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# FINAL TECHNICAL REPORT
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Project Title: **NA/CA CATALYZATION OF ILLINOIS COALS FOR GASIFICATION** DE-FG22-91PC 91334

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## ABSTRACT

Gasification for power generation via IGCC processes is expected to become an important market for high sulfur Illinois Basin coals. Fluid-bed gasifiers have significant advantages over entrained flow processes. These advantages include ease of control, large turndown capacity, high thermal efficiency, and moderate oxygen and steam requirements. Three of the most pressing technical problems in fluid-bed gasification of Illinois coals are the caking tendency, high sulfur content, and low carbon conversion and consequent large char recycle required in most systems. This program explores the use of gasification catalysts to attack these three problems. The catalysts are sodium/calcium mixtures. Another advantage of using catalysts is that gasification temperature might be lowered, leading to less expensive materials of construction and a reduction in alkali vaporization.

The results of this study indicate that these catalysts can reduce or eliminate the caking of Illinois coals. Loadings below 1 weight % were effective if the catalyst was added by impregnation at low pH (below about 5). An Na/Ca molar ratio of greater than 1 also leads to lower catalyst requirement. Characterization results suggest that at low pH, the catalyst forms exchanged carboxylate and phenolate groups on the coal surface. Gasification of catalyzed coals in a TGA apparatus indicated that the more dispersed catalysts remained active to higher levels of conversion. Presumably the more dispersed catalysts are less prone to deactivation by reaction with mineral matter. Bench-scale gasification tests demonstrated enhanced carbon conversion for catalyzed coals. Removal of mineral matter by washing or heavy liquid cleaning resulted in higher levels of conversion for a given catalyst loading. Sulfur capture correlated with catalyst loading and was as high as 50%. Sodium vaporization was low over high ash coal because Na reacts with mineral constituents to form $NaAlSiO_4$. For cleaned coal, Na losses were as high as 40% probably because less mineral matter was available to scavenge sodium.

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## EXECUTIVE SUMMARY

The goal of this program is to develop sodium/calcium catalysts which can be added to the high sulfur Illinois Basin coal at the coal preparation plant. The additives will improve the performance of these coals in fluid-bed gasification by reducing swelling, capturing sulfur, and increasing carbon conversion (or lowering the gasification temperature). It is envisioned that this enhanced coal product will be utilized in integrated gasification-combined cycle (IGCC) power generation facilities.

The test work involves coal pretreatments such as deep cleaning and oxidation upstream of catalyst addition. A typical test series includes performing the pretreatment, adding catalyst to the coal, characterization by measurement of catalyst loading, FSI, catalyst dispersion, TGA gasification rate, and FTIR, as well as testing for gasification activity and sulfur capture in a bench-scale fluid-bed gasifier. Gasifier chars are then characterized to determine the fate of the catalyst. The goal is to find the best combination of pretreatment, catalyst addition method, catalyst loading, and catalyst composition.

The most important results obtained during the first year of this project are summarized below.

### Feed Coal (IBC-105) Characterization

- Water washing resulted in ash content reduction from 18.4 to 8.9 percent. Heavy liquid cleaning reduced ash to 3.2 percent. Heavy liquid cleaning and water washing were equally effective in total sulfur reduction. Oxidation of the coal introduced nearly 7 percent oxygen.

- Water washing was effective at reducing naturally occurring sodium content from 0.115 to 0.058 weight percent.

- Cleaned coals were much less reactive than as-received coal because of lower catalytic mineral matter content.

### Preliminary Test Work

- Free swelling index (FSI) was found to be a good predictor of caking tendency under gasification conditions.

- Dry mixing as a catalyst addition technique was rejected because high catalyst loadings (5 weight percent) were required to eliminate caking.

## Characterization of Ca-Catalyzed IBC-105

- Ca addition eliminated swelling at less than 1.5 weight percent loading if added at pH less than 5. Higher loading was required at higher pH.

- Ca dispersion decreased with increasing catalyst loading but was not affected by pH.

- Ca addition at low pH resulted in the formation of Ca-exchanged carboxylate and phenolate groups on the coal surface.

- Impregnation of Ca at low pH led to high conversion and resistance to deactivation in TGA gasification tests.

- Heavy liquid cleaning and oxidation of the starting coal did not enhance the TGA reactivity of Ca-catalyzed coal.

## Characterization of Na + Ca Catalyzed IBC-105

- Na + Ca addition eliminated swelling at loadings less than 1.5 weight percent if added at low pH and Na/Ca greater than 1.

- Dispersion of this catalyst decreased with loading at Na/Ca ratio below 1. It was not affected by pH.

- At Na/Ca ratio greater than 1, dispersion was nearly constant with catalyst loading.

- Na + Ca addition at low pH resulted in formation of exchanged carboxylate and phenolate groups on the coal surface.

- Na + Ca catalysts were much more active than Ca alone in TGA gasification. Impregnation at low pH and with Na/Ca > 1 led to increased activity and resistance to deactivation.

- FSI of heavy liquid cleaned coals did not change by the addition of up to 3 weight percent Na + Ca.

- Heavy liquid cleaning, washing, and oxidation did not enhance catalytic activity.

## Bench Scale Gasification Tests

- Catalyst addition resulted in increased carbon conversion; however, there was no advantage of Na + Ca over Ca alone.

- Heavy liquid cleaning produced the greatest positive effect on catalyzed coal carbon conversion. Washing and oxidation had no great effect.

- Sulfur capture correlated with Ca content but never exceeded 50 percent.

- Sodium losses were low for high ash coal because Na reacts with aluminosilicates in the ash to form nepheline ($NaAlSiO_4$).

- Sodium losses from heavy liquid cleaned coal were as high as 40 percent, probably because of the low level of mineral matter available to scavenge the sodium.

Future work on this program will focus on understanding how coal properties influence the effectiveness of coal catalyzation methods and parameters. Special emphasis will be placed on development of improved bench-scale gasification methods. This will allow an investigation of the effect of gasification temperature and simulation of a near-commercial fluid-bed gasifier such as the U-GAS gasifier design.

## DISCLAIMER

## OBJECTIVES

This research program is investigating the effect of a number of catalyst addition variables on Illinois coal gasification. Several laboratory tests of catalyzed coal properties, as well as gasification in a bench-scale fluid-bed reactor, will be employed. The overall objective is to optimize catalyst loading, composition, and addition method for achieving high reactivity, processability, and low emissions. During 1992-1993, this objective was pursued through work in two main areas.

### Catalyzed Coal Preparation and Characterization

The effect of catalyst addition method and catalyst loading/composition on the properties of selected feed coals was evaluated. Coal pretreatment by cleaning and preoxidation was examined. The responses measured included catalyst dispersion, TGA gasification rate, and free swelling index. The starting coals were characterized. FTIR spectra of several catalyzed coals were measured.

### Bench-Scale Gasification Tests

Both the starting and catalyzed coals were gasified in a bench-scale fluid-bed gasifier. A temperature of 750°C was employed. Runs of 6 hours duration were performed. Product gases were analyzed for $CO$, $CO_2$, $H_2S$, $COS$, $CH_4$, and $H_2$ by mass spectrometry. Gasifier chars were characterized to determine carbon conversion, sulfur capture, and the fate of the catalyst.

## INTRODUCTION AND BACKGROUND

Illinois Basin coals make up an important national energy resource. Because of their high sulfur content, continued exploitation of this resource is in jeopardy. Amax Coal Industries (ACI), the third largest coal producer in the United States, operates two mines in Illinois and three mines in southwestern Indiana. These mines, managed by Amax Coal Company - Midwestern Operations, make up an important business area for ACI, and consequently, there is a strong interest within Amax in the development of new technologies for Illinois Basin coal utilization. Amax Research & Development, Inc. (Amax R&D) is the research arm of AMAX Inc., the parent company of ACI. Because of ACI's strong interest in the continued utilization of high sulfur coal resources in Illinois, Amax R&D is pursuing this program for development of gasification catalysts for Illinois coals.

Amax envisions adding the catalyst to the coal as part of coal preparation at the mine site. In this way, the catalyst

addition method and loading can be tailored for different coals and a value-added coal can be shipped from the mine. The catalyzed coal could be used as feedstock for integrated gasification combined cycle (IGCC) power generation, for the production of synthesis gas, or for the production of hydrogen. IGCC is probably the nearest term market.

Fluid-bed gasifiers would appear to be the preferred technology for IGCC because they have demonstrated high reliability, ease of operation, and high turndown capability. Additionally, they operate at lower temperatures than entrained flow gasifiers and have lower oxygen and steam requirements. The product gas contains no tar or oils.

Several problems complicate the use of Illinois coals in fluid-bed gasifiers. One problem is their tendency to swell or become plastic which leads to agglomeration. Consequently, special precautions are required such as the use of reactor designs and systems that are less efficient than would be the case otherwise. These designs include entrained and spouted beds and beds of inert material. The second problem is the low carbon conversion usually obtained in fluid-bed gasifiers which requires a high level of char recycle. To mitigate this problem, high temperatures are usually employed. This leads to an increased oxygen requirement relative to lower temperature operation. Increased oxygen demand requires a larger, more expensive oxygen plant for oxygen blown gasifiers. Higher oxygen demand leads to the production of lower Btu product gas. High temperature also requires expensive materials of construction and can increase agglomeration problems. Furthermore, higher temperatures lead to increased levels of alkali vaporization. Alkali vapors cause severe corrosion of gas turbine components. Finally, the high sulfur content of Illinois coals leads to high sulfur levels in the gasifier product gas.

Therefore, it is desirable to develop improved methods for Illinois coal gasification which mitigate the problems outlined above. This will result in reduced capital and operating costs and earlier, widespread commercialization of gasification technology. To achieve this goal, we are investigating technologies for catalyzing coal prior to gasification. Our goal is to develop a method of catalyzing coal which will result in high catalyst dispersion so that even low loadings generate high gasification reactivity at reduced temperature. The catalytic material will enhance the formation of cross-links in the coal leading to reduced agglomeration tendency. The catalyst can also capture some of the sulfur leading to the production of higher quality product gas.

The catalyst to be investigated consists of calcium mixed with sodium. Calcium and sodium have been separately shown to be good catalysts for steam/oxygen gasification of coals and chars. Potassium is probably the most commonly studied gasification catalyst, and the catalytic properties of sodium are similar. Sodium and potassium catalysts eventually deactivate by reaction with the coal mineral matter to form inactive sodium aluminosilicates (Lang and Neavel, 1982; Bruno et al., 1988). Both sodium and potassium can be converted to volatile oxides, hydroxides, chlorides, or sulfates during gasification. Several research groups have shown that alkali catalysts can be stabilized on a carbon surface by interac<sup> </sup>ion with oxygen functional groups or migration into the carbon matrix. The stabilized alkali is not volatile (Sams et al., 1985; Matsukata et al., 1989; Meijer et al., 1991). Calcium catalysts have a lower activity than sodium and tend to deactivate by sintering and agglomeration (Radovic et al., 1983).

Recently it has been demonstrated that when sodium or potassium and calcium are used in combination, a highly active catalyst is produced which maintains a high dispersion and is less reactive with ash constituents (Heinemann and Somorjai, 1991; Haga et al., 1991). Consequently, high rates of the catalyzed gasification reaction are obtained even at high levels of burn off and with low catalyst loading. No information on the effect of composite catalysts on alkali vaporization is available. This method of catalyzing coal may be economically more attractive than methods previously proposed. This is because low catalyst loading can be employed and the catalyst is not expensive.

The use of calcium and sodium compounds as agglomeration reducing agents has been investigated before (Tromp et al., 1986; Khan and Jenkins, 1989). It has been demonstrated that dispersed calcium or sodium can catalyze the formation of cross-links by bonding to carboxyl groups in the coal. However, most of these studies were directed at coal pyrolysis where cross-link formation reduces liquid yield and is, therefore, undesirable. Previous studies were also not concerned with achieving a high level of calcium dispersion. We plan to maximize dispersion and, therefore, cross-link density.

Dispersed and bulk calcium compounds have also been used as in-situ sulfur capture agents in gasification. Sulfur removal of greater than 90 percent from high sulfur coals has been demonstrated in the Lurgi circulating fluidized bed (Herbert et al., 1989).

We expect that the optimum Na/Ca ratio, loading, and addition method will be different for each of the three responses of

interest (catalyzed gasification, reduced agglomeration, and sulfur capture). The specific goal of the proposed program is to examine the effect of these variables for Illinois coals. Given the benefits of catalyzed low-temperature gasification, reduced agglomeration, and in-situ capture of most of the sulfur, the proposed system should yield substantial economic benefits.

One coal from the Illinois coal sample bank and a coal from one of Amax's Illinois coal mines were tested. Coals and catalyzed coals were characterized by measurement of their elemental composition and by FTIR spectroscopy. Dispersion of the catalyst was examined by carbon dioxide chemisorption. Gasification reactivity was tested in a bench-scale fluid-bed gasifier. Tests in this unit also provided a practical measure of agglomerating tendency. The gasifier temperature was low enough ($750^{\circ}$C) that alkali vaporization should be very low (Krishnan et al., 1990). The ability of the catalyst to serve as a sulfur capture agent was investigated as a part of the bench-scale testing. Gasifier chars were examined to determine the fate of the catalyst using X-ray powder diffraction.

## EXPERIMENTAL PROCEDURES

Because of the exploratory nature of this project, the research program focused on laboratory and bench-scale tests. To provide fundamental footing for future work, feed and catalyzed coals were characterized in some detail. The coals were also tested in a bench-scale gasifier to provide a practical indication of the success of catalyst addition methods. Details are given below.

### Catalyzed Coal Preparation

The two coals selected for testing under this project are IBC-105 from the Illinois Coal Sample Program and washed coal from Amax's Delta Mine. Both are Illinois No. 6 coals. IBC-105 is described as a pristine channel sample and has a high ash content. IBC-105 was screened to 40 by 200 mesh when received and stored in sealed plastic bags. Delta coal was received as minus 1 inch and crushed and screened to 40 by 200 mesh.

The IBC-105 coal was also pretreated by the following methods:

- Water Washing
- Heavy Liquid Cleaning
- Air Oxidation

Water washing was performed by panning several hundred grams to remove the heavier mineral constituents. Approximately 80

weight percent of the starting coal was recovered after drying in air at 50°C. Heavy liquid cleaning was performed by floating the coal off of the ash in a heavy liquid of specific gravity 1.4. This liquid was prepared from a petroleum fraction of gravity 0.75 and perchloroethylene of gravity 1.6. Approximately 40 weight percent of the starting coal was recovered as the float fraction. The heavy liquid was removed from both the float and sink fractions by drying in air at 50°C followed by vacuum drying at 50°C.

Air oxidation was performed by placing a shallow tray of coal in an oven at various temperatures from 100 to 200°C. Table 1 lists analytical results for IBC-105 oxidized for various times at several temperatures. Weight loss during oxidation was less than 5 percent for all samples. The results show that substantial oxygen can be taken up by the coal under very mild conditions. A fraction of the pyritic sulfur is converted to sulfate sulfur in the process. FSI is very low for all oxidized samples.

Table 1. Results of Air Oxidation of IBC-105

| Temperature °C | Time, Hours | Weight % | | | | |
|---|---|---|---|---|---|---|
| | | O | $S_{tot}$ | $S_{pyr}$ | $S_{sulf}$ | FSI |
| Raw IBC-105 | -- | 6.5 | 4.68 | 2.29 | 0.20 | 4.5 |
| 110 | 25 | 14.3 | 4.26 | 1.13 | 0.64 | 0.5 |
| 150 | 1 | 12.2 | 4.01 | 1.20 | 0.63 | 0.5 |
| 150 | 4 | 13.2 | 4.74 | 1.72 | 0.76 | 0.5 |
| 150 | 25 | 17.9 | 4.31 | 1.21 | 0.73 | 0 |
| 200 | 18 | 13.8 | 4.84 | 1.68 | 0.75 | 0.5 |

The reason for coal oxidation is to introduce oxygen functional groups such as carboxylic acid which can interact with the $Na^+$ and $Ca^{2+}$ ions leading to a highly dispersed catalyst (Lang and Neavel, 1982) and to the formation of non-volatile sodium species (Meijer et al., 1991). Ester groups can also be converted to carboxylic acid when heated in the presence of alkali and water. Thus, ester groups may also serve to interact with catalyst species. To evaluate the extent to which acid groups are generated during oxidation, we have characterized each of these samples using infrared spectroscopy (DRIFTS). Our methodology is described in detail below in the section on catalyzed coal characterization.

Oxidation at 150°C for 4 hours was selected for preparation of catalyzed coal samples because at this temperature, infrared spectra showed that acid and ester groups had definitely formed.

Catalyst addition is performed by impregnation of the catalyst components from aqueous solutions. Sodium hydroxide and calcium acetate are used as the catalyst precursors. Sodium and calcium are impregnated at the same time from a solution containing both components. Fifty $cm^3$ of solution per 100 grams of coal is employed. The procedure is to prepare 50 $cm^3$ of a solution of the desired concentration based on a target catalyst loading. The pH of this solution is then adjusted to the desired level using nitric acid or ammonium hydroxide. This pH adjusted solution, now having a volume slightly greater than 50 $m^3$, is mixed with the coal. The impregnated coal is dried in air at 50°C overnight. Some samples were prepared by dry mixing of NaOH and $Ca(OH)_2$ with the coal, and the variables were total catalyst loading (1 to 5 weight percent) and Na/Ca molar ratio (0 to 1).

<u>Catalyzed Coal Characterization</u>

Feed coals, catalyzed coals, and chars from the bench-scale gasifier are characterized using the following techniques:

- Proximate Analysis
- Ultimate Analysis
- Total Sulfur and Sulfur Forms
- Na, K, Ca, and Fe Analysis
- Free Swelling Index (FSI) and Pyridine Swelling
- X-ray Powder Diffraction (XRD)
- Infrared Spectroscopy (DRIFTS)
- Thermogravimetric Analysis (TGA)

Proximate analysis is performed using a Fisher 940 coal analyzer. Ultimate analysis, including an analysis for oxygen, is performed using a Carlo-Erba EA-1108 CHNO analyzer. Total sulfur is determined using a Leco SC-32 instrument. Pyritic sulfur is determined by volumetry and sulfate sulfur by gravimetry using standard ASTM procedures. For analysis of Na, K, Ca, and Fe, the coal samples are ashed in air at 625°C and fused with $LiBO_2$, and the melt is dissolved in 5 percent nitric acid and analyzed by flame atomic absorption.

Free swelling index was used as a measure of caking tendency and determined using ASTM D720. Results of several replications on one sample indicate that FSI values are accurate to ± 0.5 FSI units. Pyridine swelling was performed using the volumetric method described by Green and coworkers (1984). In preliminary tests, dry mixed and impregnated coals were treated for 10 minutes in a tube furnace at 750°C in nitrogen saturated with water vapor by bubbling through boiling water. This is referred to as a partial gasification test. The samples were contained in porcelain boats. The consistency of the cake which formed was evaluated

qualitatively to provide a rough indication of caking tendency under gasification conditions.

X-ray powder diffraction patterns are obtained using a Philips X'Pert System. Infrared spectra are acquired using a Nicolette 510P FTIR equipped with a Spectra Tech diffuse reflectance cell. Spectra are acquired on neat coal samples with a resolution of 4 $cm^{-1}$ unless stated otherwise. Typically 400 scans were averaged to produce the reported spectra. Infrared spectroscopy provides a fingerprint of the carbon-oxygen bonds present in a coal sample and how these bonds change as the coal is treated.

A Setaram TGA instrument is utilized to measure carbon dioxide gasification rates and catalyst dispersion by carbon dioxide chemisorption. Approximately 100 mg of coal is loaded into a quartz bucket and placed in the TGA chamber. The chamber is then repeatedly evacuated and purged with argon to remove oxygen, and an argon flow is initiated. The sample is heated at 30°C/minute to 800°C under argon. At this point, carbon dioxide is introduced if gasification is to be performed.

To measure catalyst dispersion, the sample is held under argon at 800°C for 5 minutes and then cooled to 300°C. Carbon dioxide is introduced and the weight gain is monitored. After 30 minutes, the gas is switched back to argon. The weight gain after this treatment is taken as the amount of $CO_2$ chemisorbed. Dispersion is calculated as the mole fraction of Na + Ca which chemisorbs $CO_2$:

$$\text{Dispersion} = \text{mmole } CO_2 \text{ adsorbed}/(\text{mmole Na + Ca}) \qquad (1)$$

The results of replication of this measurement on one sample indicate that the dispersion results may be considered accurate to ± 0.02 dispersion units (mole fraction). This chemisorption technique was first developed by Ratcliffe and Vaughn (1985) for a study of potassium catalyzed coal gasification. They observed dispersion values of 0.25 to 0.3. More recently Linares-Solano and coworkers (1990) have utilized this technique in studies of Ca catalyzed carbon dioxide gasification of pure carbons. These workers performed an extensive parametric study which indicated that 300°C was the optimum chemisorption temperature because physical adsorption was minimized and bulk reaction of carbon dioxide with Ca to form $CaCO_3$ did not occur. They observed dispersion values in the range of 0.1 to 0.2.

## Bench-Scale Gasification

Bench-scale gasification tests are performed in a 1.75-inch inside diameter fluid-bed bench-scale system. The system is operated as a batch reactor where a single charge of 75 grams

of coal is introduced into a hot reactor with established gas flows. The reactor itself consists of a Incoloy 800HT tube which is 4 feet long. The unit is heated by a three-zone furnace and strip heaters at selected locations. Gases are metered to the unit via mass flow controllers. A metering pump is used to inject water into a steam generator which is swept by the inlet gases. Product (CO, $CO_2$, COS, $H_2S$, $H_2$, $CH_4$, $O_2$, and $H_2O$) gases are analyzed by mass spectrometry. To avoid problems in analyzing for CO in nitrogen (both have a mass of 28), we utilize synthetic air where argon replaces nitrogen.

In a typical gasification test, the unit is heated to reaction temperature under a flow of synthetic air. Any tars which have accumulated on the reactor walls are burned off during this heat up period, which is continued until no carbon dioxide is observed in the product gas. The desired reactant gas flows are then initiated (steam/Ar or steam/synthetic air). The feed charge of 75 grams is then dropped into the fluid bed from a lock hopper to initiate the test. Standard conditions are:

- 750°C
- 5 psig
- 75 g Coal Feed
- 0.75 $cm^3$/min Water
- 0.25 slm of Ar of Synthetic Air
- 6-Hours Run Duration

At the end of each test, reactant gas flows are replaced with argon and the unit is cooled under argon purge. The unconverted coal char is then vacuumed from the unit and submitted for characterization for carbon, ash, sulfur, and sodium content. Additionally, chars were characterized by XRD.

Carbon conversion and sulfur retention are evaluated by comparing analyses for the feed coal and gasifier char. We assume that ash is not lost from the char during gasification. The ratios C/Ash and S/Ash are used in calculation of carbon conversion and sulfur retention:

Carbon Conversion, wt% = 100 x (1 - $[C/Ash]_{char}$/$[C/Ash]_{feed}$)   (2)

   Sulfur Retention, wt% = 100 x $[S/Ash]_{char}$/$[S/Ash]_{feed}$   (3)

A similar calculation is used to estimate sodium losses.

# RESULTS AND DISCUSSION

## Preliminary Test Work

The goals of preliminary test work were to compare dry mixing and impregnation as catalyst addition methods and to select a characterization method for prediction of caking under gasification conditions. During the initial stages of this test work, FSI was compared with pyridine swelling for prediction of caking tendency in a partial gasification test. A suite of dry mixed and impregnated samples was prepared and tested. Results are shown in Table 2. All of the dry mixed samples formed a hard to medium cake in the partial gasification test. None of the wet impregnated samples formed a hard cake probably because this preparation procedure leads to much greater catalyst dispersion and possibly to oxidation of the coal surface during drying. Many of the impregnated samples remained loose and did not form any cake.

### Table 2. Catalyzed Coal Characterization Results

| Weight % Loading | Molar Na/Ca | pH | FSI | Pyridine Swelling | Cake Consistency |
|---|---|---|---|---|---|
| Dry Mixed Samples | | | | | |
| 1 | 0:1 | | 3.5 | 2.6 | Hard Cake |
| 2 | 1:2 | | 2.0 | 2.5 | Hard Cake |
| 5 | 1:1 | | 1.5 | 2.2 | Medium Cake |
| 1 | 1:1 | | 2.5 | 2.6 | Hard Cake |
| 5 | 0:1 | | 1.0 | 2.3 | Medium Cake |
| Wet Impregnated Samples | | | | | |
| 5 | 0:1 | 3 | 0.5 | 2.5 | Loose |
| 2 | 1:2 | 6 | 2.0 | 2.7 | Medium Cake |
| 1 | 0:1 | 3 | 1.5 | 2.5 | Soft Cake |
| 5 | 0:1 | 9 | 1.5 | 2.4 | Medium Cake |
| 1 | 0:1 | 9 | 2.5 | 2.6 | Medium Cake |
| 5 | 1:1 | 3 | 0.5 | 2.3 | Loose |
| 1 | 1:1 | 3 | 1.5 | 2.5 | Soft Cake |
| 5 | 1:1 | 9 | 2.0 | 2.5 | Soft Cake |
| 1 | 1:1 | 9 | 2.0 | 2.7 | Medium Cake |

For the raw coal, an FSI value of 4.5 and a pyridine swelling value of 2.7 were measured. Pyridine swelling values for the catalyzed coals are generally in a narrow range from 2.2 to 2.7 and do not appear to correlate particularly well with cake consistency. On the other hand, FSI values do correlate

reasonably well with cake consistency, and accordingly, FSI was selected as the best method for measuring caking tendency.

Five weight percent of the physically mixed catalyst was required to significantly reduce coal swelling. For the proposed application, 5 weight percent is considered to be a very high loading, and therefore, physical mixing as a catalyst preparation technique was abandonded.

## Feed Coal Characterization

The feed coals that have been prepared to date are:

- IBC-105 screened to 40 x 200 mesh.
- Delta crushed and screened to 40 x 200 mesh.
- IBC-105 water washed (40 x 200).
- IBC-105 heavy liquid cleaned (40 x 200).
- IBC-105 oxidized in air (40 x 200).

Details of feed coal preparation have been described in the "Experimental Procedures" section.

Analytical results for each of these coals are presented in Table 3. The Delta coal, which was washed at the mine preparation plant, is seen to be lower in ash than IBC-105. Cleaning of IBC-105 resulted in reduction of ash content to 8.9 weight percent for water washing and to 3.2 weight percent for heavy liquid cleaning. Ash content of the oxidized coal is essentially unchanged. Ultimate analyses show the coals to be broadly similar with the exception of the air oxidized coal which has gained nearly 7 weight percent oxygen. Sulfur analyses indicate significantly higher sulfur for IBC-105 relative to Delta. Water washing results in a significant reduction in sulfur content, primarily by the removal of pyrite. Heavy liquid cleaning also results in a substantial reduction, primarily of pyritic sulfur. In terms of sulfur reduction, heavy liquid cleaning is only slightly more effective than water washing. Oxidation resulted in significant reduction of pyritic sulfur content, some of which was converted to sulfate. There is an apparent increase in organic sulfur, but most likely this is actually sulfide and elemental sulfur formed upon pyrite oxidation.

Analyses for sodium, potassium, and calcium were performed because these naturally occurring materials may have catalytic and sulfur capture activity. The results indicate that IBC-105 contains more than 1 weight percent of these elements. Delta coal contains considerably less, which is consistent with its lower ash content. Cleaning of IBC-105 resulted in a large reduction of sodium, potassium, and calcium content.

## Table 3. Analytical Results for Feed Coals

|  | IBC-105 | Delta | Water Washed IBC-105 | Heavy Liquid Cleaned IBC-105 | Air Oxidized IBC-105 |
|---|---|---|---|---|---|
| **Proximate Analysis, Weight %** |  |  |  |  |  |
| Moisture | 9.1 | 2.0 | 4.8 | 2.3 | 1.0 |
| Volatiles (mf) | 36.1 | 34.9 | 39.0 | 43.2 | 33.5 |
| Ash (mf) | 18.4 | 12.1 | 8.9 | 3.2 | 17.3 |
| Fixed Carbon (mf) | 45.6 | 53.0 | 52.1 | 53.7 | 49.2 |
| **Ultimate Analysis (mf), Weight %** |  |  |  |  |  |
| Carbon | 65.4 | 72.0 | 67.9 | 74.7 | 60.9 |
| Hydrogen | 4.3 | 4.8 | 5.2 | 5.3 | 4.4 |
| Nitrogen | 1.3 | 1.6 | 1.4 | 1.5 | 1.2 |
| Oxygen | 6.4 | 8.6 | 13.7 | 8.0 | 13.2 |
| **Sulfur and Forms (mf), Weight %** |  |  |  |  |  |
| Total Sulfur | 4.68 | 3.19 | 3.08 | 2.88 | 4.74 |
| Pyritic Sulfur | 2.29 | 1.17 | -- | 0.21 | 1.72 |
| Sulfate Sulfur | 0.20 | 0.31 | -- | 0.15 | 0.76 |
| Organic Sulfur (bd) | 2.19 | 1.71 | -- | 2.52 | 2.26 |
| **Selected Elements (mf), Weight %** |  |  |  |  |  |
| Sodium | 0.115 | 0.027 | 0.058 | 0.072 | 0.121 |
| Potassium | 0.278 | 0.246 | -- | 0.060 | -- |
| Calcium | 0.803 | 0.203 | 0.083 | 0.071 | 0.967 |
| Iron | 1.96 | 1.21 | -- | 0.406 | -- |
| Free Swelling Index | 4.5 | 5.0 | -- | 4.5 | 0.5 |

Sodium analyses for Delta coal and washed IBC-105 suggest that water washing can effectively reduce Na content.

In preliminary work described above, we determined that free swelling index (FSI) was a good indication of the caking tendency of catalyzed coals. FSI values for the starting coals are very similar at 4.5 to 5.0. FSI of the oxidized coal was reduced to 0.5. It is important to note that simply exposing the coal to ambient air for extended periods of time can also result in a dramatic reduction in FSI. For example, a sample of IBC-105 which was exposed to room air for several months exhibited an FSI of 1.5. Coal cleaning had little effect on FSI.

Figure 1 shows weight loss profiles for TGA gasification of the starting coals. The reaction rates are nearly constant with conversion. Heavy liquid cleaned coal converts at a slightly slower rate than the starting coal. This may be caused by the removal of catalytic mineral matter components such as Na, K, and Ca. Delta coal is much less reactive than IBC-105, and this may also be related to the removal of catalytic mineral matter during washing. Carbon dioxide chemisorption was very low for all of the starting coals.
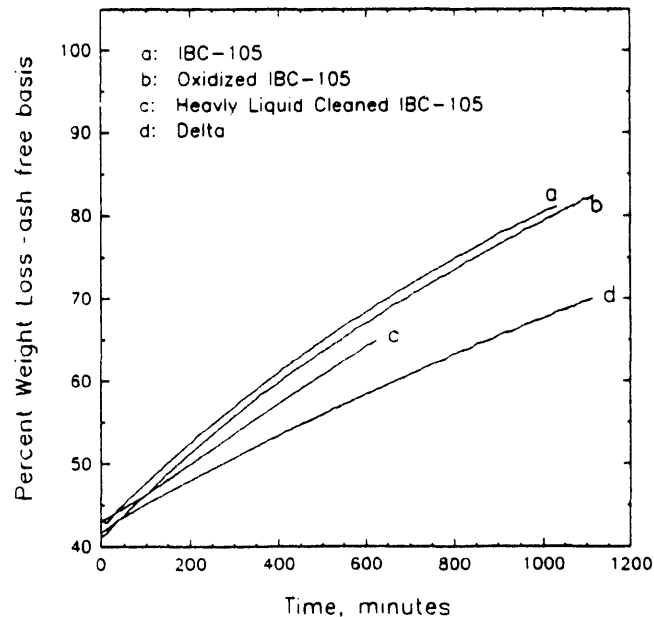


Figure 1. TGA gasification of feed coals at 800°C.

## Catalyzed Coal Characterization

### Calcium Catalyzed IBC-105

In order to provide some indication of the effectiveness of calcium alone as a gasification catalyst, sulfur capture agent, and decaking agent, several samples of IBC-105/calcium were prepared at various levels of pH. These samples were characterized by calcium analysis, measurement of FSI, calcium dispersion, IR, and TGA gasification. Results of FSI and dispersion measurement are shown in Table 4. All samples exhibit a reduced FSI relative to the raw coal (FSI = 4.5). For the range of conditions studied, elimination of swelling (FSI of 0.5 to 1.0) required low pH and a loading of 1.2 weight percent. Results for control samples prepared by impregnation of the coal with water containing ammonium hydroxide or nitric acid to adjust the pH are also reported in Table 4. The FSI of these samples is reduced to 2.5 to 3.0. It seems likely that drying of these samples (overnight at 50°C in air) results in this reduction of FSI. Reduction to lower levels is a direct result of catalyst addition.

### Table 4. FSI, Dispersion, and Catalyst Surface Area Values for IBC-105/Calcium Samples

| pH | Loading Weight % Ca | FSI | Dispersion Mole Fraction | Sample Designation |
|----|------|-----|------|------|
| 3 | 0.0 | 3.0 | -- | 1504-63-3 |
| 3 | 0.16 | 2.0 | 0.34 | 1504-94-3 |
| 3 | 0.34 | 1.5 | 0.28 | 1504-44-3 |
| 3 | 0.61 | 2.0 | 0.26 | 1504-59 |
| 3 | 1.22 | 0.5 | 0.08 | 1504-87-2 |
| 3 | 2.51 | 0.5 | 0.07 | 1504-44-1 |
| 4 | 0.85 | 1.5 | 0.20 | 1504-94-6 |
| 5 | 0.72 | 2.5 | 0.13 | 1504-94-5 |
| 6 | 0.0 | 2.5 | -- | 1504-63-6 |
| 9 | 0.0 | 2.5 | -- | 1504-63-9 |
| 9 | 0.30 | 2.5 | 0.23 | 1504-44-5 |
| 9 | 0.86 | 3.0 | 0.21 | 1504-87-1 |
| 9 | 2.30 | 2.0 | 0.08 | 1504-44-4 |

Figure 2 shows the effect of loading on FSI at various levels of pH. The data points at zero weight percent loading are the average for the control samples described above. The samples impregnated at low pH (less than 5) have consistently lower FSI values than samples with a similar loading impregnated at higher pH. The use of lower impregnation pH allows swelling to be eliminated at lower catalyst loading.
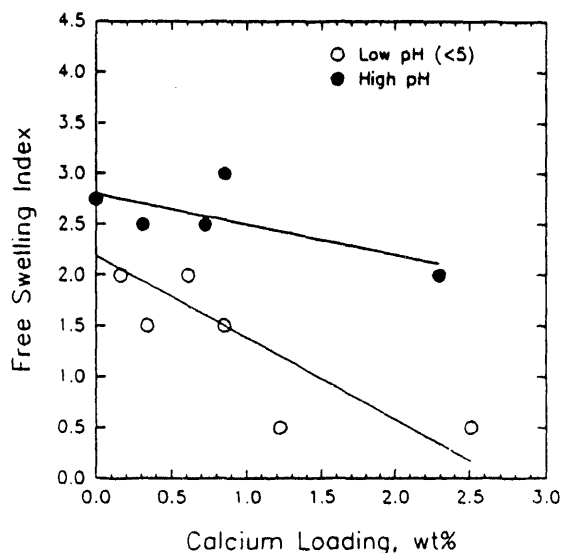
Figure 2. FSI as a function of calcium loading and impregnation pH for IBC-105.

Alkali and alkaline earth additives are thought to reduce coal swelling by catalyzing the formation of cross-links from oxygen functional groups initially present in the coal structure (Khan and Jenkins, 1985; 1989). Higher levels of calcium dispersion would be more effective at cross-link formation. It is possible that more highly dispersed Ca is produced by impregnation at low pH, leading to enhanced effectiveness for decaking.

To examine this possibility, calcium dispersion was measured for each of the Ca-catalyzed samples. The results are reported in Figure 3. It is apparent that dispersion correlates inversely with catalyst loading and there is only a very small effect of pH, if any. The fact that dispersion correlates with loading is not surprising. This occurs because a more concentrated solution of the catalyst precursor is used to prepare more highly loaded samples. With a more concentrated solution, precipitation occurs earlier in the drying process and larger particles can grow.

Another possible explanation for the pH effect on swelling is that as pH is changed, the catalyst precursor interacts with different sites or oxygen functional groups on the coal surface. Because calcium is a divalent ion, it must bind as a bridge between two oxygen functional groups. These functional groups can react to form cross-links and prevent swelling. It has been suggested that calcium can catalyze cross-link formation (Khan and Jenkins, 1985; Shams et al.,

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1992).    To  test  this  possibility,  we  have  examined  the
carbonyl region of the infrared spectra (1,500 to 2,000 $cm^{-1}$)
of  several  Ca-catalyzed  samples.     Figure  4  shows  diffuse
reflectance spectra of this region for the raw coal and Ca-
catalyzed samples prepared at pH 3 and 9 with relatively high
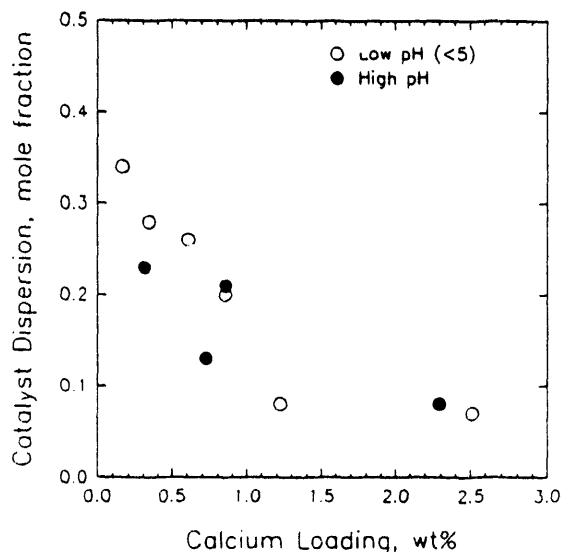loading.



Figure 3.    Calcium  dispersion  as  a  function  of  loading
             and  pH  for  IBC-105.

Comparison of the as-received coal spectrum with that of the
coal  impregnated  at  pH  3  indicates  that  the  intensity  near
1,600 declines and distinct peaks at 1,375, 1,550 and 1,700
$cm^{-1}$  appear.      Relative  intensity  at  1,640  and  1,475  is
increased.   Based on the IR band assignments of Painter and
coworkers  (1981),  these  spectral  changes  indicate  that  highly
conjugated  or  hydrogen  bonded  carboxyl  groups  at  around  1,600
have  shifted  to  form  free  carbonyl  and  carboxylate  groups  at
1,700 and Ca exchanged acid groups at 1,550 and 1,375 $cm^{-1}$.
The  shoulder  at  1,475  may  also  be  associated  with  Ca-
carboxylate, carbonate, or bicarbonate species.   There is also
a decrease in intensity of the phenoxy region (1,200 - 1,300).
This may indicate the formation of calcium exchanged phenolate
species.

Spectra of samples prepared at pH 3 with lower Ca loading (not
shown) indicated that the intensity of these spectral features
increases as loading is increased.   Control samples prepared
at pH 3 and 9 but without calcium were nearly identical to the
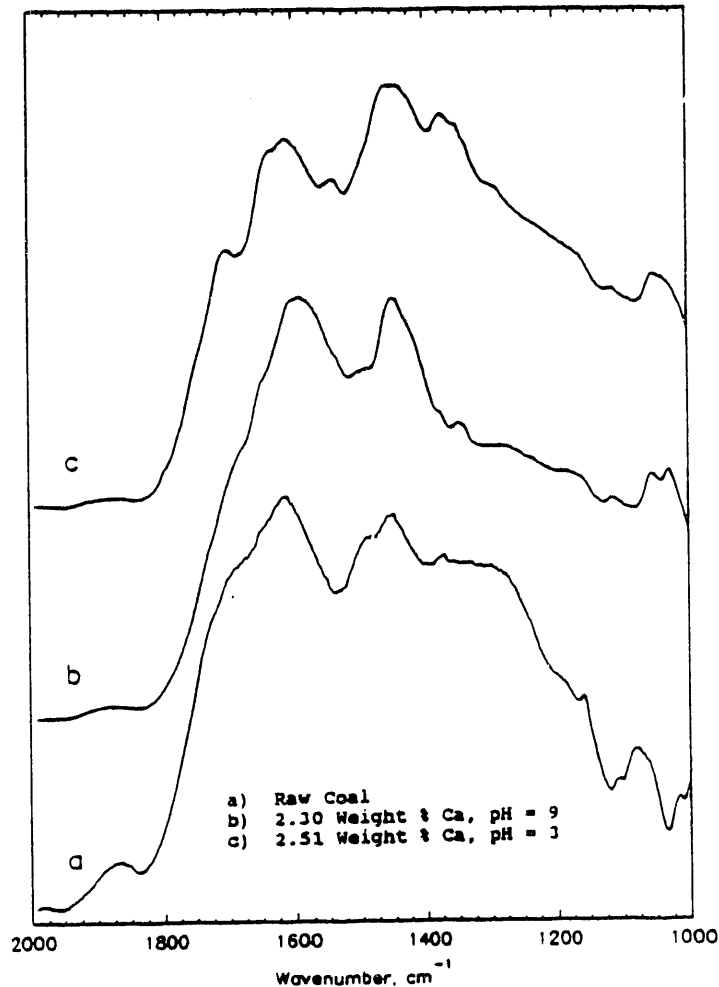starting coal.

Figure 4. IR (DRIFTS) spectra of Ca-catalyzed IBC-105.

After Ca impregnation at pH 9, there is no reduction in the intensity near 1,600 cm$^{-1}$; however, the peak is broader and the shoulder observed for the raw coal at 1,700 is less intense. No new peaks at 1,375 or 1,550 are observed. There is a decline in intensity in the 1,200 - 1,400 cm$^{-1}$ region. The carboxylate or carbonate peak at 1,475 has nearly vanished. These results suggest that there is a shift of the free carboxyl at 1,700 and exchanged carboxyl at 1,475 to form more hydrogen bonded or highly conjugated carbonyl causing broadening of the peak near 1,600. These spectral changes are the opposite of those observed for Ca addition at pH 3.

These data indicate that at pH 3, Ca interacts strongly with the oxygen functional groups of the coal resulting in the formation of free acid and Ca-exchanged carboxylate and

phenolate species. At pH 9, this interaction is not observed, and in fact, nor conjugated carbonyl and exchanged carboxyl present in the starting coal seem to have shifted to form more conjugated or hydrogen bonded material. Interaction of $Ca^{2+}$ ions with coal surface acid and hydroxyl groups should produce atomically dispersed Ca and consequently a higher level of dispersion. However, higher dispersion is not observed.

It is interesting to compare these results with those obtained by Abotsi and coworkers (1992, 1993) for ion exchange of calcium onto bituminous coal at various levels of pH. In this study, zeta potential measurements indicated that the coal surface was negatively charged over a wide range of pH. Acidic solutions were found to inhibit adsorption of calcium; however, nearly 6 weight percent calcium could be added to a demineralized bituminous coal at pH 10. These results indicate that at high pH, calcium adsorption is caused by electrostatic attraction between the negatively charged coal surface and the positively charged calcium ion. Under these conditions, calcium does not adsorb on specific surface sites but deposits non-selectively. At low pH, the surface is more positively charged and repels the positively charged Ca ion. Calcium adsorption can then occur only by exchange with a surface proton attached to a carboxylate or phenolate group.

Impregnation followed by drying is a much different situation than ion exchange; however, the results of Abotsi and coworkers (1992, 1993) may shed some light on how interaction of Ca with surface functional groups at low pH could occur. During impregnation at high pH, Ca is deposited on the surface before and during drying, but not at specific surface sites. Dispersion should decrease with increasing loading. At low pH, Ca can only interact with specific sites on the surface where it can exchange for other positively charged ions before or during the drying process. As the impregnated coal is dried, any Ca in excess of that which could be exchanged precipitates. The amount of Ca which can exchange with specific surface sites is a function of the Ca concentration in solution so that the amount of dispersed calcium increases with loading, as was observed by IR. Only a small fraction of the calcium is highly dispersed at low pH, and this gives rise to the infrared spectral features observed and may also be responsible for swelling reduction. The TGA chemisorption technique of dispersion measurement may not be sensitive enough to distinguish this small fraction of highly dispersed material. This interpretation agrees with the FSI and dispersion measurements as well as with the infrared data.

Dispersion is also expected to have a significant effect on the gasification activity of Ca. TGA gasification of the Ca catalyzed coals was performed in $CO_2$ at 800°C. Figure 5 shows

the effect of impregnation pH on TGA gasification curves. All catalyzed samples gasified much more rapidly than the feed coal. The highest conversion level and gasification rates were obtained for the coal impregnated at the lowest pH, even though this coal also had the lowest Ca loading. All of the samples had very similar gasification rates at low conversion. As conversion proceeds, the reaction rate decreases, and this decrease occurs faster for samples impregnated at higher pH. This decrease in reaction rate indicates catalyst deactivation which may occur by sintering, reaction with mineral matter, or reaction with sulfur.
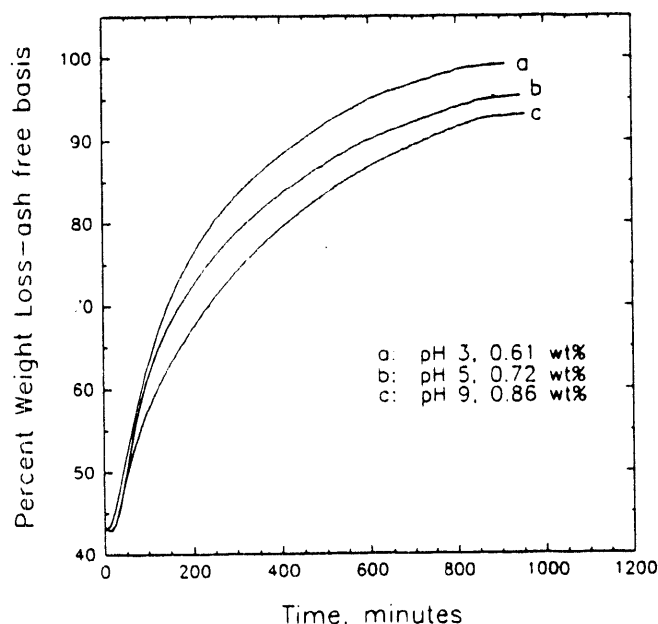


Figure 5. Effect of pH on TGA gasification of Ca-catalyzed IBC-105.

The highly dispersed material shown by IR may account for the increased conversion and resistance to deactivation of the low pH sample. At higher catalyst loadings, the gasification rate is substantially faster, but the effect of pH is less pronounced.

## Ca-Catalyzed/Pretreated IBC-105

A few samples of Ca-catalyzed and pretreated IBC-105 were prepared. Data for these samples are listed in Table 5. A sample was prepared from the heavy liquid cleaned coal using a low Ca loading of 0.4 weight percent. A low loading was selected based on the hypothesis that the low ash and sulfur

content of this coal would lead to reduced catalyst requirement. The free swelling index of this sample was reduced to roughly the same extent as the raw coal with a similar Ca loading. The dispersion level is also similar. Infrared spectra (not shown) exhibited similar features to those of the raw coal impregnated with Ca at pH 3.

### Table 5. Results for Ca-Catalyzed and Pretreated IBC-105

| Pretreatment | pH | Loading Weight % Ca | FSI | Dispersion Mole Fraction | Sample Designation |
|---|---|---|---|---|---|
| Heavy Liquid | 3 | 0.40 | 2.0 | 0.28 | 1547-9 |
| Oxidation | 3 | 0.92 | -- | 0.24 | 1547-23 |
| Oxidation | 9 | 0.84 | -- | 0.07 | 1547-24 |

Two samples were prepared from the oxidized coal at pH 3 and 9. Oxidation reduced the FSI of this coal to 0.5, so FSI was not measured for the catalyzed samples. Dispersion is higher for the pH 3 sample than for a similarly loaded raw coal. Dispersion for the pH 9 sample is significantly lower than observed for a similarly loaded raw coal. No IR data are available for the oxidized coal samples.

TGA gasification results for these coals and comparably loaded raw coal samples were obtained (not shown). The heavy liquid cleaned coal exhibited a reduced $CO_2$ gasification rate relative to raw coal with the same loading. This may indicate that at this low loading of added catalyst, the catalytic mineral matter has a significant effect and accounts for the reduced reactivity. On the other hand, this might indicate that treatment with the heavy liquid alters the coal surface to inhibit catalytic activity. The oxidized coal samples exhibited very similar levels of reactivity to similarly catalyzed raw coal. The sample prepared at low pH was slightly more reactive.

### Sodium/Calcium Catalyzed IBC-105

Table 6 lists the loading, Na/Ca ratio, FSI, and dispersion for this set of samples. Elimination of swelling (FSI <1.0) is only accomplished at pH 4 or less. The data are somewhat skewed by the fact that only highly loaded samples were prepared at pH 9. The variables controlled during catalyst preparation were impregnation pH, catalyst loading, and catalyst composition expressed as Na/Ca molar ratio. All of these variables had an effect on swelling reduction.

## Table 6. FSI, Dispersion, and Catalyst Surface Area Values for IBC-105/Sodium + Calcium Samples

| pH | Loading, Weight % | | | Na/Ca | FSI | Dispersion Mole Fraction | Sample Designation |
|----|------|------|-------|-------|-----|--------------------------|--------------------|
| | Ca | Na | Total | | | | |
| 2 | 0.87 | 0.62 | 1.49 | 1.23 | 0.5 | 0.12 | 1547-11 |
| 3 | 0.00 | 0.00 | 0.00 | -- | 3.0 | -- | 1504-63-3 |
| 3 | 0.05 | 0.21 | 0.26 | 8.74 | 1.5 | -- | 1504-44-7 |
| 3 | 0.22 | 0.05 | 0.27 | 1.33 | 2.0 | 0.12 | 1547-5 |
| 3 | 0.24 | 0.01 | 0.25 | 0.08 | 2.0 | 0.18 | 1504-94-2 |
| 3 | 0.26 | 0.10 | 0.95 | 0.67 | 2.5 | 0.11 | 1547-2 |
| 3 | 0.74 | 0.91 | 1.65 | 2.14 | 0.5 | 0.20 | 1504-81 |
| 3 | 0.84 | 0.03 | 0.87 | 0.06 | 2.0 | -- | 1504-94-4 |
| 3 | 1.07 | 0.54 | 1.61 | 0.88 | 2.0 | 0.07 | 1504-88-1 |
| 3 | 1.18 | 0.78 | 1.96 | 1.15 | 0.5 | 0.14 | 1504-44-6 |
| 3 | 1.70 | 0.40 | 2.10 | 0.41 | 0.5 | 0.04 | 1547-4 |
| 3 | 1.73 | 0.96 | 2.69 | 0.96 | 0.5 | 0.07 | 1504-79-2 |
| 4 | 0.64 | 0.02 | 0.66 | 0.06 | 2.0 | -- | 1504-94-1 |
| 4 | 0.78 | 0.91 | 1.69 | 2.00 | 0.5 | 0.13 | 1504-79-3 |
| 6 | 0.00 | 0.00 | 0.00 | -- | 2.5 | -- | 1504-63-6 |
| 6 | 0.63 | 0.33 | 0.99 | 0.93 | 2.0 | 0.09 | 1504-44-2 |
| 6 | 1.41 | 0.75 | 2.16 | 0.91 | 2.0 | 0.05 | 1504-79-1 |
| 9 | 0.00 | 0.00 | 0.00 | -- | 2.5 | -- | 1504-63-9 |
| 9 | 0.88 | 0.60 | 1.48 | 1.20 | 0.5 | 0.05 | 1547-6 |
| 9 | 2.72 | 1.47 | 4.19 | 0.94 | 2.0 | 0.02 | 1504-44-8 |

Figure 6 shows the effect of Na + Ca loading and pH on FSI for samples with a Na/Ca ratio of less than 1. Samples prepared at low pH exhibited a lower degree of swelling. As was observed for Ca-catalyzed coal, catalyst dispersion depended upon loading and not upon pH for these samples, as shown in Figure 7. The Na + Ca mixtures were about as effective as calcium only for FSI reduction. Dispersion values are also in the same range.

Infrared spectra of Na + Ca-catalyzed coals prepared at different levels of pH are shown in Figure 8. The results are very similar to those reported above for IBC-105/calcium catalyzed coals. At pH 3, the highly conjugated carbonyl originally present at 1,600 has shifted to 1,650 and 1,700. The peak at 1,475 assigned to carboxylate or carbonate is enhanced. There is an increase in intensity in the 1,400 to 1,300 region consistent with the formation of exchanged carboxylate. At higher pH, the 1,475 peak has been reduced in intensity relative to the raw coal and the carbonyl peaks at

1,650 and 1,700 have not appeared. One difference between the Na + Ca samples and the Ca only samples is the peak at 1,550 which was assigned to Ca exchanged carboxylic acid for the Ca only sample prepared at pH 3 but is not present in the Na + Ca sample.
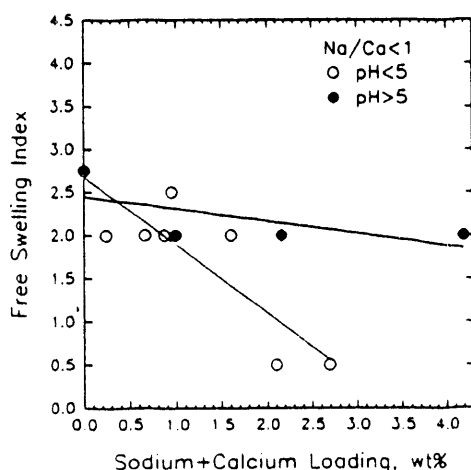


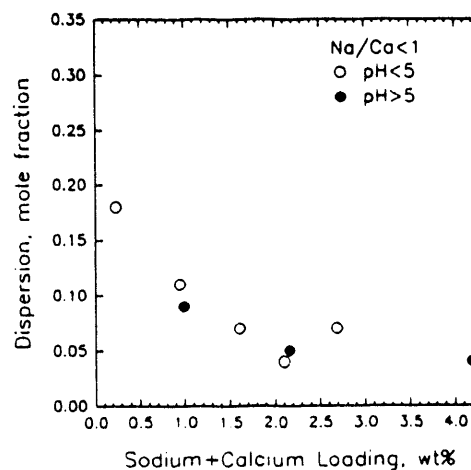Figure 6. Free swelling index as a function of Na + Ca loading and pH.

Figure 7. Na + Ca catalyst dispersion as a function of loading and pH.

These IR data lead to the same interpretation proposed for Ca only samples. That is at low pH, some fraction of the catalyst ions interact with coal carboxylate and phenolate groups to produce highly dispersed catalyst. At high pH (above 4), this is not observed. The absence of a Ca exchanged acid peak at 1,550 might be caused by the lower Ca loading of the Na + Ca sample or by some interaction between Na and Ca. IR data show that exchanged carboxylate and possibly phenolate species are formed, however.

Figure 9 shows the effect of Na + Ca loading and Na/Ca ratio on FSI for samples prepared at low pH. A high Na/Ca ratio leads to reduced FSI. Catalyst dispersion measurements shown in Figure 10 suggest that this is at least partially caused by increased levels of dispersion for samples with Na/Ca of greater than 1. Dispersion is nearly constant with loading for these samples. Infrared spectra of samples with varying Na/Ca ratio at constant pH and similar loadings were acquired
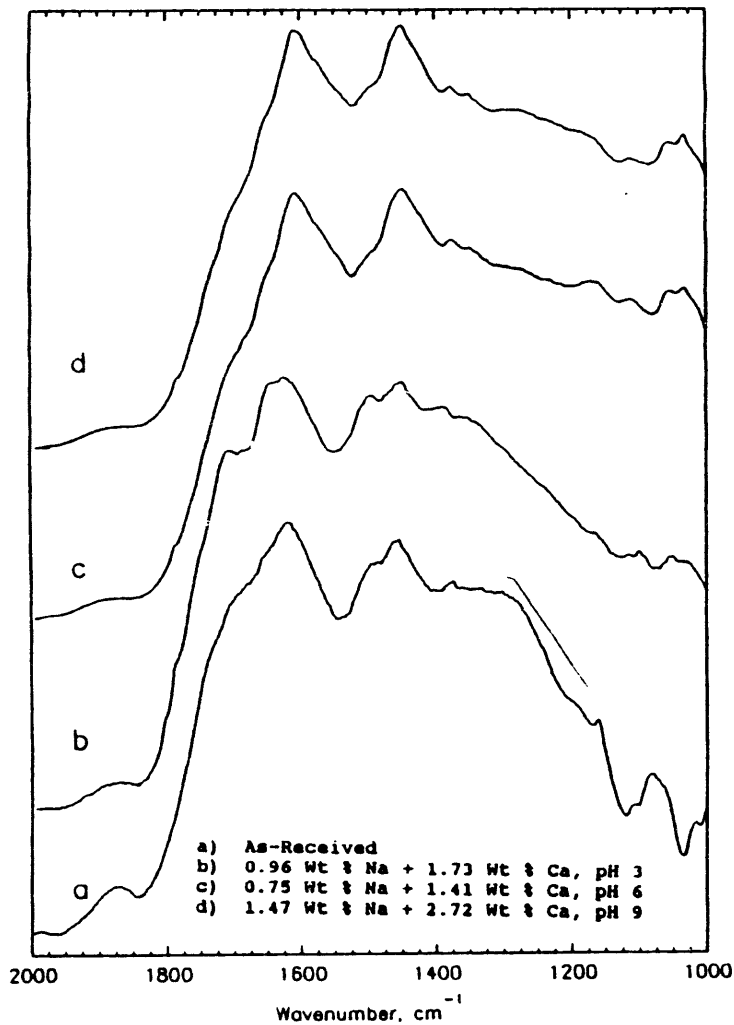
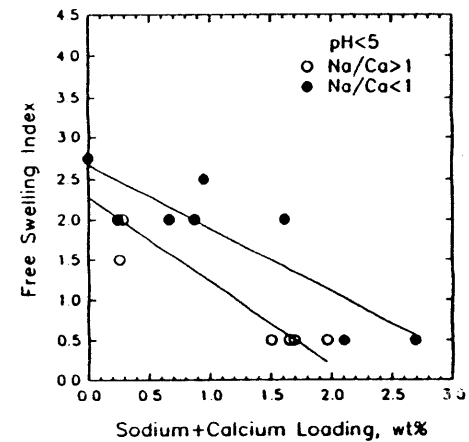Figure 8. IR spectra of Na + Ca catalyzed IBC-105 at varying pH (Na/Ca <1).



Figure 9. Free swelling index as a function of Na + Ca loading and Na/Ca ratio.
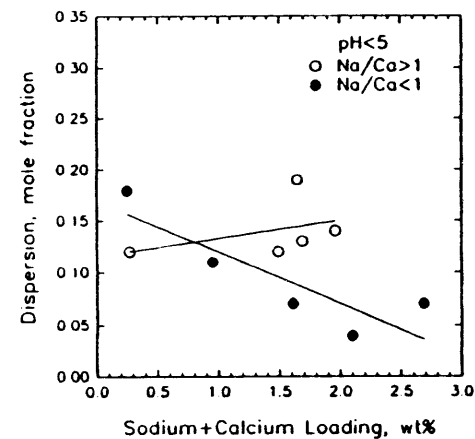


Figure 10. Na + Ca catalyst dispersion as a function of catalyst loading and Na/Ca ratio.

(not shown). Only very minor differences between the two levels of Na/Ca ratio were observed. As the ratio is increased, the carbonyl peak at 1,650 increases. More data will be required to explain this effect of Na/Ca ratio.

Several of the Na + Ca catalyzed samples were also gasified in the TGA apparatus. These catalyzed coal samples were significantly more reactive than those containing Ca as the only catalyst, as is shown in Figure 11. Samples prepared at lower pH and with Na/Ca ratio greater than 1 exhibited higher gasification rates (not shown).
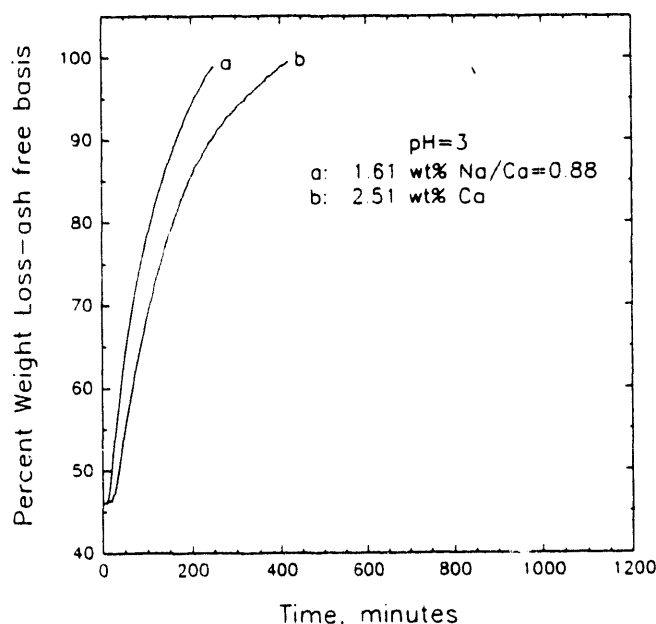


Figure 11. Comparison of TGA gasification curves for Na + Ca catalyzed and Ca only catalyzed coal.

## Na + Ca Catalyzed/Pretreated IBC-105

Samples were prepared from heavy liquid cleaned (HLC), water washed, and oxidized IBC-105. Table 7 lists FSI and dispersion values for the heavy liquid cleaned samples. In no case was the FSI reduced to 1 or less; however, there is a weak trend towards lower FSI values at lower pH. The data set is somewhat skewed because Na/Ca ratio is less than 1 for all samples.

The most surprising aspect of the results for the heavy liquid cleaned coal is that swelling was not eliminated, even at

total catalyst loadings above 3 weight percent. This loading
level reduced FSI to 1 or less for the raw coal. Catalyst
dispersion was low for all samples which is also surprising.
Neither dispersion nor FSI were correlated with loading or pH.
Additional characterization results will be required to
explain these results. Perhaps the heavy organic liquid used
to prepare these samples altered the coal surface chemistry or
pore structure in some way that prevented interaction of the
catalyst with the coal surface.

### Table 7. FSI Values for Heavy Liquid Cleaned IBC-105/Catalyst Samples

| pH | Loading, Weight % Ca | Na | Total | Na/Ca | FSI | Dispersion Mole Fraction | Sample Designation |
|----|------|------|-------|-------|-----|--------------------------|--------------------|
| 2 | 0.37 | 0.15 | 0.52 | 0.67 | 2.5 | – | 1504-96-2 |
| 3 | 0.14 | 0.05 | 0.19 | 0.67 | 2.5 | – | 1547-3 |
| 3 | 0.61 | 0.26 | 0.87 | 0.75 | 2.5 | 0.04 | 1504-90-2 |
| 3 | 0.70 | 0.34 | 1.04 | 0.86 | 2.5 | 0.05 | 1504-96-1 |
| 3 | 0.76 | 0.15 | 0.91 | 0.32 | 2.0 | – | 1504-90-1 |
| 3 | 1.11 | 0.56 | 1.67 | 0.87 | 1.5 | 0.03 | 1547-12 |
| 3 | 2.19 | 0.99 | 3.18 | 0.78 | 2.5 | 0.13 | 1504-90-4 |
| 3 | 2.97 | 0.65 | 3.62 | 0.39 | 2.5 | – | 1504-90-3 |
| 4 | 0.30 | 0.12 | 0.42 | 0.67 | 2.5 | – | 1504-96-3 |
| 6 | 1.53 | 0.57 | 2.10 | 0.66 | 3.0 | – | 1504-90-5 |
| 7 | 0.63 | 0.25 | 0.88 | 0.72 | 2.5 | 0.03 | 1504-90-11 |
| 7 | 0.77 | 0.14 | 0.91 | 0.32 | 3.0 | – | 1504-90-10 |
| 8 | 0.60 | 0.25 | 0.85 | 0.75 | 2.5 | 0.05 | 1504-90-7 |
| 8 | 0.77 | 0.15 | 0.92 | 0.36 | 2.5 | – | 1504-90-6 |
| 8 | 2.39 | 1.12 | 3.51 | 0.81 | 3.5 | 0.08 | 1504-90-9 |
| 8 | 2.99 | 0.57 | 3.56 | 0.33 | 3.5 | – | 1504-90-9 |
| 9 | 1.00 | 0.45 | 1.45 | 0.80 | 2.5 | 0.03 | 1547-13 |

The reactivity of catalyzed, heavy liquid cleaned coal was
measured by TGA. Results are shown in Figure 12 for two heavy
liquid cleaned coals and a similarly loaded raw coal. Heavy
liquid cleaning did not result in enhanced gasification
reactivity.

A small number of samples have been prepared from washed and
oxidized coal. These samples are listed, along with
characterization results, in Table 8. The results are
consistent with observations reported above for raw coal. TGA
gasification results are shown in Figure 13. Catalyst
loadings are not comparable, so direct comparisons are

difficult to make. It can be said that pH had little effect on the reactivity of the oxidized coals.
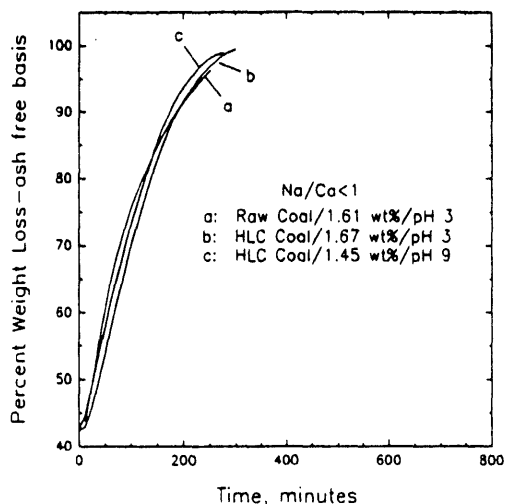


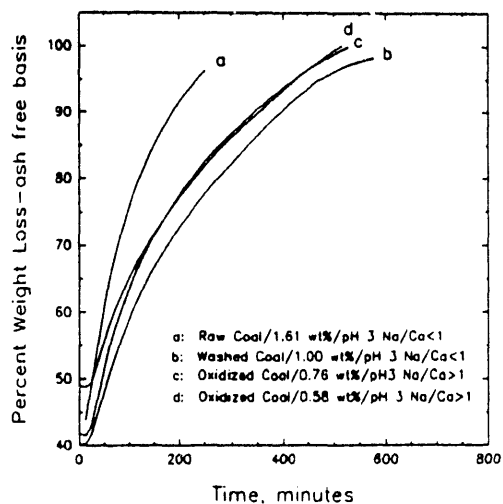Figure 12. TGA gasification results for selected heavy liquid cleaned, IBC-105 samples.



Figure 13. TGA gasification results for pretreated, Na + Ca catalyzed IBC-105.

Table 8. Results for Na + Ca Catalyzed and Pretreated IBC-105

| Pretreatment | pH | Loading, Weight % | | | FSI | Dispersion Mole Fraction | Sample Designation |
|---|---|---|---|---|---|---|---|
| | | Ca | Na | Total | | | |
| Washed | 3 | 0.64 | 0.36 | 1.00 | -- | 0.09 | 1547-25 |
| Oxidized | 3 | 0.42 | 0.34 | 0.76 | 0.0 | 0.24 | 1547-28 |
| Oxidized | 9 | 0.24 | 0.34 | 0.58 | 0.0 | 0.05 | 1547-29 |

## Bench Scale Gasification Tests

All of the feed coals, several Ca-catalyzed coals, and a suite of Na + Ca-catalyzed coals were tested in the bench-scale gasification system. Gasification conditions were selected to simulate a hypothetical low-temperature, low-oxygen requirement gasification process. Material balances for carbon, sulfur, and sodium were attempted. In most runs,

balances were not particularly good.  Results are reported
only for runs with material balances of 85 to 115 percent.

Carbon conversion, percent sulfur capture, and sodium loss
were calculated from the char analysis, as noted in the
"Experimental Procedures" section.  These results are shown in
Table 9.

Inspection of results for carbon conversion in Table 9 shows
that the addition of catalyst increased conversion in all
cases.  However, the use of Na + Ca appears to have no real
advantage over Ca alone under these conditions.  Treatment of
the coal to remove mineral matter by heavy liquid cleaning had
the greatest effect on conversion.

Cumulative conversion to carbon-containing gases (CO, $CO_2$, and
$CH_4$) as a function of time is shown in Figure 14 for several
samples.  In all cases, the addition of catalyst leads to
faster conversion and higher levels of conversion.  It is
notable that for the cleaned coal samples, much lower catalyst
loadings were required to obtain a comparable conversion
level.  Calcium only catalyzed samples exhibit the highest
reactivity.  The Na/Ca catalyzed cleaned coal samples exhibit
a lower reactivity level than expected.  This may be caused by
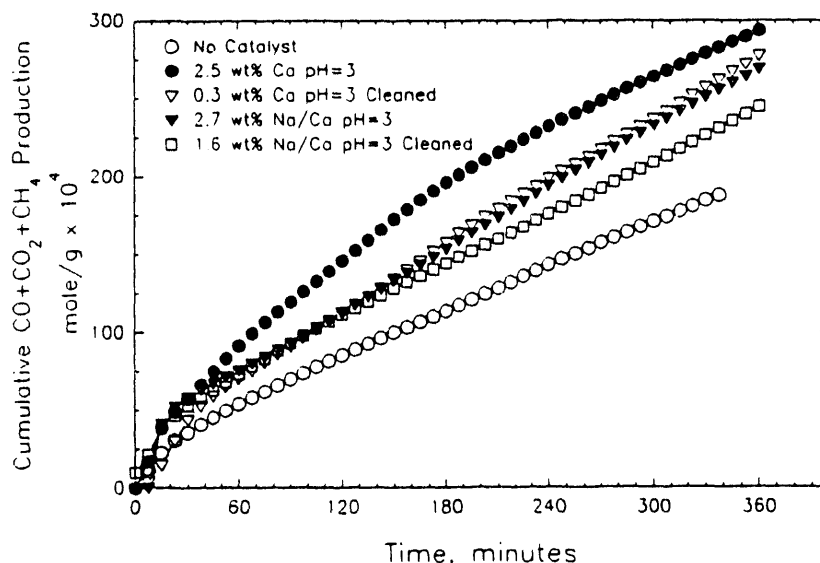large sodium losses as discussed below.



Figure 14.  Cumulative conversion to carbon-containing
gases for several catalyzed coal samples
gasified in the bench-scale system.

Table 9. Results of Bench-Scale Gasification Tests

| Coal or Pretreatment | pH | Weight % Ca | Weight % Na + Ca | Na/Ca | Char Analysis | | | | Weight % Carbon Conversion | Weight % Sulfur Capture | Weight % Sodium Loss |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Weight % C | Weight % Ash | Weight % S | Weight % Na | | | |
| **Raw Coals (No Catalyst)** | | | | | | | | | | | |
| IBC-105 | | | | | 54.8 | 38.8 | 3.81 | 0.26 | 48 | 51 | +7 |
| HLC IBC-105 | | | | | 85.2 | 9.2 | 1.93 | -- | 63 | 22 | -- |
| Wash IBC-105 | | | | | 70.6 | 20.4 | 2.20 | -- | 57 | 32 | -- |
| Oxid IBC-105 | | | | | 63.5 | 30.8 | 4.17 | -- | 42 | 50 | -- |
| Delta | | | | | 67.4 | 22.7 | 2.56 | -- | 50 | 43 | -- |
| **Ca-Catalyzed Coals** | | | | | | | | | | | |
| IBC-105 | 3 | 2.51 | | | 54.1 | 43.2 | 4.41 | | 58 | 48 | |
| IBC-105 | 3 | 0.34 | | | 58.0 | 39.8 | 3.21 | | 58 | 33 | |
| IBC-105 | 9 | 2.30 | | | 54.9 | 45.4 | 4.37 | | 60 | 44 | |
| HLC IBC-105 | 3 | 0.33 | | | 74.3 | 21.2 | 2.30 | | 82 | 14 | |
| Oxid IBC-105 | 3 | 0.91 | | | 51.7 | 47.2 | 3.77 | | 67 | 31 | |
| Oxid IBC-105 | 9 | 0.83 | | | 61.7 | 38.5 | 3.36 | | 53 | 34 | |
| **Na + Ca-Catalyzed Coals** | | | | | | | | | | | |
| IBC-105 | 3 | | 1.95 | 1.15 | 55.6 | 42.5 | 3.89 | -- | 57 | 43 | -- |
| IBC-105 | 3 | | 2.09 | 0.41 | 58.8 | 39.6 | 3.65 | 1.06 | 51 | 42 | +8 |
| IBC-105 | 9 | | 1.47 | 1.18 | 50.5 | 46.3 | 4.33 | 1.74 | 65 | 42 | +7 |
| IBC-105 | 2 | | 1.49 | 1.22 | 53.3 | 45.6 | 4.84 | 1.38 | 63 | 48 | 16 |
| HLC IBC-105 | 3 | | 0.19 | 0.65 | 83.1 | 9.5 | 2.29 | 0.27 | 56 | 31 | 18 |
| HLC IBC-105 | 3 | | 1.67 | 0.88 | 72.0 | 19.3 | 2.40 | 1.44 | 75 | 22 | 42 |
| HLC IBC-105 | 9 | | 1.45 | 0.78 | 66.3 | 22.9 | 2.25 | 1.17 | 78 | 19 | 48 |
| Wash IBC-105 | 3 | | 1.01 | 0.99 | 69.5 | 26.7 | 2.53 | -- | 63 | 31 | -- |
| Oxid IBC-105 | 3 | | 0.75 | 1.43 | 57.0 | 37.8 | 3.78 | -- | 55 | 78 | -- |
| Oxid IBC-105 | 9 | | 0.57 | 2.51 | 59.4 | 36.8 | 3.38 | -- | 53 | 35 | -- |
| Delta | 3 | | 1.00 | 1.02 | 62.4 | 29.1 | 2.64 | -- | 61 | 38 | -- |

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It is difficult to compare these samples in terms of sulfur capture because of the relatively wide range of conversions obtained. Sulfur capture is expected to correlate inversely with conversion because at low conversion much of the sulfur has not been gasified. However, for the group of samples prepared from IBC-105 sulfur capture did increase with Ca content as shown in Figure 15. In future test work, one of our goals will be to operate under conditions providing high carbon conversion for all samples so that a more meaningful comparison of catalyst effects on sulfur capture can be made.
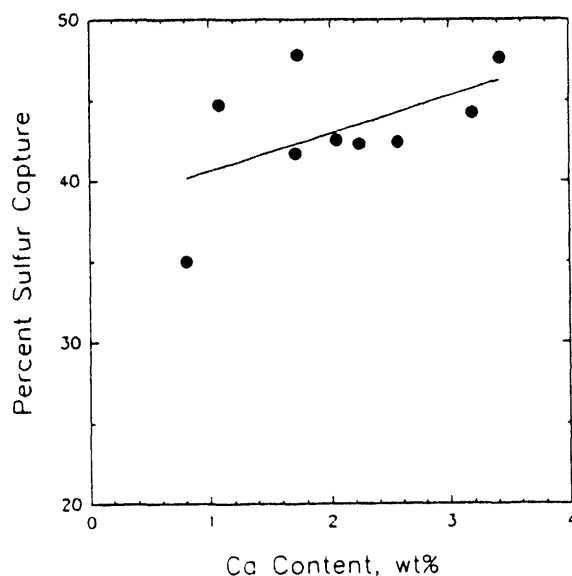


Figure 15. Sulfur capture as a function of Ca content for IBC-105.

A few numbers on sodium loss are available. For some samples, there appeared to be a slight increase in sodium content and these are listed with a plus in Table 9. The apparent sodium gains are less than 10 weight percent and provide some indication of the error of this analysis. For uncatalyzed IBC-105, there is an apparent gain which we take to mean that no significant sodium losses occurred. Some losses were observed from the Na + Ca catalyzed samples and they were very significant in the case of heavily liquid cleaned coal.

We have investigated the fate of sodium remaining on the char by X-ray diffraction. Some of the results we obtained are shown in Figure 16. Here it can be seen that for uncleaned coal, sodium reacts with aluminosilicate constituents of the

mineral matter to form nepheline ($NaAlSiO_4$). It seems likely that sodium losses are higher for the heavy liquid cleaned coal because less mineral matter is available to scavenge the sodium.
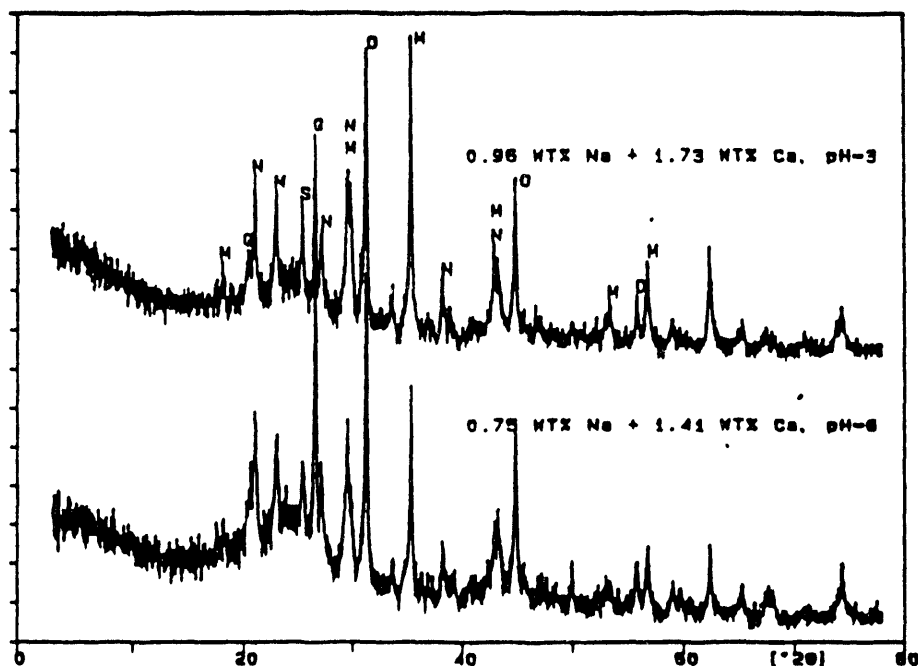


Figure 16. X-ray diffraction results for Na + Ca catalyzed chars. Q = quartz, M = magnetite, N = nepheline, O = CaS (oldhamite), S = $CaSO_4$ (anhydrite).

## CONCLUSIONS AND RECOMMENDATIONS

Ca and Na + Ca added by impregnation can eliminate caking. Decaking effectiveness is enhanced if the catalyst is added at low pH. A high (>1) Na/Ca molar ratio also enhances decaking. The effect of low pH is to generate exchanged carboxylate and phenolate groups on the coal surface. Presumably reaction of these groups to form cross-links is responsible for the reduction in plastic behavior. The reasons for the enhanced effectiveness at high Na/Ca molar ratios is not understood; however, these catalysts exhibited high dispersion even at high loading.

The additives were effective at catalyzing gasification. Loadings in the range of 1 to 2 weight percent produced dramatic increases in TGA gasification rates. Sodium +

calcium additives produced higher rates at lower total loading. However, in bench-scale gasification, there was no advantage to using Na + Ca catalysts. Calcium only coals were equally reactive. Cleaning of the coal with a heavy liquid to reduce mineral matter to a very low level produced a large increase in bench-scale carbon conversion. Washing and low temperature oxidation did not produce a noticeable positive effect.

Sulfur capture in the bench-scale gasifier correlated with the calcium content of the catalyzed coals. The highest level of sulfur capture achieved was 50 percent. Sodium losses from Na + Ca catalyzed raw coal were low. X-ray diffraction indicated that sodium had reacted with mineral matter to form $NaAlSiO_4$ (nepheline). Sodium losses were much higher (up to 40 percent) from the heavy liquid cleaned coal. In this case there was little mineral matter left to scavenge the sodium, leading to the high losses by vaporization.

During the second year of this project, it is planned to develop improved methods for bench-scale gasification. These methods will be used to investigate the effect of temperature on catalyst effectiveness, deactivation, and sodium losses. A series of bench-scale tests designed to simulate a commercial or near-commercial fluid-bed gasifier will be conducted. Also, the effect of coal properties on catalyst requirements will be examined using several other coals from the Illinois Coal Sample Bank.

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PROJECT MANAGEMENT REPORT
June 1, 1993 through August 31, 1993

Project Title: **NA/CA CATALYZATION OF ILLINOIS COALS FOR GASIFICATION**

Principal Investigator:   Mahesh C. Jha, Amax Research &
                          Development Center
Other Investigator:       Robert L. McCormick, Amax Research
                          & Development Center
Project Manager:          Daniel D. Banerjee, Illinois Clean
                          Coal Institute
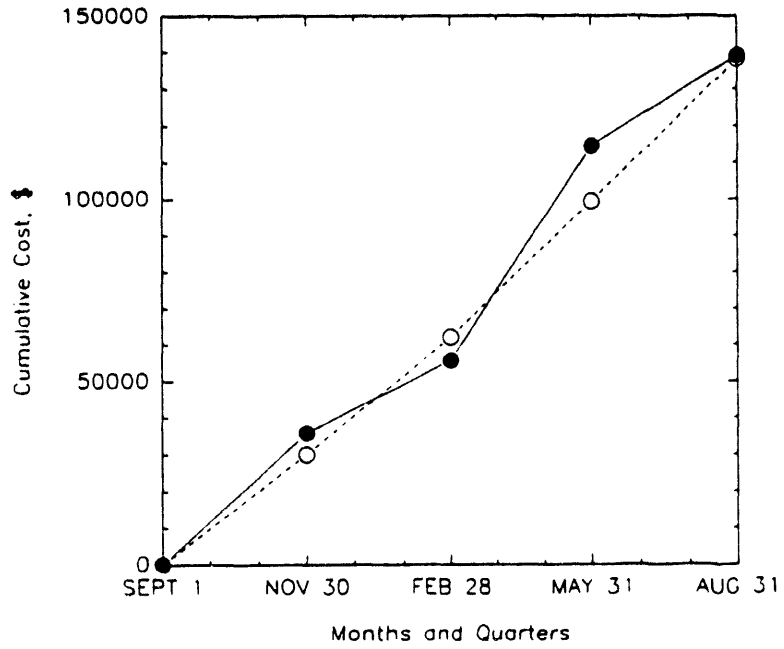
## Projected and Estimated Expenditures by Quarter

| Quarter[a] | Types of Cost | Direct Labor | Fringe Benefits | Materials and Supplies | Travel | Major Equipment | Other Direct Costs | Indirect Cost | Total |
|---|---|---|---|---|---|---|---|---|---|
| 9/1/92 to 11/30/92 | Projected | 7,393 | 4,065 | 1,000 | 0 | 0 | 3,700 | 12,053 | 28,211 |
| | Actual | 9,763 | 4,833 | 2,660 | 0 | 0 | 892 | 17,811 | 35,959 |
| 9/1/92 to 2/28/93 | Projected | 19,162 | 10,538 | 3,200 | 0 | 0 | 5,300 | 31,244 | 69,444 |
| | Actual | 16,076 | 7,958 | 2,703 | 0 | 0 | 4,565 | 24,327 | 55,629 |
| 9/1/92 to 5/31/93 | Projected | 28,750 | 15,811 | 3,800 | 0 | 0 | 9,500 | 46,877 | 104,738 |
| | Actual | 27,385 | 13,917 | 3,503 | 0 | 0 | 20,173 | 49,464 | 114,442 |
| 9/1/92 to 8/31/93 | Projected | 37,708 | 20,737 | 4,000 | 1,300 | 0 | 12,900 | 61,482 | 138,127b |
| | Estimated | 34,121 | 17,340 | 3,124 | 1,133 | 0 | 21,779 | 61,631 | 139,128 |

a  Cumulative by quarter.
b  Includes $12,000 of Amax cost share.

2

# COSTS BY QUARTER

## NA/CA CATALYZATION OF ILLINOIS COALS FOR GASIFICATION



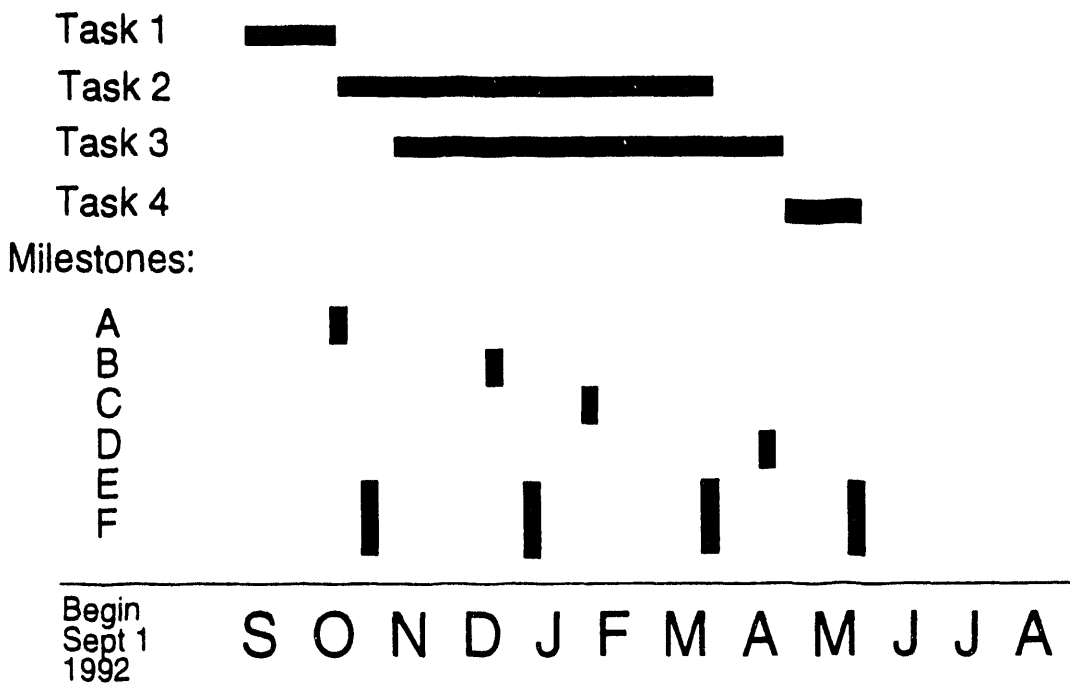○ Projected Expenditures
● Estimated Actual Expenditures

Total Project Budget $138,127*
*Includes $12,000 in Amax Cost Share
and $126,127 in ICCI award

**SCHEDULE OF PROJECT MILESTONES**

**NA/CA CATALYZATION OF ILLINOIS COALS FOR GASIFICATION**



Task 1
Task 2
Task 3
Task 4
Milestones:
A
B
C
D
E
F

Begin
Sept 1
1992

S O N D J F M A M J J A

A Coal and equipment acquisition
B Initial study of catalyst addition methods
C Selection of standard gasification test conditions
D Completion of gasification tests
E Technical reports prepared and submitted
F Management reports prepared and submitted