the inputs from GPIF. As can be seen, the overall contribution to the emissions is very small; a total of 0.45 lb/h of additional ash will be emitted compared to 336 lb/h under normal operation.

Table 13. Partitioning of GPIF Fly Ash by the ESP

Element	Fly Ash In (lb/h)	Fly Ash Out (lb/h)	ESP Hopper (lb/h)	ESP Eff. (%)
Antimony	0.006	0.000043	0.006	99.3
Arsenic	0.061	0.001220	0.06	98.0
Barium	0.102	0.00051	0.101	99.5
Beryllium	0.002	0.000012	0.002	99.4
Boron	0.131	0.00815	0.122	93.8
Cadmium	0.001	0.000008	0.001	99.2
Chromium	0.017	0.000204	0.017	98.8
Cobolt	0.004	0.00002	0.004	99.5
Copper	0.014	0.000114	0.014	99.2
Lead	0.016	0.000237	0.016	98.5
Manganese	0.028	0.000176	0.028	99.4
Mercury	0.001	0.000901	0.0001	9.9
Molybdenum	0.003	0.000037	0.003	98.8
Nickel	0.016	0.000128	0.016	99.2
Selenium	0.007	0.000779	0.006	88.9
Vanadium	0.02	0.000166	0.02	99.2
Uranium	0.001	0.000005	0.001	99.5
Thorium	0.002	0.00001	0.002	99.5
Total Fly Ash	90	0.45	89.55	

1.4 Significance of Trace Metal Emission from GPIF

The preceding sections have given a description of the flows at Fort Martin and the proposed GPIF facility. To make a comparison a number of caclulations were performed. First, the ash flow into all the hoppers is combined. For the Fort Martin facility, the hoppers are the air heater, economizer, ESP and furnace bottom ash hoppers. For the GPIF, the hoppers are the drum filter discharge hopper and an estimate of the flow to the ESP hoppers resulting from the GPIF fly ash. Combining the hoppers was performed to simplify the comparison, and since all the hoppers are combined on site to be sent to the settling pond. As stated in the analysis, all the ash from the GPIF facility is at least as stable and non-leachable as the normal hopper ash. Therefore the only issue is the change in flow rate. The more important issue is a comparison of the flow of trace metals up the stack. Analyses for the normal facility and the GPIF were performed and can be compared to each other.

Two ways of comparing the flows were addressed. In the first case, the expected case, the total coal input remains constant. This implies that the steam generated by the GPIF makes up for the steam lost by the plant. The second case, the worst case, assumes that the GPIF is 20% less efficient than the Fort Martin Facility. Therefore, the coal flows into the overall facility is 624,400 lb/hr (12,000 for the GPIF, and 2,400 additional firing increment for Fort Martin).

Tables 14a and 14b present the results of this analysis. In Table 14a the expected case is presented. The first four columns present the flow rates into the hoppers and stack for the Fort Martin facility and the GPIF, both at maximum load. The next two columns are the combined flow rate assuming 12,000 lb/h of coal through the GPIF and a 610,000 lb/h through the Fort Martin Facility.

First, the flow rates through the GPIF can be seen to be small compared to the normal flow rates. Second, the distribution between hopper and stack is different for the GPIF. In the case of the GPIF, a larger fraction of the ash and trace metals go to the hoppers for disposal in the settling pond. When the combined flow in the stack is compared to the normal flow in the stack, there is a net decrease in every trace metal and overall flow

Table 14a. Effect of GPIF Facility - Expected Case

Element	Comb. Hoppers Fort Martin Normal Operation (lb/h)	Stack Fort Martin Normal Operaton (lb/h)	GPIF Hopprs (lb/h)	Stack GPIF (lb/h)	Comb. Hoppers Fort Martin with GPIF (lb/h)	Comb. Stack with GPIF (lb/h)	Change Hopprs (%)	Ch'g Stack (%)
Antimony	0.74	0.004	0.03	0.000043	0.75	0.004	1.57	-0.91
Arsenic	14.67	0.26	0.29	0.001220	14.68	0.252	0.05	-1.45
Barium	105.36	0.38	2.04	0.000510	105.37	0.372	0.01	-1.79
Beryllium	1.36	0.006	0.03	0.000012	1.36	0.006	0.05	-1.74
Boron	27.23	3.05	0.62	0.008150	27.33	3.001	0.36	-1.66
Cadmium	0.29	0.002	0.006	0.000008	0.29	0.002	0.14	-1.51
Chromium	9.24	0.09	0.18	0.000204	9.24	0.088	0.03	-1.70
Cobalt	3.78	0.01	0.07	0.000020	3.78	0.013	0.03	-1.78
Copper	9.89	0.06	0.19	0.000114	9.90	0.057	0.02	-1.73
Lead	6.76	0.08	0.13	0.000237	6.76	0.082	0.05	-1.64
Manganese	26.63	0.12	0.55	0.000176	26.66	0.119	0.15	-1.78
Mercury	0.01	0.19	0.001	0.000901	0.01	0.184	6.87	-1.45
Molybdenum	2.03	0.02	0.05	0.000037	2.04	0.019	0.28	-1.74
Nickel	8.65	0.06	0.17	0.000128	8.65	0.056	0.01	-1.70
Selenium	1.56	0.35	0.03	0.000779	1.757	0.341	0.18	-1.71
Vanadium	13.6	0.09	0.27	0.000166	13.61	0.086	0.08	-1.74
Uranium	1.3	0.005	0.03	0.000005	1.30	0.005	0.15	-1.82
Thorium	1.98	0.007	0.04	0.000010	1.98	0.007	0.04	-1.79
Total Fly Ash	92964	336	2531	0.45	92972.5	330	0.009	-1.8

Table 14b. Effect of GPIF Facility - Worst Case

Element	Comb. Hoppers Fort Martin Normal Operation (lb/h)	Stack Fort Martin Normal Operaton (lb/h)	GPIF Hoppers (lb/h)	Stack GPIF (lb/h)	Comb. Hopprs Fort Martin with GPIF (lb/h)	Comb. Stack with GPIF (lb/h)	Change Hopprs (%)	Ch'g Stack (%)
Antimony	0.74	0.004	0.026	0.000043	0.757	0.004	1.96	-0.52
Arsenic	14.67	0.256	0.290	0.001220	14.736	0.253	0.43	-1.07
Barium	105.36	0.379	2.040	0.000510	105.78	0.373	0.39	-1.41
Beryllium	1.36	0.006	0.027	0.000012	1.368	0.006	0.44	-1.36
Boron	27.23	3.052	0.622	0.008150	27.431	3.013	0.74	-1.28
Cadmium	0.29	0.002	0.006	0.000008	0.292	0.002	0.52	-1.12
Chromium	9.24	0.089	0.181	0.000204	9.279	0.088	0.42	-1.32
Cobalt	3.73	0.014	0.074	0.000020	3.796	0.013	0.41	-1.40
Copper	9.89	0.058	0.193	0.000114	9.934	0.057	0.41	-1.35
Lead	6.76	0.083	0.134	0.000237	6.789	0.082	0.44	-1.26
Manganese	26.63	0.012	0.553	0.000176	26.767	0.012	0.53	-1.09
Mercury	0.01	0.186	0.001	0.000901	0.013	0.184	7.26	-1.06
Molybdenum	2.03	0.019	0.045	0.000037	2.047	0.019	0.67	-1.35
Nickel	8.65	0.057	0.168	0.000128	8.686	0.056	0.40	-1.32
Selenium	1.56	0.347	0.033	0.000779	1.573	0.343	0.57	-1.32
Vanadium	13.60	0.088	0.273	0.000166	13.659	0.087	0.46	-1.35
Uranium	1.30	0.005	0.027	0.000005	1.308	0.005	0.53	-1.44
Thorium	1.98	0.007	0.039	0.000010	1.992	0.007	0.42	-1.40
Total Fly Ash	92964	336	2531	0.45	94103	331	1.23	-1.41

by 0.85 to 1.83%. The hoppers show both increases and decreases, ranging from 0.00 to +5.93%. The increases into the hoppers occur mainly because there is a decrease in stack emissions. Some of the increase can be attributed to the $CaCO_3$ added for SO_2 control.

The worst case scenario is in Table 14b. In this case, since the GPIF boiler is assumed too be 20% less efficient than the Ft. Martin Station boilers, the overall combined emissions must increase, because the overall coal input is increasing from 622,000 to 624,400 lb/h. Once again the main increases are in the hoppers, which is positive. The stack emissions still decrease by 0.13% overall. All but one of the trace elements solid waste increases by less than 1%

In summary, the change in trace element emissions due to GPIF is rather small. In the expected scenario, the stack emissions decrease slightly and the emissions to the settling pond stay about constant. In the worst case, there is a very small, less than 1%, increase in ash emissions, with a 1 to 3% increase in emissions to the land fill.

2. CRITERIA POLLUTANTS

Emissions of criteria pollutants (SO_2, NO_x, total particulate matter, PM-10, and CO) for the GPIF are based on conventional fixed-bed gasification experience. The following paragraphs summarize the expected emission of each pollutant from the package boiler prior to exhausting the flue gas into the stack at Fort Martin station.

2.1 SO_2 Emissions

It is expected that all of the coal sulfur will be converted to H_2S, COS, or CS_2 during the gasification process. H_2S is expected to constitute greater than 95% of the sulfur products. During tests when limestone was injected with the coal in pyrolyzer tube experiments, up to 95% sulfur retention of volatilized organic sulfur as CaS was achieved lending credence that PyGas™ gasifier may achieve similar reductions. It is therefore likely that greater than 50% of the H_2S will be captured and removed with the gasifier bottom ash. Therefore 10 to 100% of the coal's sulfur will be emitted as SO_2 from the package boiler. So long as the GPIF utilizes low sulfur coal, the combined Ft. Martin Station and GPIF facilities are expected to produce less SO2 emissions than the Ft. Martin Station currently does and normally will without the GPIF in service.

2.2 NO_x Emissions

The bound nitrogen contained in the coal is converted to molecular nitrogen, tar, ammonia, and cyanide during gasification. N_2 is the predominant product, but NH_3, HCN, and tar can total 10 to 40% of the coal nitrogen depending on gasifier temperature, steam/air ratio, pyrolysis conditions, and coal type.

Experience with the Riley-Morgan fixed-bed gasifier indicates that NH_3 (200 to 2000 ppm) is greater than HCN (~100 ppm) in the product gas. If tars are cracked in the upper gasifier, tar nitrogen will be converted to either N_2 or HCN. Therefore, the HCN content of the gas leaving the PyGas™ reactor may include more HCN then from previous fixed-bed gasifiers. Whether the fuel bound nitrogen is contained in the tar or cracked to HCN will have little impact on NOx emissions.

Table 15 shows measured conversion rates of fuel nitrogen to NH_3 in 2-ft diam Wellman-Galusha gasifier. High NH_3 concentrations corresponded to low gasifier outlet

Table 15. Conversion of Coal Nitrogen to Ammonia in a 2-ft Diam Wellman-Galusha Gasifier

Run	NH_3 Conc. (ppm)	lb Steam / Std. cu ft $(CO + H_2)$	Coal Nitrogen (wt%)	Molar Conversion of N to NH_3 (%)
1	1940	2.26	1.54	35.0
2	622	2.19	1.54	12.0
3	385	1.81	1.54	5.2
4	666	1.76	1.54	9.0
5	486	2.19	1.54	5.3
6	658	2.26	1.54	7.2
7	452	1.84	1.54	6.8
8*	1170	7.29	1.08	5.0

*Pure O_2 as the oxygen source.

temperatures and high steam flows into the gasifier. Since the PyGas™ reactor will operate at higher outlet temperatures and minimize steam flows, these conversion rates are considered to be an upper bound.

Figure 7 shows the conversion of NH_3 to NO_x using a conventional swirl burner in a refractory-lined furnace. Note that the conversion rate decreases markedly as the NH_3 content of the gas increases, a common observance during oil combustion. The thermal NO_x contribution during these tests was about 100 ppm. The total NO_x emission ranged from 200 to 300 ppm, implying that the conversion of N to NO_x in a gasification or combustion process is less than 10%.

During cracking within the upper PyGas™ vessel, significant ammonia may be reduced to N2 and H2 further reducing NOx emissions potential.

Based on these data, we expect the NO_x emission from the package boiler to be less than 300 ppm (0.4 lb/MBtu). In contrast, the NO_x emission from the Fort Martin boilers are in the range of 525 to 900 ppm (0.7 to 1.2 lb/MBtu). Therefore, the combined Ft. Martin Station and GPIF facilities are expected to produce less SO2 emissions than the Ft. Martin Station currently does and normally will without the GPIF in service.

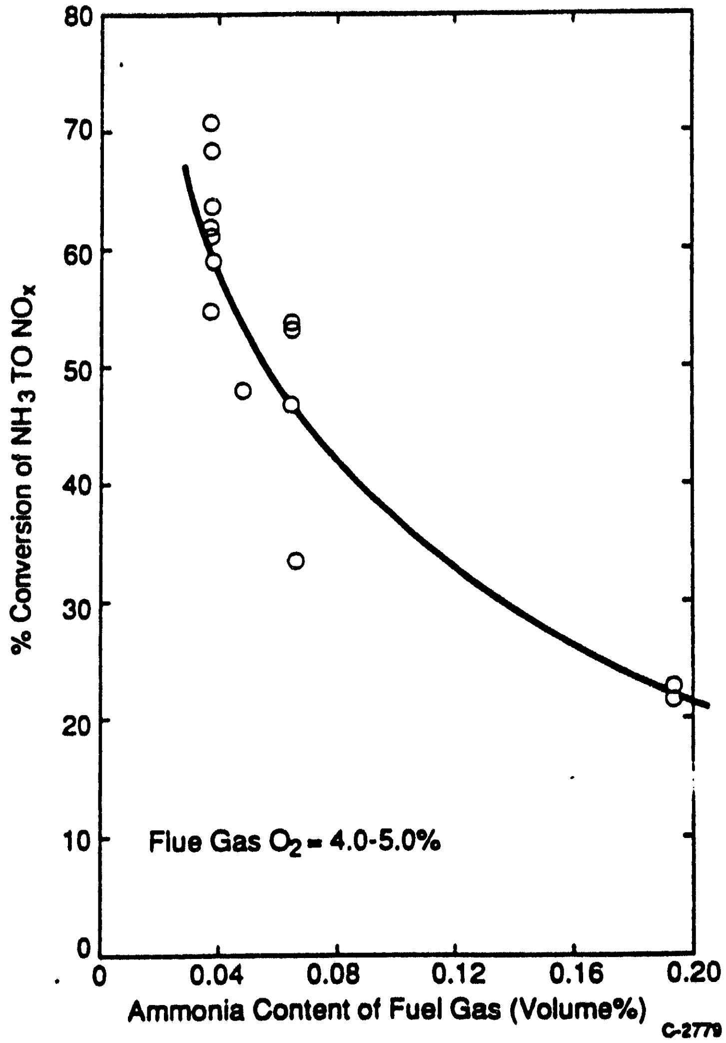


Figure 7. Conversion of ammonia to NO_x in a turbulent diffusion flame.

2.3 CO Emissions

The package boiler will utilize a burner capable of burning low-Btu gas having a range of heating values between 100 to 170 Btu/SCF. During periods when poorer quality gas is being produced, the facility will be fired with auxiliary #2 fuel oil. Good combustion will be maintained for all conditions, thus maintaining CO emissions from the package boiler to less than 100 ppm.

3. NEPA ASSESSMENT OF PSIT FACILITIES

PSI Technology Company, a subcontractor to CRS Sirrine on the Gasification Process Improvement Facility (GPIF), project DE-RP21-91MC28202, may conduct limited laboratory experimentation during the project. Such experiments would utilize existing laboratory reactor facilities for coal gasification experiments to determine the alkali-sorbent potential of coal ash. Limited experiments may also be conducted to assess the interaction of trace metals within the coal ash, again using existing facilities.

Note that indoor bench-scale research projects or conventional laboratory operation within existing experimental facilities are cited as categorical exclusions to NEPA requirements, as noted in Section B.3.6 of Appendix B, Subpart D, 10 CFR 1021. This PSIT portion of this project clearly falls within this definition.

For completeness, a description of expected emissions from these laboratory activities is described in outline form in the following sections. The format follows that identified by DoE/METC in pages A-10 through A-12 of Part IV, Section J, Attachment A, Exhibit I of the Request for Proposals for this project.

3.1 Brief Description of PSIT Laboratory Facilities to be Used in this Project

If requested by CRSS, PSIT shall conduct bench-scale experiments to assess alkali-ash and/or trace metal-ash interactions during gasification. It is anticipated that a maximum of 3 kg total of coal would be gasified throughout the duration of Phase I. Assuming that work on this project commences in March 1993 and proceeds for two years, the average coal consumption rate in the PSIT facility is 0.125 kg or 0.28 lb/month.

All experiments shall be conducted in existing PSIT bench-scale laboratory facilities. The two reactors being considered for these experiments are extremely small, with coal-feed capacities of approximately 5 g/min coal feed and 0.5 g/min coal feed.

Solid ash deposited on the collection filters is either sent to an analytical lab, or archived at PSIT for future reference. Because the ash is considered a non-hazardous substance, and because of the small (mg) quantities generated, it can also be disposed of in the general office (laboratory) trash.

used for this analysis (data published by Finkelman (1992) for the National Coal Resources Data System (NCRDS) of the U.S. Geological Survey). These were:

Sb	1.2 ppm
As	24
Be	2.2
Cd	0.47
Cr	15
Co	6.1
Pb	11
Mn	43
Hg	0.17
Ni	14
Se	2.8

With a coal ash content of 15%, the following concentrations and emission rates (corresponding to an average ash emission rate of 11 mg/h) are obtained:

Sb	8ppm	0.09 μg/h
As	150	1.7
Be	15	0.2
Cd	3	0.03
Cr	100	1.1
Co	41	0.5
Pb	73	0.8
Mn	287	3.2
Hg	1	0.01
Ni	93	1.0
Se	19	0.2

Other Issues: Because of the extremely low values of these emissions, no impact on air quality is expected. As the only water used in these laboratory systems is recirculated cooling water, there will be zero impact on water resources from this project. Local noise levels will not be increased as a result of this project.

Worker Safety: Laboratory workers routinely wear laboratory coats to protect clothing, and use particulate filter masks when handling coal or ash.

Summary: No environmental impact of any type should occur as a result of this small-scale laboratory project.

3.3 Permits Required

No permits are required for operation of the PSIT laboratory facilities. State requirements exempt facilities consuming less than 100 tons of coal per year or having a thermal input of greater than 3×10^6 Btu/h; the PSIT facility consumes approximately 10 lb of coal per year and is rated at 8×10^3 Btu/h maximum.

Note that indoor bench-scale research projects or conventional laboratory operation within existing experimental facilities are cited as categorical exclusions to NEPA requirements, as noted in Section B.3.6 of Appendix B, Subpart D, 10 CFR 1021. This PSIT portion of this project clearly falls within this definition.

3.4 Agency Contacts

Mr. Thomas Parks, Massachusetts Department of Environmental Protection, Northeast Regional Office, Division of Air Quality, 10 Commerce Way, Woburn, MA 01810, (617) 935-2160.

Ms. Judy Perry, Massachusetts Department of Environmental Protection, 1 Winter Street, Boston, MA, (617) 292-5673.

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