This project is in direct support of the Foster Wheeler Development Corporation integrated partial gasification process. That process utilizes mild gasification conditions to give only gas and char products.

Most of the chlorine present in the coal is released at temperatures below those employed for gasification. Over the range of particle sizes (128-425µm), temperature (846-965°C), and quantity of dolomite added (0 or 16% of the coal weight), several statistically significant effects were observed. An average of 11.9% of the potassium and 20.7% of the sodium was found to enter the gas phase under gasification conditions. The responses of the removal of sodium to changes in the values of the variables studied were more significant than those for potassium, especially for the effect of dolomite, where a negative relationship was observed at the 99% confidence level.

Solid analyses were consistent with the above findings; the major portion of the alkali metals is retained in the solid phase during gasification. TGA performed on selected samples of the product char produced curves similar to those obtained with the Foster Wheeler chars. The gasification solid product is fairly unreactive, as indicated by the relatively high temperatures required for ignition.
EXECUTIVE SUMMARY

Objectives

The overall objective of the project was to support the integrated partial gasification process being developed by the Foster Wheeler Development Corporation. That process utilizes mild gasification conditions to give only gas and char products. Limestone addition to the gasifier captures much of the sulfur released during the gasification; the fate of chlorine and the alkali metals (Na and K) is unknown. This proposal addresses that issue, in terms of the following specific project goals: 1) determination of the rates and extent of removal of sodium, potassium, and sulfur, in addition to chlorine, from the solid phase under pre-gasification and gasification conditions, 2) evaluation of the chemical transformations of the elements that occur under partial gasification conditions, and 3) to assess the reactivity of the product char from the experiments.

The results of this project are being complemented by those of a companion project that is determining the sulfur and nitrogen oxide emissions from the combustion of the residual char from the Foster Wheeler gasifier. Together, the results will aid in determination of the required operating conditions to allow high-sulfur/high-chlorine Illinois coals to be utilized in advanced combined-cycle power generation and co-generation systems.

Background

Foster Wheeler Development Corporation (FWDC), as a subcontractor in this proposal, is presently working on two DOE contracts that are developing the major components and processes as follows: DOE Contract DE-AC21-86MC21023 - Second-Generation Pressurized Fluidized Bed Cycle, and the second, DOE Contract DE-AC22-91PC91154 - Development of a High-Performance Coal-Fired Power Generating System with a Pyrolysis Gas- and Char-Fired High-Temperature Furnace, which is part of the "Combustion 2000" program. Both of these programs utilize a partial gasification process to produce fuel gas for powering a gas turbine and combustion of the char residual from the partial gasification process to raise steam and/or preheat air for the gas turbine cycle. A variation of these two cycles for near-term use involves using the partial gasification process to drive the gas turbine and combustion of the char in an atmospheric pressure circulating fluidized bed combustor to raise steam.

Foster Wheeler is committed to commercialization of integrated partial gasification systems. The proposed systems are capable, using today's gas and steam turbine technology, of achieving energy conversion efficiencies of 45-48% HHV at a cost of electricity up to 20% below today's costs using
pulverized coal-fired steam generating boiler plants at emission rates well below today's standards.

To meet gas turbine requirements concerning sulfur, alkali and particulate content, a high-temperature ceramic barrier filter is used to remove particulate from the fuel gas. None of the coals tested, including the Illinois No. 6, had as high an alkali content as, for instance, the IBC-109 coal in the Illinois sample bank, nor has sufficient work been done to be able to determine the fate of these alkalies, nor how and in what form they remain in a gaseous state or how they form on the residual char.

The results of this study are being correlated to the pilot plant work at Foster Wheeler. With such correlations in hand, commercial-size design of a high-efficiency combined cycle utilizing Illinois coals can be undertaken at minimum risk in the near term.

We have previously investigated the kinetics of chlorine release from coal under an inert atmosphere, and have reported rate constants and activation energy over a temperature range of 350-385°C.

**Experimental Procedure**

**Description of Equipment** The previous reports have described the details of the partial gasification system. Briefly, air and nitrogen flow from gas tanks through tubular preheaters, after which water is added. The steam and nitrogen enriched air is further heated and enters a 2 inch ID stainless steel column after passing through a bed support screen, where coal or coal/dolomite mixtures are added to the column, usually in increments of 5 g. On runs where dolomite is used, it is added in the same ratio with respect to coal as employed at the Foster Wheeler pilot plant. Measured samples are withdrawn continuously from the gas stream above the bed through a heated stainless steel sampling port. The samples are passed through 400 ml of distilled water, held in plastic sampling bottles, and analyzed by use of ion-specific probes and, on selected samples, by Inductively Coupled Plasma (ICP) spectroscopy. The main gas stream passes through a cyclone to separate entrained solids, and is sampled for analysis of the major gas components by gas chromatography. Unconverted coal and dolomite are removed from the column following each run, by injection of nitrogen through a port located above the bed support screen.

**Coals Used** Most runs have been performed with the IBC-109 coal and another Illinois No. 6 coal (FW IL #6) that has been used at the Foster Wheeler pilot plant at Livingston, New Jersey. The major difference between the two coals is the chlorine content. The IBC-109 coal is high in chlorine
content (0.4 %), while the other Illinois No. 6 coal contains only 0.06 % chlorine. Thus, any effect of chlorine on the rate and extent of release of the alkali metals to the vapor phase should be evident.

Results and Discussion

Chlorine Behavior Under Pre-gasification Conditions. A relation was found between percent chlorine lost to the gas phase and the % volatile loss for IBC-109 coal under pre-gasification conditions (most of this data is from our previous study, that involved thermal treatment to temperatures of only 420°C). In spite of the fact that the data were obtained over a range of times, temperatures, and particle sizes, the correlation with volatile loss is apparent. Note that most of the chlorine was removed from the coal at temperatures well below that employed in the gasifier. This suggests that little chlorine would remain in the coal at gasification temperatures, and thus not be available to facilitate transport of the alkali metals to the gas phase.

Sodium and Potassium Behavior Under Gasification Conditions. Although most absorber samples were also analyzed for sodium and potassium by ICP in addition to the ion-specific probe method, review of the data indicated interference with the ICP (especially the sodium values) resulted in false high values for the smaller particle size coals. Thus the absorber sample results presented here are calculated based on the ion specific probe values. The nature of the interference in the ICP measurements is not known at this time; one possibility is that colloidal particles carrying the interfering substance pass through the filter used prior to analysis.

The mean value for percent potassium released was 11.9%, and that for sodium released 20.7%. Translated to concentrations in the product gas stream, these values are comparable to concentrations reported previously for the Foster Wheeler pilot plant operation.

For potassium, Dolomite and Particle Size were indicated to be significant variables at the 83.5% and 86% confidence levels, respectively.

For sodium, the effect of adding dolomite shows a most probable reduction of 10% in the sodium released, with 99% confidence there is an effect. When the pure error mean square, rather than error evaluated by the fitted line, was used to determine the confidence intervals, significant effects were indicated for all variables: The higher chlorine content coal (IBC-109) exhibited slightly less sodium evolution, the larger particle size coal showed increased
potassium evolution, and higher temperatures decreased potassium evolution.

**Solid Analyses.** Selected samples of chars resulting from the partial gasification of the coals used, with and without Dolomite addition, were analyzed. Some samples that were processed under pre-gasification conditions were also analyzed, as were char samples provided by Foster Wheeler. Proximate analyses, total sulfur, and alkali metals were determined.

Analyses of selected solid samples from the gasification runs indicate that the greater portion of the alkali metals are retained in the solid phase. This is consistent with the absorber data. The sodium and potassium values on the product chars were comparable to those measured in the Foster Wheeler char (which was from a Pittsburgh seam coal).

**Conclusion(s) and Recommendation(s)**

Most of the chlorine present in the coal is released at temperatures below those employed for gasification. Over the range of particle sizes (128-425μm), temperature (846-965°C), and quantity of dolomite added (0 or 16% of the coal weight), the following observations may be made:

* an average of 11.9% of the potassium enters the gas phase under gasification conditions.

* the response of the removal of potassium to changes in the values of the variables studied was not significant.

* an average of 20.7% of the sodium enters the gas phase under gasification conditions.

* the response of the removal of sodium to changes in the values of the variables studied were more significant, especially for the effect of dolomite, where a negative relationship was observed at the 99% confidence level.

* Solid analyses were consistent with the above findings; the major portion of the alkali metals is retained in the solid phase during gasification.

* TGA performed on selected samples of the product char produced curves similar to those obtained with the Foster Wheeler chars. The gasification solid product is somewhat unreactive, as indicated by the fairly high temperatures required for ignition and burnout.

* The analytical procedure involving ashing followed by sequential extraction with HCl and HF has proven to be a useful technique for determination of the alkali metal concentration in the coals and product chars.
OBJECTIVES

The overall objective of the project was to support the integrated partial gasification process being developed by the Foster Wheeler Development Corporation. That process utilizes mild gasification conditions to give only gas and char products. Limestone addition to the gasifier captures much of the sulfur released during the gasification; the fate of chlorine and the alkali metals (Na and K) is unknown. This proposal addresses that issue, in terms of the following specific project goals: 1) determination of the rates and extent of removal of sodium, potassium, and sulfur, in addition to chlorine, from the solid phase under pre-gasification and gasification conditions, 2) evaluation of the chemical transformations of the elements that occur under partial gasification conditions, and 3) to assess the reactivity of the product char from the experiments.

The results of this project are being complemented by those of a companion project that is determining the sulfur and nitrogen oxide emissions from the combustion of the residual char from the Foster Wheeler gasifier. Together, the results will aid in determination of the required operating conditions to allow high-sulfur/high-chlorine Illinois coals to be utilized in advanced combined-cycle power generation and co-generation systems.

To meet the stated objectives of the project, the following tasks have been scheduled.

Task A, Equipment Modification: The existing fluidized bed system requires modification to attain the higher temperatures required for the gasification reactions, to incorporate means to introduce steam at controlled rates to the fluidizing column.

Task B, Obtain and Prepare Coal Samples: In addition to the IBC-109 coal that we have been using for previous chlorine removal rate studies, samples of the Pittsburgh No. 8 coal and an additional Illinois coal will be obtained from Foster Wheeler. Coals will be carefully prepared by riffling sub-samples and grinding to the desired particle size (down to -200 mesh). Samples will be maintained under nitrogen during storage.

Task C, Perform Baseline Runs: Coal will be charged to the reactor after reaction temperature is attained, without limestone and under an inert atmosphere. Rates of release of chlorine, sodium, potassium and sulfur will be measured over the temperature range 400-1000°C, or until significant agglomeration occurs.

Task D, Perform Fluidized Bed Runs under Gasification Conditions: After preheating the reactor, limestone will be
charge to the reactor and brought to the desired reaction temperature. Coal will then be charged to the reactor. Chlorine, alkali metal, and sulfur evolution rates will be measured, and kinetic parameters determined. The fluidizing phase used will be the steam/air mixture specified for the gasification process. Temperatures up to 1000°C will be evaluated.

**Task E, Determine Reactivity of Char:** In addition to analysis for chlorine, alkali metals and proximate analysis, selected samples will be evaluated for char reactivity by TGA combustion profile procedures. Isothermal reactivities with CO₂, as well as steam reactivity employing an Exxon miniature gasifier will be performed.

**Task F, Perform Gas and Solid Analyses.** The gas samples will be analyzed by use of a gas chromatograph. Solid samples will be subjected to water and acid leaching and the leachates analyzed for chloride and the alkali metals, in addition to proximate and sulfur analyses.

**Task G, Analyze Data:** Rate constants and activation energies will be calculated for the constituents studied, and a mechanistic model developed to explain the observed distribution of products between the gas and solid phases. Evaluation of scale-up procedures will be performed, with respect to process operation with larger column diameter fluidized beds (Foster Wheeler personnel will perform the scale-up evaluation).

**INTRODUCTION AND BACKGROUND**

Foster Wheeler Development Corporation (FWDC), as a subcontractor in this proposal, is presently working on two DOE contracts that are developing the major components and processes as follows: DOE Contract DE-AC21-86MC21023 — Second-Generation Pressurized Fluidized Bed Cycle, and the second, DOE Contract DE-AC22-91PC91154 — Development of a High-Performance Coal-Fired Power Generating System with a Pyrolysis Gas- and Char-Fired High-Temperature Furnace, which is part of the "Combustion 2000" program. Both of these programs utilize a partial gasification process to produce fuel gas for powering a gas turbine and combustion of the char residual from the partial gasification process to raise steam and/or preheat air for the gas turbine cycle. A variation of these two cycles for near-term use involves using the partial gasification process to drive the gas turbine and combustion of the char in an atmospheric pressure circulating fluidized bed combustor to raise steam.

Foster Wheeler is committed to commercialization of integrated partial gasification systems. The proposed systems are capable, using today's gas and steam turbine technology, of achieving energy conversion efficiencies of 45-48% HHV at
a cost of electricity up to 20% below today's costs using
pulverized coal-fired steam generating boiler plants at
emission rates well below today's standards.

Common to all three schemes is the partial gasifier. Under
DOE Contract DE-AC21-86MC21023, over 500 hours of testing of
this gasifier with a coal feed capacity of 400 lb/hr has
demonstrated excellent performance. Most of the work has
been conducted using a Pittsburgh No. 8 coal. Limited runs
have been performed with a western (Eagle Butte coal) and an
Illinois No. 6 coal.

To meet gas turbine requirements concerning sulfur, alkali
and particulate content, a high-temperature ceramic barrier
filter is used to remove particulate from the fuel gas.
Sulfur content of the fuel gas is controlled by feeding
dolomite or limestone to the gasifier. Alkali content of
the fuel gas for the coal used indicates that to meet the
gas turbine requirements, it may be necessary to cool the
fuel gas to approximately 1000°F from the gasifier operating
temperature of approximately 1750°F to condense sufficient
alkali to meet those requirements. However, none of the
coals tested, including the Illinois No. 6, had as high an
alkali content as, for instance, the IBC-109 coal in the
Illinois sample bank, nor has sufficient work been done to
be able to determine the fate of these alkalies, nor how and
in what form they remain in a gaseous state or how they form
on the residual char.

The residual char produced in the gasifier would, in the
near-term scheme, be combusted in a circulating fluid bed.
This char, which contains organic sulfur as well as ash and
calcium sulfide, has been characterized for the three coals
tested. However, this has not been done for high-chlorine/
high-sulfur Illinois coals. Both the gasification work
proposed here and the combustion work proposed in a compan-
ion proposal will be conducted in small bench-scale systems
which are available at Southern Illinois University at
Carbondale. The results will be correlated to the pilot
plant work at Foster Wheeler. With such correlations in
hand, commercial-size design of a high-efficiency combined
cycle utilizing Illinois coals can be undertaken at minimum
risk in the near term.

The fate of sodium and potassium in the pressurized fluid-
ized bed combustion and gasification of peat over the
temperature range 700-1000°C has been reported by Mojtabahdi
and Backman5,6. They found the volatile phase compounds of
sodium and potassium consisted primarily of chlorides and
hydroxides, and the condensed phase contained chlorides and
carbonates. Up to 20% of the sodium and 70% of the potassi-
um were found present in the vapor phase at 800°C under
their gasification conditions. High chlorine content
enhanced volatilization of the alkali metals.
The literature is more extensive in the areas of pyrolysis and combustion, compared to gasification. Solomen, et al. have recently published an extensive review of 357 publications related to experiments involving kinetic rates and mechanisms of coal pyrolysis. Their review compares results from various reactor types, and provides a critical analysis of previously reported pyrolysis data. There is little mention, however, of chlorine and alkali metal behavior. Gibb and Angus performed bomb combustion tests with coals and found, contrary to previous theory, that sodium did not appear to exert an important control on potassium release. Manzoori and Agarwal studied fluidized bed combustion of high sodium, high sulfur low ash coals, and found evidence of the formation of a low melting point eutectic; the molten ash consisted of a matrix of mixed alkali sulfates.

We have previously investigated the kinetics of chlorine release from coal under an inert atmosphere, and have reported rate constants and activation energy over a temperature range of 350-385°C.

EXPERIMENTAL PROCEDURE

Description of Equipment

The previous reports have described the details of the partial gasification system that is shown in Figure 1. Briefly, air and nitrogen flow from gas tanks through tubular preheaters, after which water is added. The steam and nitrogen enriched air is further heated and enters a 2 inch ID stainless steel column after passing through a bed support screen, where coal or coal/dolomite mixtures are added to the column, usually in increments of 5 g. On runs where dolomite is used, it is added in the same ratio with respect to coal as employed at the Foster Wheeler pilot plant. Measured samples are withdrawn continuously from the gas stream above the bed through a heated stainless steel sampling port. The samples are passed through 400 ml of distilled water, held in plastic sampling bottles, and analyzed by use of ion-specific probes and, on selected samples, by Inductively Coupled Plasma (ICP) spectroscopy. The main gas stream passes through a cyclone to separate entrained solids, and is sampled for analysis of the major gas components by gas chromatography. Unconverted coal and dolomite are removed from the column following each run, by injection of nitrogen through a port located above the bed support screen.

Coals Used

The primary coals used were the IBC-109 coal and another Illinois No. 6 coal (FW-IL #6) that has been used at the Foster Wheeler pilot plant at Livingston, New Jersey. Table
1 compares the characteristics of the two coals. Note that the major difference between the two coals is the chlorine content. The IBC-109 coal is high in chlorine content (0.4 %), while the other Illinois No. 6 coal contains only 0.06 % chlorine. Thus, any effect of chlorine on the rate and extent of release of the alkali metals to the vapor phase should be evident.

TABLE 1
Analysis of Coals Used

<table>
<thead>
<tr>
<th>Analysis %, dry basis)</th>
<th>IBC-109</th>
<th>FW IL #6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Carbon</td>
<td>57.6</td>
<td>49.3</td>
</tr>
<tr>
<td>Ash</td>
<td>7.63</td>
<td>13.2</td>
</tr>
<tr>
<td>Volatile</td>
<td>34.7</td>
<td>37.5</td>
</tr>
<tr>
<td>K</td>
<td>0.17</td>
<td>0.2</td>
</tr>
<tr>
<td>Na</td>
<td>0.07</td>
<td>0.1</td>
</tr>
<tr>
<td>Cl</td>
<td>0.4</td>
<td>0.06</td>
</tr>
<tr>
<td>S</td>
<td>1.13</td>
<td>2.86</td>
</tr>
</tbody>
</table>

Analytical Procedures

Proximate, Sulfur, and Chlorine Analyses The coal and char samples were analyzed by proximate analysis and sulfur by the Southern Illinois University Coal Testing Lab at the Carterville Coal Development Park. The chlorine content of the samples were determined by ASTM D 2361 - 91.

Analysis of Coal and Char for Sodium and Potassium A simplified analytical procedure for analysis of sodium and potassium in coal has been developed. The procedure involves high temperature ashing followed by sequential extraction with HCl and HF. Agreement with published values for three Argonne coal samples has been previously reported.

Determination of Sodium, Potassium, and Chlorine Released to the Gas Phase The procedure applied for determination of the sodium, potassium and chlorine released to the gas phase during gasification was based on water absorption, followed by analysis of the aqueous samples. The bed sample port was kept hot water by an electric resistance heating tape to minimize deposition of sodium and potassium. This sample port was located as close to the fluidized bed as physically possible, but was limited by the bed ceramic heater and possible interference with fluidization. The water of the absorber was analyzed with a model EA 940 expandable ion analyzer by Orion for sodium, potassium and chlorine. ICP spectroscopy was also performed for sodium and potassium.
Experimental Design and Data Analysis

The variables that were investigated in this study are indicated in Table 2.

<table>
<thead>
<tr>
<th>Variable</th>
<th>low level</th>
<th>High Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>FW II#6</td>
<td>ICB-109</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0</td>
<td>0.16, ratio dolomite/coal</td>
</tr>
<tr>
<td>Mesh size</td>
<td>-60 + 100</td>
<td>-30 + 60</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>850</td>
<td>950</td>
</tr>
</tbody>
</table>

An experimental design and data analysis program (RS/1) was utilized to minimize the test matrix, and facilitate statistical analysis of the data obtained. The measured system responses are the transfer of potassium and sodium from the solid to the gaseous phase, expressed as percent of the constituent in the original coal.

RESULTS AND DISCUSSION

Sodium, Potassium and Chlorine Behavior Under Pre-gasification Conditions.

Figure 2 presents the relation between percent chlorine lost to the gas phase and the % volatile loss for IBC-109 coal under pre-gasification conditions (most of this data is from our previous study, that involved thermal treatment to temperatures of only 420°C). In spite of the fact that the data were obtained over a range of times, temperatures, and particle sizes, the correlation with volatile loss is apparent. Note that most of the chlorine was removed from the coal at temperatures well below that employed in the gasifier. This suggests that little chlorine would remain in the coal at gasification temperatures, and thus not be available to facilitate transport of the alkali metals to the gas phase.

Difficulties with analysis of the absorber samples for chlorine by probe measurement were encountered, presumably due to the interference of sulfide present in the sample. Thus chlorine values are not reported for the runs under gasification conditions.

Although most absorber samples were also analyzed for sodium and potassium by ICP in addition to the ion-specific probe method, review of the data indicated interference with the ICP (especially the sodium values) resulted in false high values for the smaller particle size coals. Thus the absorber sample results presented here are calculated based on the ion specific probe values. The nature of the interference in the ICP measurements is not known at this time;
one possibility is that colloidal particles carrying the interfering substance pass through the filter used prior to analysis.

Table 3 presents the descriptive statistics for the controlled variables studied, and the response variables "percent potassium released to the gas phase" (PKINGSP) and "percent sodium released to the gas phase" (PNAINGSP). Q1, Q3, and IQR refer to the first quartile, third quartile, and inter-quartile range, respectively. The mean value for percent potassium released was 11.9%, and that for sodium released 20.7%. Translated to concentrations in the product gas stream, these values are comparable to concentrations reported previously for the Foster Wheeler pilot plant operation.

<table>
<thead>
<tr>
<th>Variable</th>
<th>DOLOMITE % of coal wt.</th>
<th>PART_SIZE μm</th>
<th>TEMP °C</th>
<th>PKINGSP %</th>
<th>PNAINGSP %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Count</td>
<td>49.0</td>
<td>49.0</td>
<td>49.0</td>
<td>48.000000</td>
<td>47.000000</td>
</tr>
<tr>
<td>Mean</td>
<td>5.9</td>
<td>278.2</td>
<td>903.5</td>
<td>11.858228</td>
<td>20.727000</td>
</tr>
<tr>
<td>Stdev</td>
<td>7.8</td>
<td>114.3</td>
<td>41.9</td>
<td>14.499829</td>
<td>12.739409</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.0</td>
<td>128.0</td>
<td>846.0</td>
<td>0.419727</td>
<td>0.000000</td>
</tr>
<tr>
<td>Q1</td>
<td>0.0</td>
<td>200.0</td>
<td>860.0</td>
<td>3.115259</td>
<td>13.714834</td>
</tr>
<tr>
<td>Median</td>
<td>0.0</td>
<td>200.0</td>
<td>915.0</td>
<td>7.169205</td>
<td>18.445110</td>
</tr>
<tr>
<td>Q3</td>
<td>16.0</td>
<td>425.0</td>
<td>928.0</td>
<td>14.779629</td>
<td>28.745465</td>
</tr>
<tr>
<td>Maximum</td>
<td>16.0</td>
<td>425.0</td>
<td>965.0</td>
<td>82.352941</td>
<td>59.870410</td>
</tr>
<tr>
<td>IQR</td>
<td>16.0</td>
<td>225.0</td>
<td>68.0</td>
<td>11.664370</td>
<td>15.030630</td>
</tr>
</tbody>
</table>

Utilizing the data represented by the summary given in table 2, plus the variable "Flow" and the two coals studied, the RS/1 program was used to generate multiple regression models to fit the data obtained. Table 4 presents the regression results for the response "percent potassium released to the gas phase". The last column, "Signif.", indicates the extent to which the given variable appears to have a significant effect on the response variable. For example, a significance value of 0.10 implies 90% confidence there is an effect. Note that none of the variables exhibited significance at the 90% confidence level; Dolomite and Particle Size were indicated to be significant at the 83.5% and 86% confidence levels, respectively. The variable "Flow", the flow rate of the sample stream through the absorber, was included in the initial equation and exhibited a significance value of 0.81, indicating that changes in flow rate through the absorber did not have a significant effect on
absorber efficiency. This term was then eliminated from the model. Figure 3 presents the effects of the controlled variables on the response variable. If the 95% error bars overlap the "zero effect" line, the presence of an effect cannot be claimed with 95% confidence. The tick marks at the center of each error bar indicates the most probable effect on the response variable, as it is changed from the minimum to maximum value. Table 5 and Figure 4 were generated after elimination of the "flow" variable; only slight improvements in the significance level of the remaining variables are evident.

Table 6 and Figure 5 present the regression results for the response "percent sodium released to the gas phase", using the same controlled variables as described for the potassium evolution. Again, the "Flow" variable did not demonstrate a significant effect, and was eliminated from the model; Table 7 and Figure 6 were then generated. Note that the effect of adding dolomite shows a most probable reduction of 10% in the sodium released, with 99% confidence there is an effect. Figure 7 was prepared using pure error mean square, rather than error evaluated by the fitted line, to determine the confidence intervals. Note that significant effects are now indicated for all variables.

Solid Analyses

Selected samples of chars resulting from the partial gasification of the coals used, with and without Dolomite addition, were analyzed. Some samples that were processed under pre-gasification conditions were also analyzed, as were char samples provided by Foster Wheeler. Proximate analyses, total sulfur, and alkali metals were determined. Table 8 presents proximate and total sulfur analyses; the alkali metal analyses are given in Table 9. The concentrations of sodium and potassium resulting from sequential digestion of the ashed samples with hydrochloric and hydrofluoric acids are presented. The total concentration of each of these components in the original char sample was calculated by summing the removals obtained with each acid. The first 5 runs listed in Table 9 were conducted under pre-gasification conditions, under a nitrogen atmosphere. The numbers given in the sample name indicate the percent removal of chlorine obtained by the thermal treatment. Solid recoveries for these runs were greater than 90%. Thus, if no alkali metals were lost to the gas phase, a slight increase in concentration in the treated coal would be expected. This was observed for sodium. However, the potassium concentration decreased slightly. Nevertheless, it is evident that the greater portion of the alkali metals are retained in the solid phase. This is consistent with the absorber data. The sodium and potassium values on the product chars were comparable to those measured in the Foster Wheeler char (which was from a Pittsburgh seam coal).
TGA Analyses

Selected samples of the chars produced were subjected to reactivity evaluation by TGA. A typical result is shown in Figure 8. The TGA analyses indicate that in general the chars were of moderate to poor reactivity, as indicated by relatively high ignition temperatures.

CONCLUSION(S) AND RECOMMENDATION(S)

Most of the chlorine present in the coal is released at temperatures below those employed for gasification. Over the range of particle sizes (128-425μm), temperature (846-965°C), and quantity of dolomite added (0 or 16% of the coal weight), the following observations may be made:

* An average of 11.9% of the potassium enters the gas phase under gasification conditions.

* The response of the removal of potassium to changes in the values of the variables studied was not significant.

* An average of 20.7% of the sodium enters the gas phase under gasification conditions.

* The response of the removal of sodium to changes in the values of the variables studied were more significant, especially for the effect of dolomite, where a negative relationship was observed at the 99% confidence level.

* Solid analyses were consistent with the above findings; the major portion of the alkali metals is retained in the solid phase during gasification.

* TGA performed on selected samples of the product char produced curves similar to those obtained with the Foster Wheeler chars. The gasification solid product is fairly unreactive, as indicated by the fairly high temperatures required for ignition.

* The analytical procedure involving ashing followed by sequential extraction with HCl and HF has proven to be a useful technique for determination of the alkali metal concentration in the coals and product chars.

REFERENCES


Figure 1. Flow diagram of experimental set up.

Figure 2. Chlorine removal related to volatile loss under pre-gasification conditions.
TABLE 4.
Least squares coefficients for the response of % potassium removal resulting from changes in coal used, dolomite added, particle size, temperature, and flow rate.

Least Squares Coefficients, Response PK, Model FWM11

<table>
<thead>
<tr>
<th>Term</th>
<th>Coeff.</th>
<th>Std. Error</th>
<th>T-value</th>
<th>Signif.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1</td>
<td>-23.017537</td>
<td>47.637226</td>
<td>0.6000</td>
<td></td>
</tr>
<tr>
<td>2 C&lt;1df&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 IL#6</td>
<td>-1.196258</td>
<td>2.263720</td>
<td>-0.53</td>
<td>0.6000</td>
</tr>
<tr>
<td>4 IBC-109</td>
<td>1.196258</td>
<td>2.263720</td>
<td>0.53</td>
<td>0.6000</td>
</tr>
<tr>
<td>5 D</td>
<td>-0.371731</td>
<td>0.274976</td>
<td>-1.35</td>
<td>0.1837</td>
</tr>
<tr>
<td>6 P</td>
<td>-0.025143</td>
<td>0.020335</td>
<td>-1.24</td>
<td>0.2232</td>
</tr>
<tr>
<td>7 T</td>
<td>0.050358</td>
<td>0.051764</td>
<td>0.97</td>
<td>0.3362</td>
</tr>
<tr>
<td>8 F</td>
<td>-0.023570</td>
<td>0.099314</td>
<td>-0.24</td>
<td>0.8136</td>
</tr>
</tbody>
</table>

No. cases = 48  R-sq. = 0.1442  RMS Error = 14.19
Resid. df = 42  R-sq-adj. = 0.0423  Cond. No. = 67.42

Mulreg FWM11, Model FWM11
Main Effects on Response PKINGSP
(with 95% Confidence Intervals)

C: "IL#6" to "IBC-109"
D: 0 to 16
P: 128 to 425
T: 846 to 965
F: 23 to 122.27

Figure 3. Effects box plot for the response of % potassium removal resulting from changes in coal used, dolomite added, particle size, temperature, and flow rate.
TABLE 5.

Least squares coefficients for the response of % potassium removal resulting from changes in coal used, dolomite added, particle size and temperature.

<table>
<thead>
<tr>
<th>Term</th>
<th>Coeff.</th>
<th>Std. Error</th>
<th>T-value</th>
<th>Signif.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1</td>
<td>-23.683208</td>
<td>47.029868</td>
<td></td>
<td>0.5163</td>
</tr>
<tr>
<td>2 C&lt;1df&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 IL#6</td>
<td>-1.378353</td>
<td>2.106222</td>
<td>-0.65</td>
<td>0.5163</td>
</tr>
<tr>
<td>4 IBC-109</td>
<td>1.378353</td>
<td>2.106222</td>
<td>0.65</td>
<td>0.5163</td>
</tr>
<tr>
<td>5 D</td>
<td>-0.380399</td>
<td>0.269532</td>
<td>-1.41</td>
<td>0.1653</td>
</tr>
<tr>
<td>6 P</td>
<td>-0.027178</td>
<td>0.018235</td>
<td>-1.49</td>
<td>0.1434</td>
</tr>
<tr>
<td>7 T</td>
<td>0.050095</td>
<td>0.051181</td>
<td>0.98</td>
<td>0.3332</td>
</tr>
</tbody>
</table>

No. cases = 48  
R-sq. = 0.1431  
RMS Error = 14.03  
Resid. df = 43  
R-sq.-adj. = 0.0633  
Cond. No. = 59.95

Mulreg FWM1, Model FWM11_COPY
Main Effects on Response PKINGSP
(with 95% Confidence Intervals)

Figure 4. Effects box plot for the response of % potassium removal resulting from changes in coal used, dolomite added, particle size and temperature.
TABLE 6.
Least squares coefficients for the response of % sodium removal resulting from changes in coal used, dolomite added, particle size, temperature, and flow rate.

**Least Squares Coefficients, Response PN, Model FWM31**

<table>
<thead>
<tr>
<th>Term</th>
<th>Coeff.</th>
<th>Std. Error</th>
<th>T-value</th>
<th>Signif.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1</td>
<td>69.154578</td>
<td>40.752853</td>
<td></td>
<td>0.4184</td>
</tr>
<tr>
<td>2 &lt;ldf&gt;</td>
<td></td>
<td></td>
<td></td>
<td>0.4184</td>
</tr>
<tr>
<td>3 IL#6</td>
<td>1.518997</td>
<td>1.858260</td>
<td>0.82</td>
<td>0.4184</td>
</tr>
<tr>
<td>4 IBC-109</td>
<td>-1.518997</td>
<td>1.858260</td>
<td>-0.82</td>
<td>0.4184</td>
</tr>
<tr>
<td>5 D</td>
<td>-0.582935</td>
<td>0.231842</td>
<td>-2.51</td>
<td>0.0159</td>
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<tr>
<td>6 P</td>
<td>0.020051</td>
<td>0.017185</td>
<td>1.17</td>
<td>0.2500</td>
</tr>
<tr>
<td>7 T</td>
<td>-0.050192</td>
<td>0.043928</td>
<td>-1.14</td>
<td>0.2598</td>
</tr>
<tr>
<td>8 F</td>
<td>-0.070033</td>
<td>0.004327</td>
<td>-0.93</td>
<td>0.3602</td>
</tr>
</tbody>
</table>

No. cases = 47, R-sq. = 0.2104, RMS Error = 11.99
Resid. df = 41, R-sq-adj. = 0.1141
Cond. No. = 67.28

**Mulreg FWM3, Model FWM31**

Main Effects on Response PNAINGSP
(with 95% Confidence Intervals)

C: "IBC-109" to "IL#6"
D: 0 to 16
P: 128 to 425
T: 846 to 965
F: 23 to 122.27

Figure 5. Effects box plot for the response of % sodium removal resulting from changes in coal used, dolomite added, particle size, temperature, and flow rate.
Least squares coefficients for the response of % sodium removal resulting from changes in coal used, dolomite added, particle size and temperature.

**Least Squares Coefficients, Response PN, Model FWM41**

<table>
<thead>
<tr>
<th>Term</th>
<th>Coeff.</th>
<th>Std. Error</th>
<th>T-value</th>
<th>Signif.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1</td>
<td>65.087021</td>
<td>40.445725</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 C&lt;1df&gt;</td>
<td></td>
<td></td>
<td>0.5651</td>
<td></td>
</tr>
<tr>
<td>3 IL#6</td>
<td>1.031488</td>
<td>1.778964</td>
<td>0.58</td>
<td>0.5651</td>
</tr>
<tr>
<td>4 IBC-109</td>
<td>-1.031488</td>
<td>1.778964</td>
<td>-0.58</td>
<td>0.5651</td>
</tr>
<tr>
<td>5 D</td>
<td>-0.612498</td>
<td>0.229237</td>
<td>-2.67</td>
<td>0.0107</td>
</tr>
<tr>
<td>6 P</td>
<td>0.013572</td>
<td>0.015667</td>
<td>0.87</td>
<td>0.3913</td>
</tr>
<tr>
<td>7 T</td>
<td>-0.049079</td>
<td>0.043836</td>
<td>-1.12</td>
<td>0.2692</td>
</tr>
</tbody>
</table>

No. cases = 47  
R-sq. = 0.1939  
RMS Error = 11.97

Resid. df = 42  
R-sq-adj. = 0.1171  
Cond. No. = 59.63

**Mulreg FWM3, Model FWM32**

Main Effects on Response PNAINGSP  
(with 95% Confidence Intervals)

C: "IBC-109" to "IL#6"

D: 0 to 16

P: 128 to 425

T: 846 to 965

![Graph](image)

Figure 6. Effects box plot for the response of % sodium removal resulting from changes in coal used, dolomite added, particle size and temperature.
Mulreg FWM4, Model FWM41
Main Effects on Response PNAINGSP
(with 95% Confidence Intervals)

C: "IBC-109" to "IL#6"
D: 0 to 16
P: 128 to 425
T: 846 to 965

Increase in PN

Figure 7. Effects box plot for the response of % sodium removal resulting from changes in coal used, dolomite added, particle size and temperature; confidence intervals based on pure error mean square.

DELTA SERIES TGA7

Figure 8. Typical TGA performed on a product char.
Table 8
Proximate and Sulfur analyses on selected solid samples

Proximate Analyses

<table>
<thead>
<tr>
<th>Run</th>
<th>Shot</th>
<th>Coal</th>
<th>Particle size (μm)</th>
<th>Temp. (°C)</th>
<th>Volatile (%)</th>
<th>Ash (%)</th>
<th>F-Carbon (%)</th>
<th>Sulfur (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>final</td>
<td>IL#6</td>
<td>200</td>
<td>957</td>
<td></td>
<td></td>
<td></td>
<td>0.8895</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>IBC-109</td>
<td>200</td>
<td>965</td>
<td></td>
<td></td>
<td></td>
<td>1.695</td>
</tr>
<tr>
<td>12</td>
<td>4</td>
<td>IBC-109D</td>
<td>200</td>
<td>963</td>
<td></td>
<td></td>
<td></td>
<td>0.798</td>
</tr>
<tr>
<td>13</td>
<td>4</td>
<td>IBC-109D</td>
<td>425</td>
<td>915</td>
<td></td>
<td></td>
<td></td>
<td>1.56</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>IBC-109</td>
<td>3</td>
<td>1.25</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>15</td>
<td>3</td>
<td>IBC-109</td>
<td>425</td>
<td>920</td>
<td></td>
<td></td>
<td></td>
<td>1.145</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>IBC-109</td>
<td>200</td>
<td>876</td>
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<td>79.26</td>
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<td>0.0417</td>
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<tr>
<td>char</td>
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<td></td>
<td>890</td>
<td>5.45</td>
<td>88.15</td>
<td>6.4</td>
<td></td>
<td>16.2</td>
</tr>
<tr>
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<td></td>
<td>425</td>
<td>0.88</td>
<td>99.12</td>
<td>0</td>
<td></td>
<td>21.5</td>
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<tr>
<td>char</td>
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<td></td>
<td>200</td>
<td>2.15</td>
<td>97.85</td>
<td>0</td>
<td></td>
<td>19.55</td>
</tr>
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</table>
Table 9: Sodium and Potassium analyses of selected solid samples

<table>
<thead>
<tr>
<th>Run</th>
<th>Shot</th>
<th>Coal</th>
<th>Particle size μm</th>
<th>Temp. °C</th>
<th>Weight g</th>
<th>Na ppm</th>
<th>K ppm</th>
<th>Na ppm</th>
<th>K ppm</th>
<th>Na %</th>
<th>K %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tony65.6</td>
<td>1</td>
<td>IBC-109</td>
<td>200</td>
<td>350</td>
<td>1.003</td>
<td>3.127</td>
<td>4.575</td>
<td>2.445</td>
<td>4.374</td>
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<td>0.178</td>
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<tr>
<td>Tony75.2</td>
<td>1</td>
<td>IBC-109</td>
<td>200</td>
<td>400</td>
<td>1.036</td>
<td>2.313</td>
<td>1.644</td>
<td>2.135</td>
<td>2.029</td>
<td>0.086</td>
<td>0.071</td>
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<tr>
<td>Tony69.6</td>
<td>1</td>
<td>IBC-109</td>
<td>128</td>
<td>350</td>
<td>1.011</td>
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<td>4.64</td>
<td>2.293</td>
<td>3.485</td>
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<td>0.161</td>
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<tr>
<td>Tony82.8</td>
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<td>IBC-109</td>
<td>128</td>
<td>400</td>
<td>1.037</td>
<td>2.836</td>
<td>5.54</td>
<td>2.033</td>
<td>3.402</td>
<td>0.094</td>
<td>0.172</td>
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<td>Tony90.0</td>
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<td>IBC-109</td>
<td>128</td>
<td>450</td>
<td>1.017</td>
<td>2.97</td>
<td>8.135</td>
<td>1.965</td>
<td>-0.329</td>
<td>0.097</td>
<td>0.154</td>
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</table>

<table>
<thead>
<tr>
<th>200ml extract</th>
<th>in HCL</th>
<th>in HF</th>
<th>Total, in solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.099</td>
<td>0.147</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.105</td>
<td>0.298</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.130</td>
<td>0.314</td>
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</tr>
<tr>
<td>12</td>
<td>0.103</td>
<td>0.298</td>
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<tr>
<td>13</td>
<td>0.111</td>
<td>0.302</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.107</td>
<td>0.300</td>
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<td>0.070</td>
<td>0.036</td>
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</tr>
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<td>Char</td>
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<tr>
<td>Char</td>
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</table>
This work has been sponsored by the Illinois Department of Energy and Natural Resources through its Coal Development Board and Illinois Clean Coal Institute. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of IDENR and the ICCI.