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# Interaction of Sodium, Sulfur, and Silica during Coal Combustion

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# Interaction of Sodium, Sulfur, and Silica during Coal Combustion

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The interaction of sodium, sulfur, and silica at conditions typical in a pulverized coal furnace was investigated by using both model mixtures and a synthetic coal. The model mixtures consisted of selected inorganic constituents that were well mixed in proportions typically found in low-rank coal. The synthetic coal consisted of a furfuryl alcohol polymer with appropriate amounts of sodium, sulfur, and silica to duplicate the characteristics of low-rank coal. The model mixtures and synthetic coal were burned in a laminar flow (drop-tube) furnace at 900, 1100, 1300, and 1500 °C and residence times of 0.1, 0.5, 1.5, and 2.4 s. The resulting char and fly ash particles were quickly quenched, collected, and analyzed with a scanning electron microscope (SEM) to determine size and composition. Results indicated that the formation of sodium silicates is favored by higher temperatures and longer residence times. Thermodynamic calculations and the model mixture studies indicated above 1100 °C there is little interference in the formation of sodium silicates by sodium sulfates. In the synthetic coal studies, sodium sulfate particles were detected on the surface of the larger sodium silicate fly ash particles formed at lower temperatures. The size and prevalence of the sodium sulfate particles decreased as temperature was increased. Fly ash particle formation was characterized by fragmentation followed by coalescence. Fragmentation was more prevalent at higher temperatures and smaller fly ash particles were formed. Larger particles were formed at lower temperatures, indicating more complete coalescence with some cenosphere formation.

## Introduction

The objective of this study is to determine the effect that temperature and residence times, found in typical industrial pulverized-coal boilers, have on the formation of sodium silicates and sodium sulfates from the inorganic constituents of coal. Western coals contain significant quantities of sodium, sulfur, and silica. The inorganic constituents of coal pass through the combustion zone as solids, liquids, or vapors and ultimately react or condense to form fly ash particles. Some of the fly ash particles are transported to the heat exchange surfaces and form a deposit which grows with time. As these deposits increase they insulate the heat-transfer surface, decreasing the thermal efficiency of the boiler.

A significant effort has been dedicated to the problems associated with inorganic constituents of coal, but a need exists for better fundamental understanding of the formation of ash deposits with closely controlled, laboratory-scale experimental techniques and for application of theoretical models to predict ash-melting behavior.

This study investigates the interaction of three inorganic constituents commonly found in subbituminous and lignite coals: sodium, sulfur, and silica. Sodium volatilizes upon combustion, becomes dispersed through the gas stream, and later condenses on other ash particles and on the metal surfaces. Wibberly and Wall[1] proposed that sodium-containing materials provide a binding matrix that fuses ash particles together. The mechanism of formation of such a material may be the key to understanding the deposition processes of western coals. Studies by Sondreal and others[2] on low-rank coals from the western U.S. revealed that the severity of ash fouling deposits correlates not only with

sodium concentration, but also with total ash content.

One of the major problems in studying the roles of inorganics during coal combustion is the complexity of coal. To alleviate this problem, the interactions of the three inorganic constituents were studied in model systems: first without any coal matrix,[3] and then with use of a synthetic coal (glassy carbon) incorporated with the desired inorganics.[4]

The objectives of this investigation were to determine the effect of temperature and residence time on the formation of sodium sulfates and sodium silicates, more specifically to (1) determine the effect of temperature on the formation of sodium sulfates and sodium silicates, (2) determine the temperature at which sodium silicates are preferentially formed over sodium sulfates, (3) determine the effect of the addition of a carbon (coal) matrix, (4) determine the effect of residence time on ash formation, and (5) determine the surface compositions and homogeneity of the resulting fly ash particles.

The two major competing reactions of interest are

$$Na_2O(g) + 2SiO_2(s) \rightarrow Na_2Si_2O_5(s) \qquad (1)$$

$$Na_2O(g) + SO_2(g) + (1/2)O_2 \rightarrow Na_2SO_4(s) \qquad (2)$$
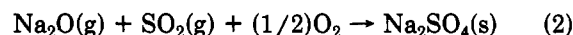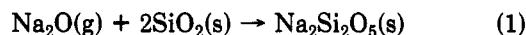
During the reaction, sodium oxide bonds with either the sulfur or silica to form the appropriate compound. The sodium sulfate reaction is a gaseous reaction which will

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(1) Wibberly, L. J.; Wall, T. F. *Fuel* 1982, 61, 87–92.
(2) Sondreal, E. A.; Tufte, P. H.; Beckering, W. *Combust. Sci. Technol.* 1977, 16, 95–110.
(3) Erickson, T. A. The Role of Sodium and Sulfur in High Temperature Reaction with Silica Particles. Senior Honors Thesis, University of North Dakota, Grand Forks, ND, 1988.
(4) Erickson, T. A. The Fate of Flame Volatilized Sodium During the Combustion of Pulverized Coal in Reaction with Silica and Sulfur (Studied with the Aid of a Synthetic Coal). M.S. Thesis, University of North Dakota, Grand Forks, ND, 1990.

proceed quite rapidly whereas the formation of sodium silicate requires the sodium to diffuse into a molten quartz particle.

Wibberly and Wall[1] found that sodium reacts to form multiple products during combustion. They indicated that sodium sulfate, condensed on boiler tubes, may have resulted from the sulfanation of condensed chlorides on the metal surface by

$$2NaCl + SO_2 + (1/2)O_2 + H_2O \rightarrow Na_2SO_4 + HCl \quad (3)$$
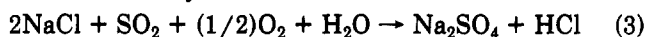
This reaction has also been suggested by Boll and Patel.[5]

Raask[6] found that sodium and calcium sulfates are decomposed by silicates to produce a melilite by the following:

$$(xNa_2SO_4 + yCaSO_4) + Al_2O_3-zSiO_2 \rightarrow$$
$$xNa_2O-yCaO-Al_2O_3-zSiO_2 + (x + y)SO_3 \quad (4)$$
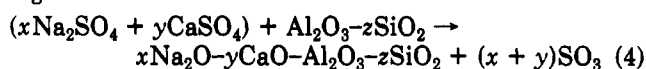
This reaction takes place at the surface of the silicate fly ash particles. Wibberly and Wall[1] indicated that the silica particles with evidence of heterogeneous nucleation have rounded edges. This effect is caused by the reaction of sodium or calcium with the silica to form sodium silicates and calcium silicates.

The proposed mechanisms suggest that sodium reacts in two different ways in the combustion zone. Gaseous sodium oxide reacts with the $SO_2$ to form a sodium sulfate with homogeneously condenses out in the cooler portions of the combustor. Gaseous sodium oxide will also adsorb onto the silica to form a melilite. Raask[6] indicated that approximately 60% of the sodium is adsorbed and dissolved in the silicate and the remainder forms sodium sulfates.

Wibberly and Wall[1] performed experiments with sodium chloride and quartz and found that when the two were heated together they formed a low-viscosity sodium silicate which condensed to form a deposit on the walls of a tube. When the quartz was heated alone no deposit formed. They also found that below 1030 °C the sodium sulfate formation inhibited the sodium silicate formation. Sodium and sulfur oxides are considered volatile inorganic constituents and the boiling temperatures (892 and 445 °C, respectively) are lower than 1500 °C, a common temperature achieved in pulverized coal boilers.

The primary component of coal other than carbon and oxygen is silicates, which have a large amount of inorganic cations associated with them. Sulfur is often present in coal in both mineral form (pyrite, gypsum, etc.) and associated with the organic matrix of the coal. Sulfur forms oxides during combustion and these oxides form inorganic sulfites and sulfates when they interact with other inorganic constituents. Vapor pressure measurements and calculations by Scandrett and Clift[7] indicate that vapor-phase sodium hydroxides or chlorides are present in significant quantities only above approximately 950 °C. Below 950 °C the alkalies are present mainly as condensed sulfates. In addition, reactions of alkali-metal sulfates with aluminosilicates are thermodynamically favored over reactions with silica and quartz, and the reaction with aluminosilicates should occur above approximately 730 °C.

## Experimental Method

The test matrix for this study consisted of two parts[3,4] and is shown in Table I. All of the samples in the test matrix were burned in a laminar flow furnace which allows precise control of the combustion environment. The residence time and temperature

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(6) Raask, E. *Mineral Impurities in Coal Combustion*; Hemisphere Publishing Co.: New York, 1985.

(7) Scandrett, L. A.; Clift, R. *J. Inst. Energy* **1984**, *12*, 391-397.

**Table I. Test Matrix**

| run | composn[e] | temp, °C | residence time, s | analysis[d] |
|---|---|---|---|---|
| model mixture | | | | |
| 1 | A | 1500 | 1.4 | R |
| 2 | A | 900 | 1.4 | R |
| 3 | B | 1500 | 1.4 | R |
| 4 | B | 1300 | 1.4 | R |
| 5 | B | 1000 | 1.4 | R |
| 6 | C | 1500 | 1.4 | R |
| 7 | D | 1500 | 1.4 | R |
| 8 | B | 1500-1300[a] | 2.4 | R |
| 9 | D | 1500-1300[a] | 2.4 | R |
| 10 | D | 1500-1100[a] | 2.4 | R |
| 11 | D | 1500-900[a] | 2.4 | R |
| synthetic coal | | | | |
| 12 | E | 1500 | 0.1[b] | C, R, T |
| 13 | E | 1500 | 0.5[b] | C, R, T |
| 14 | E | 900 | 0.1[b] | C, R, T |
| 15 | E | 900 | 0.5[b] | C, R, T |
| 16 | E | 1500 | 1.4 | R, P, I |
| 17 | E | 1300 | 1.4 | R, P, I |
| 18 | E | 1100 | 1.4 | R, P, I |
| 19 | E | 900 | 1.4 | R, P, I |
| 20 | E | 1500 (N_2 atm) | 1.4 | R |
| 21 | F | 1500 | 1.4 | R |
| 22 | F | 900 | 1.4 | R |

[a] Two furnaces, temperature of each furnace. [b] Short residence time probe used. [c] Composition: A, 100% $SiO_2$; B, 95% $SiO_2$, 5% Na; C, 99.8% $SiO_2$, 0.2% S; D, 94.8% $SiO_2$, 5% Na, 0.2% S; E, 84% SynCoal, 10% $SiO_2$, 5% Na, 1% S; F, 89.6% SynCoal, 10% $SiO_2$, 0.4 S. [d] Analysis: C, CCSEM; R, morphology; P, point count; T, TGA; I, image analysis.

profile can be varied. Longer residence times can be achieved by using two furnaces; shorter residence times can be achieved with a short residence time probe. The furnace assembly will be described in more detail in the equipment section. After passing through the furnace, the particles enter a quenching probe which instantly cools the sample and quenches the reaction with an inert atmosphere. The resulting char and fly ash are collected on filter paper.

The test matrix allows determination of the effects of both residence time and combustion temperature on the interaction of sodium, sulfur, and silica both with and without a carbon matrix (synthetic coal). In the test matrix, model mixture refers to inorganics burned in the absence of a carbon matrix and synthetic coal refers to inorganics burned in the presence of a carbon matrix. The coal was fed at a rate of 0.3 g/min with a gas flow rate of approximately 4 $dm^3$/min of air and nitrogen. In all cases the temperature refers to the wall temperature of the furnace(s). The actual gas-phase temperature is expected to be slightly higher than the wall temperature when the synthetic coal mixtures are burned due to the energy released from combustion. The residence time for a particle is calculated from Stoke's law and depends on temperature, length of furnace, and particle size and assumes that all particles achieve terminal velocity upon entering the heated zone of the furnace.

Runs 1-12 used model mixtures of the inorganic constituents without the presence of a carbon matrix. Runs 1 and 2 are used to determine fragmentation of the quartz particles in the absence of the burning synthetic coal particle and to see if there is a temperature effect. Runs 3-5 and 8 study the effect of temperature and residence time on the formation of sodium silicates without any competition from the formation of sodium sulfates. Run 6 studies the interaction between the sulfur and the quartz in the absence of sodium oxide. Runs 7 and 9-11 study the effects of temperature and residence time on the competition between the sodium silicate and sodium sulfate reactions.

Runs 12-22 tested the effects of the addition of a synthetic coal matrix. Runs 12-16 and 19 investigate the effect of residence time on ash formation. Runs 16-19 are used to determine the temperature effect. Run 20 is heated in a nitrogen atmosphere and is used to determine the effect of temperature on the synthetic coal matrix in the absence of combustion. Runs 21 and 22 are used to look at the ash formed in the absence of sodium.

**Table II. Synthetic Coal Characterization**

| method of analysis | % SiO$_2$ | % Na | % S | % ash |
|---|---|---|---|---|
| TGA | | | | 15.9 |
| ICP | 11.3 | 4.0 | | |
| CCSEM | 9.3 | | | |
| proximate–ultimate | | | 1.0 | 15.0 |

BET surface area 50.3 m$^2$/g

The primary method of analysis is the scanning electron microscope/microprobe (SEM) with an energy-dispersive X-ray detector with the aid of an image analysis system. Two analytical programs were used in conjunction with the SEM: scanning electron microprobe point count (SEMPC), which is an automated point count program, and computer-controlled scanning electron microscopy (CCSEM), which is an automated particle sizing and compositional program. Other analyses included thermal gravimetric analysis (TGA), Malvern particle size analysis, X-ray diffraction (XRD), proximate–ultimate analysis, and nitrogen BET surface area from gas adsorption data.

## Equipment and Technique

**Model Mixtures.** Samples containing silica, sulfur, and sodium were made at the compositions (A–D) shown in Table I. Sodium bicarbonate was used to introduce the sodium. Sublimed sulfur and sodium bicarbonate were manually combined with the quartz (silica). The quartz was sized from 10 to 20 μm and the sodium bicarbonate and sulfur were less than 1 μm. These samples were burned in the laminar flow furnace with a gas stream composition of 94% nitrogen and 6% oxygen. This composition compares with the downstream composition of a standard boiler operating with approximately 3% excess air.

**Synthetic Coal.** *Preparation.* The purpose of a synthetic coal is to be able to study the interactions of coal combustion in a system not as complex as actual coal. The synthetic coal must have similar combustion characteristics as well as lending itself to the addition of minerals in a quantitative manner. A furfuryl alcohol polymer has been found to be such a substance.[8-10]

The preparation of the synthetic coal was developed by Flagan and Senior.[9,11] The technique was slightly modified for this study and is described in detail elsewhere.[4] In brief, the quartz (which had been sized to 5 μm) was added prior to the polymerization so that it would behave as an included mineral. After the polymer was cured, the synthetic coal was ground and sized. Analysis of the sized coal indicated that 0.4 wt % sulfur was inherent in the synthetic coal polymer due to the *p*-toluenesulfonic acid which is used as a catalyst for the polymerization. Additional sublimed sulfur was added extraneously and mixed with the ground synthetic coal so that the final composition would consist of 1% sulfur. Sodium was added by using a solution of sodium benzoate in an ethanol solution. The sodium benzoate/alcohol solution was mixed with the ground coal and the alcohol evaporated. This has been found[12] to effectively load the sodium on the coal so that it will easily volatilize.
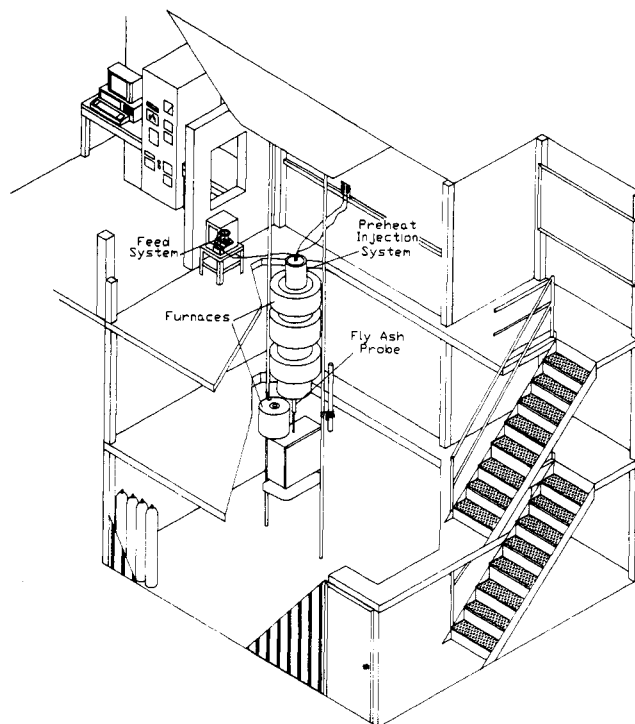


**Figure 1.** Laminar flow furnace orientation and assembly.
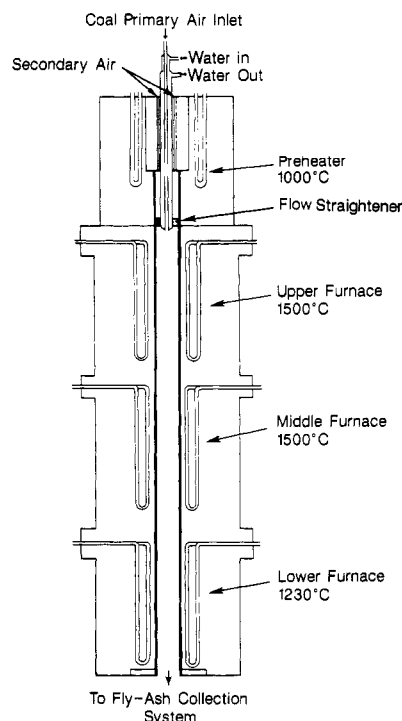


**Figure 2.** Laminar flow furnace heated zones.

*Characterization.* The chemistry of the polymerization of furfuryl alcohol to form a glassy carbon has been studied extensively.[13-17]

For this study, characterization of the synthetic coal included analysis by CCSEM, TGA, proximate–ultimate, inductively coupled plasma (ICP) (with acid digestion and

(8) Schmitt, J. L. Carbon Molecular Sieves as Selective Catalyst Supports. Ph.D. Thesis, Pennsylvania State University, University Park, PA, 1976.
(9) Senior, C. L.; Flagan, R. C. *Twentieth International Symposium on Combustion*; The Combustion Institute: Pittsburgh, PA, 1984; pp 921–929.
(10) Levendis, Y. A.; Flagan, R. C. *Combust. Sci. Technol.* **1987,** *53,* 117–136.
(11) Senior, C. L. Submicron Aerosol Production During Combustion of Pulverized Coal. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1984.
(12) Mills, M. E. Sodium Release from Solids in Flames Studied Using Laser Induced Fluorescence Spectroscopy. Ph.D. Thesis, University of North Dakota, Grand Forks, ND, 1989.

(13) Dunlop, A. P.; Peters, F. N. *Ind. Eng. Chem.* **1953,** *34,* 814.
(14) Riesz, C. H.; Susman, S. *Proceedings of the 4th Carbon Conference*; Pergamon Press: Oxford, U.K., 1960.
(15) Conley, R. T.; Metil, I. *J. Appl. Polym. Sci.* **1963,** *7,* 37–52.
(16) Wewerka, E. M.; Walters, K. L.; Moore, R. H. *Carbon* **1968,** *7,* 129–141.
(17) Fitzer, E.; Schaefer, W.; Yamada, S. *Carbon* **1969,** *7,* 643–648.

lithium boride extraction), and BET surface area from nitrogen adsorption. The results are shown in Table II. By formulation, the synthetic coal included 10% $SiO_2$ (quartz), 7% $Na_2O$, and 3% $SO_3$ by weight, which compares well with the results presented in Table II.

The weight loss with respect to temperature results from the TGA were in qualitative agreement with TGA results for a low-rank coal. The BET surface area of the synthetic coal is 50.3 $m^2/g$.

The prepared samples of synthetic coal were burned in the laminar flow furnace with 20% excess air (to ensure complete combustion) according to the test matrix given in Table I.

**Laminar Flow Furnace.** Figure 1 shows the laminar flow furnace, control room, and collection system. Figure 2 is a diagram of the three furnaces which make a heated core of up to 60 in. long with preheat injector. The furnaces can be used in series to allow for variable residence times and are designed so that they can be swiveled in and out of position with ease. For this study, only the top two furnaces were used. The various heating zones can be individually controlled and the controllers are interfaced with a computer which is used to set the temperature and control the heating and cooling of furnaces when they are being placed in operation. The model mixtures or synthetic coal is fed mechanically and then fluidized with part of the feed gas before being added to the furnace. The solids feeding rate is maintained at approximately 0.3 g/min.

To achieve residence times shorter than 1 s, a short residence time probe is inserted through the bottom of the furnace to the appropriate position which will give the desired residence time. The probe quickly cools the sample and quenches the reaction with an inert atmosphere. A suction pyrometer can also be inserted in the bottom of the furnace assemble to determine the temperature profile of the gas flowing through the system without the effects of radiation from the furnace walls. Details of the laminar flow furnace, the short residence probe, and the suction pyrometer are given elsewhere.[4,18]

**Scanning Electron Microscope.** A Jeol JXA-35 scanning electron microprobe was used in conjunction with a Tracor Northern (TN) energy-dispersive detector with ultrathin window. In addition, a TN automated stage, digital beam control, and image analysis system were used. Three different techniques[19] were used to study the samples: (1) manual mapping, point analysis, image analysis, and morphology, (2) SEMPC, scanning electron microprobe point count, and (3) CCSEM, computer-controlled scanning electron microprobe. Each of these procedures will be described in more detail. Standard beam conditions for all analysis were 15 kV and 400 pA.

Manual procedures on the SEM refer to sampling and characterization of single particles and points as specified by the operator. Mapping allows a visual representation of the composition of an area. Up to 16 different element compositions can be viewed on one map. The map is qualitative, with no numerical values given. The image information can be stored in the image analysis system and analyzed to determine size and other physical aspects. Manual techniques were used mainly to investigate single particles with interesting characteristics to gain further understanding into particle formation.

SEMPC is a Flextran program which does point analysis on a sample. The program will acquire a spectra on a point, and if there are enough predetermined X-ray counts, it will continue acquiring for 25 s total. If the counts are not adequate, the program will move to the next point. The points are set up by designating a distance for the automated stage to move each time. The samples for the SEMPC are adhered to a carbon plug with double-stick tape. The sample is coated with sputtered carbon to allow the discharge of electrons from the sample while being analyzed. This method allows analysis of the surface of the particles with the X-rays coming from the first 5 $\mu$m of depth.

CCSEM is a program which digitally controls the beam to scan across a field and pick out the mineral particles by their level of brightness. CCSEM uses the backscatter electron imaging to differentiate the minerals from the background. The higher atomic number of the minerals relative to the carbon matrix leads to a brighter appearance in the backscatter mode. The program will size each particle with eight different diameters and analyze the center of the mineral for its composition. When the entire frame is completed, the automated stage moves to the next preset field. Two thousand points can be analyzed by using this technique.

The samples for the CCSEM are polished epoxy mounts where the sample is mounted in epoxy, polished with silicon carbide paper, polished with diamond paste, and sputter-coated with carbon. The samples are cross sectioned to investigate the internal detail of the ash and coal samples.

The sample volume of the electron beam is estimated to be a 5-$\mu$m sphere. Many of the particles analyzed were smaller than 5 $\mu$m, so sample volume is important.

**Thermodynamic Calculations.** *Theory.* SOLGASMIX is a theoretical application of thermochemical equilibrium written by Liao and Spear.[20] It determines the compounds that will give a minimum Gibb's free energy for a given system. Data bases put together by the National Institute of Testing and Standards (NITS) are used for the thermodynamic data. The basic techniques used in equilibrium calculations are based on free energy minimization.[21] Gibb's phase rule relates the number of phases $P$, and the degrees of freedom $F(p,T,x)$, to the number of components $C$ by the following:

$$F = C - P + 2 \tag{5}$$

The activities must also obey the Gibb–Duhem constraint:

$$\sum n_i \, d(\ln a_i) = 0 \tag{6}$$

In addition, if the quantity of a substance drops below $10^{-10}$ mol during the iteration process, the species will be deleted in order to increase the rate of convergence. After the mixture that minimizes the free energy of the system has been determined, additional tests are applied for condensed phases (of pure nature only) with invariant stoichiometry. If the test indicates that the phase in question must be included, the compositions of the liquid and solid mixtures are redetermined, and then the final equilibrium phases are found.

## Results

**Thermodynamic Model (SOLGASMIX) Results.** *Model Mixture.* Figure 3 shows the results of the SOLGASMIX calculations for the model systems with a composition of

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(19) Steadman, E. M.; Zygarlicke, C. J.; Benson, S. A.; Jones, M. L. *Seminar on Fireside Fouling Problems*; Advanced Combustion Engineering Research Center: Brigham Young University, Provo, UT, 1990.

(20) Liao, P. K.; Spear, K. E. SOLGASMIX with HETTA for the IBM-PC and Compatibles; *Material Research Laboratories: University Park, PA, 1986.*
(21) Eriksson, G. *Chem. Scr.* **1975**, *8*, 100.
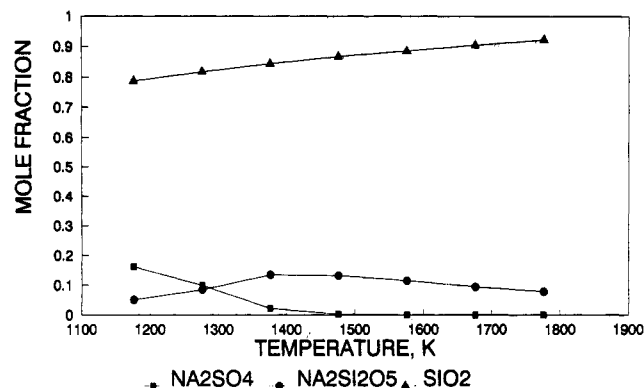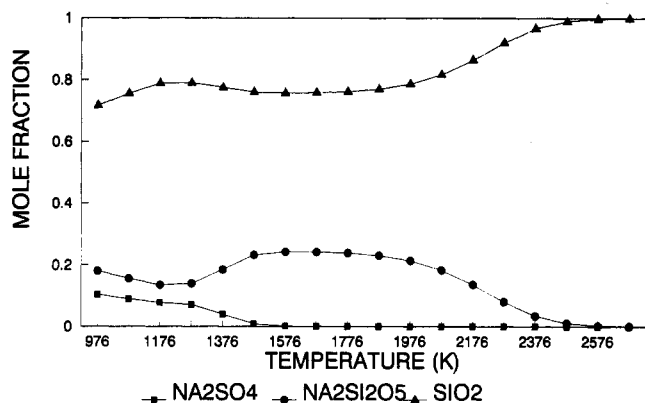
**Figure 3.** SOLGASMIX results from model mixture studies.



**Figure 4.** SOLGASMIX results from synthetic coal system.

**Table III. Model Mixture Results**

| | initial | | | composition | | |
|---|---|---|---|---|---|---|
| run | composn[b] | temp, °C | time, s | Na₂O | SiO₂ | SO₃ |
| | | | | $Na_2O$ | $SiO_2$ | $SO_3$ |
| 1 | A | 1500 | 1.4 | | 100.0 | |
| 2 | A | 900 | 1.4 | | 100.0 | |
| 3 | B | 1500 | 1.3 | 15.0 | 85.0 | |
| 4 | B | 1300 | 1.3 | 21.5 | 78.5 | |
| 5 | B | 1000 | 1.3 | 86.8 | 13.2 | |
| 6 | C | 1500 | 1.3 | | 100.0 | |
| 7 | D | 1500 | 1.3 | 16.5 | 83.5 | |
| 8 | B | 1500–1300[a] | 2.4 | 6.0 | 94.0 | |
| 9 | D | 1500–1300[a] | 2.4 | 5.5 | 91.5 | 3.0 |
| 10 | D | 1500–1100[a] | 2.4 | 3.0 | 94.5 | 2.5 |
| 11 | D | 1500–900[a] | 2.4 | 38.0 | 13.0 | 49.0 |

[a] Two furnaces, temperature of each furnace. [b] Composition: A, 100% $SiO_2$; B, 95% $SiO_2$, 5% Na; C, 99.8% $SiO_2$, 0.2% S; D, 94.8% $SiO_2$, 5% Na, 0.2% S.

edges of the quartz particles. Also, at least some spherical sodium silicate particles were formed at each temperature. The average surface composition determined for several of these sodium silicate spheres is reported in Table III (the SEM microprobe can only determine the compositions in the first few micrometers of the particles). At the higher temperatures and longer residence times, more interaction is expected. These results are demonstrated in Table III. At the higher temperatures, the surface concentration of silicates increases, and the sodium concentration decreases. This indicates that more of the silicate is reacting with the sodium, and the sodium is diffusing further into the particles at the higher temperature and residence times. If the sodium oxides were merely remaining in the gas phase and being swept out of the reactor at the higher temperatures, then there would not be a residence time effect.

Auger surface analysis of run 3 indicated that the sodium extended only to between 50 and 100 Å into the particle. This indicates that the sodium is present mainly at the particle surface. At the high temperature (run 3), only about 5–15% of the silica particles interacted with sodium, as determined by rounded edges and/or spherical sodium–silica particles. Even fewer particles interacted at the lower temperatures (runs 4 and 5). At the longer residence time (run 8) the silica content at the surface increases, which indicates more interaction. The physical appearance of these particles is very close to those of the shorter residence time (run 3); only the spherical particles are more abundant at the longer residence time.

No interaction was found between the silica and sulfur in run 6 as expected. No sulfur could be traced after the particles passed through the furnace. Apparently all of the sulfur was volatilized and left the furnace in the gas phase.

Comparison of runs 3 and 7 indicates that, in the presence of sulfur, there is a slight decrease in the surface concentration of silicates. This indicates that the sodium had not diffused into the silica to the same extent as when sulfur was not present. Some of the sodium may have reacted with the sulfur and been swept out of the reactor.

Runs 9–11 also examined the competing reaction of sulfur and silica with sodium. For particles exiting the second furnace at 1100 °C or above, little or no sodium sulfate was found. At the higher temperatures, most of the interaction had occurred between the sodium and silica, with only a small amount of sulfur being observed. However, run 11 produced some particles that contained up to 50% sulfur and 40% sodium on the surface. This suggests that the temperature where sodium silicates begin dominating over sodium sulfates lies between 900 and 1100 °C. The sodium sulfate particles formed from the model
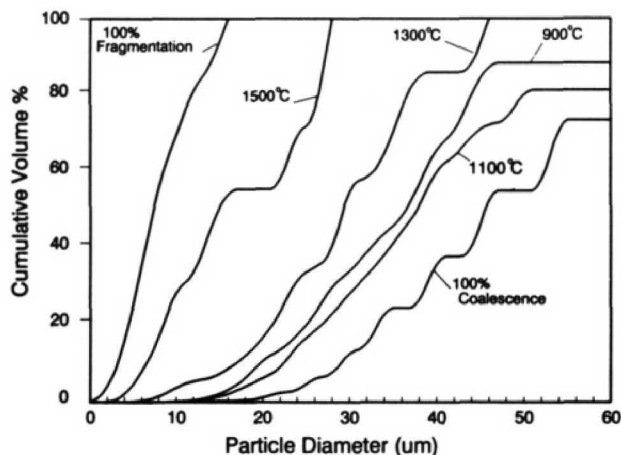
94.8% silica, 5% sodium, and 0.2% sulfur (composition D, Table I). From the figure the competition for sodium between silica and sulfur can be seen as a function of temperature. The calculations indicate that a crossover between the formation of $Na_2SO_4$ and $Na_2Si_2O_5$ occurs at approximately 1050 °C which agrees with the experimental data.

*Synthetic Coal.* Figure 4 shows the results of the SOLGASMIX calculations on the synthetic coal sample. The temperatures range from 700 to 2400 °C. The formation of sodium sulfate competes with the sodium silicate formation at lower temperatures. Above 1100 °C the competition is minimal and sodium silicates are formed more readily. This is similar to the model mixture results (Figure 3) except that the sodium sulfates never dominate but they do interfere. These results assume equilibrium has been reached between the components. The temperatures listed are the actual combustion temperatures which may be higher than the wall temperature due to the exothermic reaction of coal combustion. The combustion temperature depends on excess air.

**Model Mixtures.** *SEM Results.* Table III gives the composition data from the resulting fly ash created when the model mixtures were burned. The composition data was collected by analyzing the surfaces of the collected samples with the SEM using manual operation, and the data reported are the averages from multiple particles.

SEM analysis of the pure silica particles that passed through the furnace (runs 1 and 2) found that the particles retained the sharp, jagged edges found in the quartz before combustion. This was expected since no reaction should occur. No evidence of fragmentation of the particles was observed, and no temperature effect was noted.

In runs 3–5 and 8, the effect of temperature and residence time on the sodium/silica reaction is demonstrated. The SEM analysis of these samples found that at all temperatures there was evidence of a rounding of the sharp

**Figure 5.** Synthetic coal fly ash particle-size distribution.

**Table IV. Particle Surface Compositions**

| temp, °C | bulk composition | | | gray area composition | | | white moiety composition | | |
|---|---|---|---|---|---|---|---|---|---|
| | Na | S | Si | Na | S | Si | Na | S | Si |
| 900 | 24 | 5 | 61 | 19 | 1 | 80 | 39 | 18 | 43 |
| 1500 | 19 | 1 | 80 | 5 | 0 | 95 | 6 | 1 | 93 |

mixture were primarily spherical in form and resembled the sodium–silica particles. The sodium sulfate particles were smaller and more abundant than the sodium silicate particles.

**Synthetic Coal.** In runs 15–18, the same synthetic coal was burned at 1500, 1300, 1100, and 900 °C with approximately the same residence time of 1.4 s (equivalent to passing through the first furnace). The SEM analysis of the four resulting fly ashes can be described in terms of particle size distributions, surface characteristics, and morphology and inner composition.

Figure 5 shows the particle-size distribution of the resulting fly ash particles. These results were determined by manually sizing 125 particles with the aid of the image analysis system. The following are also shown in Figure 5: (1) the theoretical diameter distribution of fly ash particles assuming 100% coalescence of inorganic species and homogeneous distribution of the inorganics throughout the coal, and (2) the distribution of the quartz particles before combustion. The implications of these results have been described elsewhere.[22]

The surface characteristics of the particles are similar in that they are spherical and are covered with small white particles or moieties. Figure 6 shows a fly ash particle produced at 900 °C. The abundance and size of the moieties decrease with increasing temperature. At 900 °C the approximate size of the white moieties is 0.5–2 μm; at 1500 °C the moieties are, at most, half that size. The compositions of the 1500 and 900 °C samples were determined in three specific areas with the SEM/microprobe X-ray detection system. The three areas analyzed were bulk composition (average over entire particle), gray area composition (the large fly ash particle), and the white moieties composition. Table IV shows the results. The results are averages of several samplings on similar areas and indicate that the larger particles comprise sodium and silica with sodium sulfate particles (white moieties) sticking to the surface. The white moieties are believed to be pure sodium sulfate, and the silica and some of the sodium found in the analysis are interference coming from below
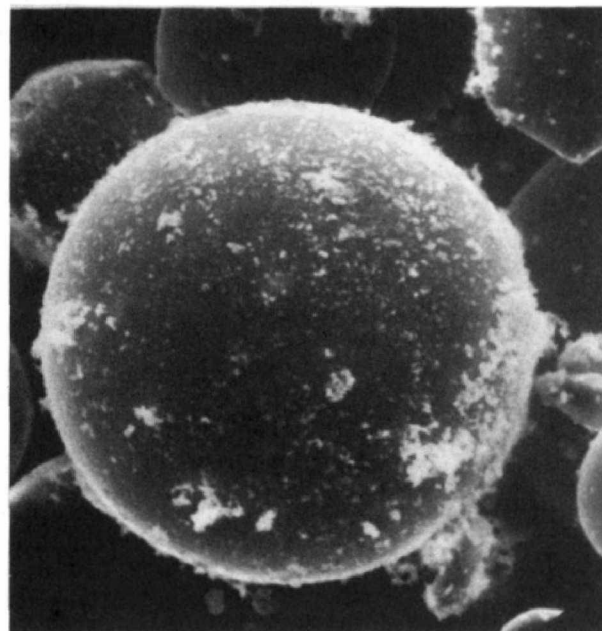
(22) Erickson, T. A.; Ludlow, D. K.; Benson, S. A. *Fuel*, submitted for publication.



**Figure 6.** Synthetic coal fly ash, 900 °C, 1.5 s. Note white moieties on surface.

the moieties because the sample excitation volume of the electron beam is larger than the moiety volume. It is also evident that the sulfur content in the overall composition of the sample decreases with increasing temperature. This is expected since more of the sulfur is expected to leave in the gas stream at the higher temperatures.

Cross-sectioned samples were also analyzed. The particles formed at 900 °C were not homogeneous in many respects. Many particles were heterogeneous being composed of areas that contained pure silica and areas that contained both sodium and silica. Other particles appeared to be cenospheres, with the center of the particles being either hollow or containing unburned carbon. The 1500 °C particles appeared to be completely homogeneous with both silica and sodium existing throughout. This could be explained by either highly molten quartz intermixing and reacting to form sodium silicates with the reaction occurring readily, or by the diffusion of sodium into the quartz to form an amorphous glass in which the sample does not contain a specific crystalline form, but is an agglomeration of the two components.

*Residence Time Studies.* The residence time studies focused on the early transformations and reactions that take place during coal combustion. Residence times of 0.1 and 0.5 s which constitute the first 7% and 35% of the combustion processing time (assuming full residence time of 1.4 s) were achieved with the short residence time probe. Short residence time data were collected at 900 and 1500 °C.

All four samples were analyzed by using CCSEM, TGA, and morphology. The results are given in Table V along with the results for unburned synthetic coal.

For the CCSEM analysis, the particles were mounted in epoxy, cross sectioned, and polished so that both included minerals and mineral moieties on the surface of the char could be measured. The CCSEM technique analyzes at least 1000 mineral particles. The average particle size of the minerals in the short residence time samples are very similar and only slightly larger than the average mineral size within the unburned synthetic coal. This implies that no appreciable coalescence has occurred in the first 35% of the combustion stage. The average particle diameter of the 1500 °C, 0.1-s sample is slightly higher than the
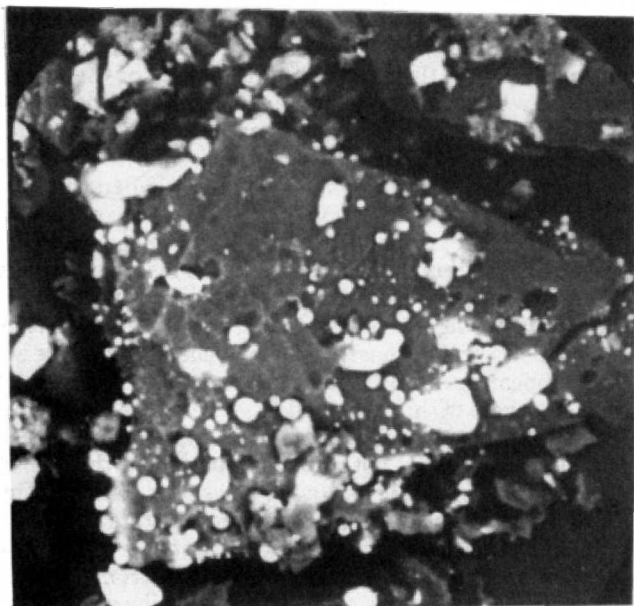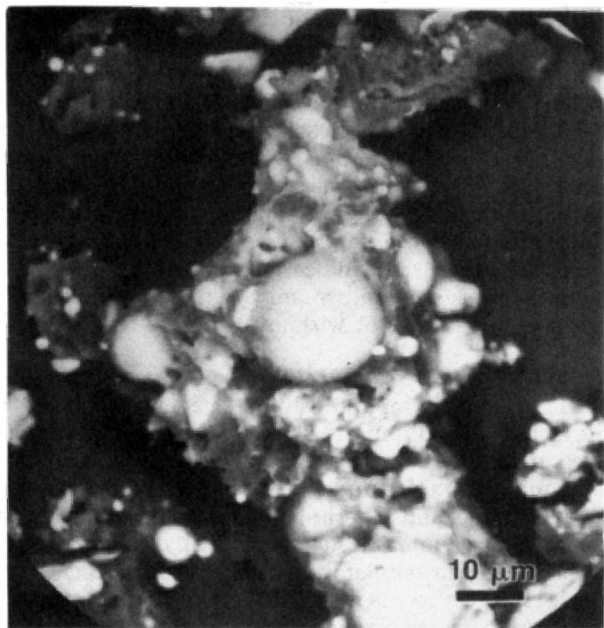
**Figure 7.** Synthetic coal char, 900 °C, 0.1 s.



**Figure 8.** Synthetic coal char, 900 °C, 0.5 s.

**Table V. Short Residence Time Results**

| combust. temp, °C | residence time, s | mineral diameter,[a] $\mu$m | sodium silicates,[b] % | carbon loss,[c] % | BET surf. area, $m^2/g$ |
|---|---|---|---|---|---|
| 900 | 0.1 | 4.04 | 1.2 | 14.3 | 55.1 |
| 900 | 0.5 | 4.06 | 18.9 | 66.5 | 124.4 |
| 1500 | 0.1 | 5.06 | 11.0 | 48.7 | 110.4 |
| 1500 | 0.5 | 4.20 | 45.4 | 83.5 | N/A[d] |
| synthetic coal | | 3.84 | | | 50.3 |

[a] Average diameter determined from CCSEM analysis. [b] Area percentage of particles with >5% Na and <5% S (CCSEM analysis). [c] TGA analysis. Carbon loss compared to unburned synthetic coal. [d] Sample too small to accurately determine surface area.



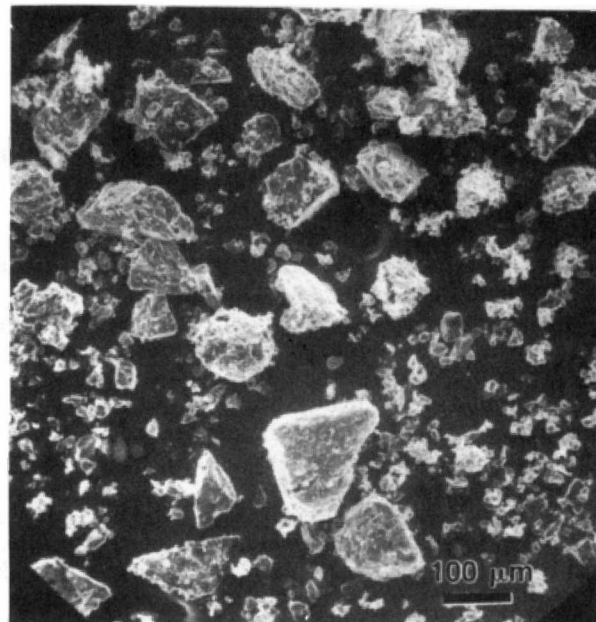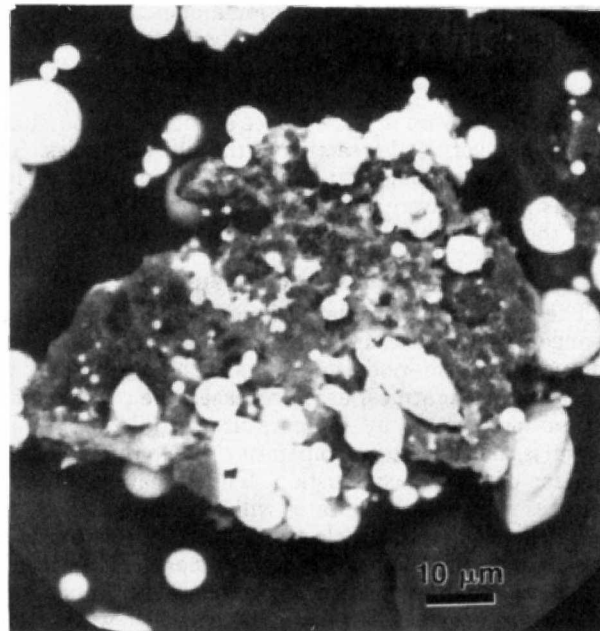**Figure 9.** Synthetic coal char, 1500 °C, 0.1 s.



**Figure 10.** Synthetic coal char, 1500 °C, 0.5 s.

other samples and is attributed to random error in sampling and sample preparation since the 1500 °C, 0.5-s sample has a smaller average mineral diameter.

The CCSEM technique characterizes the composition of the mineral particles it analyzes. The area percentage of sodium silicates present in the samples is also shown in Table V. The CCSEM technique categorizes a particle as sodium silicates if at least 5% sodium is found with the silica and if there is no more than 5% sulfur. The CCSEM results indicate that, at higher temperatures and longer residence times, a larger fraction of the quartz particles have reacted with sodium to form sodium silicates. No appreciable evidence of sodium sulfate formation was indicated by the CCSEM technique. However, the CCSEM technique as used will only analyze particles greater than 1 $\mu$m and will exclude most sodium silicate particles (white surface moieties in Figure 6) that have formed during the early stages of combustion.

Figures 7–10 are SEM photographs of the four different residence time runs. The sample at 1500 °C and 0.1 s (run

12) appears to have bimodal size distribution of char: the large particles in the range of 100 $\mu$m and the smaller particles around 20 $\mu$m. It appears that the smaller particles are fragments from the larger particles since no appreciable amount of the fine particles was evident with the unburned synthetic coal samples. Analysis of the sample

indicated that sodium and sulfur were present on the char surface but not in appreciable conjunction with the quartz particles. This could demonstrate the early formation of sodium sulfates. However, the sodium and sulfur concentrations did not correspond to any physical morphological structure of the surface that was visible.

For the 1500 °C, 0.5-s sample (run 13), the amount of carbon remaining had decreased substantially. The mineral particles formed were as large as 30 μm which is larger than the mineral particles after 1.4 s of combustion. This is an indication of cenosphere formation during the early stages of combustion. The large-sized particles demonstrated that coalescence had occurred. The quartz particles had about 5% of sodium associated with them which is on the same scale as the sodium present in the full combustion samples. CCSEM analyses also determined that a small amount of sulfur was present with the unburned carbon. The sulfur was not associated with the sodium.

The sample from 900 °C, 0.1 s (run 14), had a bimodal distribution similar to run 12. However, the lower temperature sample (run 14) showed a lesser degree of combustion and coalescence than the higher temperature sample (run 12). Approximately 5–10% of the large particles investigated had cracks which indicated that fragmentation had occurred. The larger particles had evidence of combustion (spherical moieties of mineral matter), whereas few of the smaller particles had evidence of combustion. Run 20, the heating of synthetic coal in an inert atmosphere, gave no evidence of molten quartz particles. The quartz particles remained jagged and apparently unaffected by the passage through the laminar flow furnace.

The char particles produced at 900 °C and 0.5 s (run 15) were much smaller and more homogeneous in size than those produced at 0.1 s (run 14). The average particle size of the char produced in run 15 was 20 μm. The char sample was expected to be smaller due to more complete combustion. However, the char particles were too small to be the remnants of combustion alone. This indicates that fragmentation has occurred. There is a greater extent of coalescence of the minerals than at the shorter residence time.

The samples run in the absence of sodium (runs 21 and 22) showed very little reaction of the silica particles. The quartz particles remained relatively jagged as the carbon matrix burned away, and there was only minor evidence that the quartz had become molten.

## Discussion of Results

The addition of the synthetic coal matrix significantly changed the interaction between sodium, sulfur, and silica compared to the model mixtures. The addition of the burning carbon atmosphere decreased the production of sodium sulfates at all temperatures studied. A major reason is the increase in temperature due to the exothermic reaction of the coal combustion. The formation of sodium silicates over sodium sulfates will dominate due to temperature effects, with little effect due to the reducing atmosphere of the combustion environment. This accentuates the need for the study of combustion products with the use of a model coal or synthetic coal which will decrease the number of components interacting by the investigators choice, while maintaining the atmosphere of actual coal combustion.

The formation of sodium silicates during coal combustion is favored by longer residence times and higher temperatures, as shown by the model mixture and residence time studies. The formation of sodium sulfates does not interfere to any large degree with the formation of sodium

silicates due to the high temperature of combustion taking place within the burning coal environment. In the model mixture studies, the rounding of the edges of the quartz particles was attributed to interaction with sodium. In the synthetic coal studies there was an increased prevalence of spherical quartz particles produced due to both the interaction with sodium and the higher temperatures associated with the combustion of the synthetic coal matrix.

At the higher temperature, there is a prevalence of homogeneous sodium silicate particles. This may actually be an amorphous glass in which the sodium diffused into the quartz during its molten state. At lower temperatures, the particles are not nearly as homogeneous, with the sodium appearing on the surface of the quartz particles and inside pockets within the particle. The pockets probably formed by the sodium being caught up in the formation of molten quartz, but not diffusing throughout the quartz.

The size of sodium sulfate particles decreases with increasing temperature from a few micrometers to submicrometer particles. This makes the particles difficult to identify and analyze with the current instrumentation.

Though serendipitous to the study of the inorganics, the following conclusions can be made of the combustion characteristics of the synthetic coal. The formation of fly ash during the combustion of the synthetic coal appears to be dominated by both fragmentation and coalescence. From the temperature studies it appears that there is a formation by coalescence at the lower temperatures and that larger fly ash particles are formed. At higher temperatures, fly ash formation by fragmentation of the coal occurs first followed by coalescence resulting in smaller fly ash particles being formed. The residence time studies showed that at both temperature extremes fragmentation had occurred. There is indication that the larger particles found at lower temperatures may be due to the formation of cenospheres, with or without complete carbon loss.

## Conclusions

The effect of temperature and residence time on the interaction of sodium and sulfur with silica was investigated at conditions typical in a pulverized coal combustor using model mixture and a synthetic coal. The thermodynamic model and experimental results indicate that the formation of sodium silicates is favored by longer residence times and higher temperatures. The results indicate that above 1100 °C there is little interference in the formation of sodium silicates by sodium sulfates.

The addition of the coal matrix effected the interaction of sodium, sulfur, and silica. The higher particle temperatures, due to the exothermic combustion of the synthetic coal, lead to conditions where molten silica is present. Under these conditions, the sodium becomes more dispersed throughout the silica particles. The higher temperatures also lead to a decrease in the formation of sodium sulfates, and more sulfur is swept through the reactor without reacting.

The residence time studies indicate that fragmentation occurs in the early stages of combustion of the synthetic coal followed by a coalescence of the minerals (both included and extraneous). Larger fly ash particles are formed at lower temperatures. This is caused by a combination of less fragmentation with more complete coalescence and by cenosphere formation.

Analysis of the surface composition of the fly ash particles indicates that the bulk of the surface consists of sodium silicates. At the lower temperatures, small sodium sulfate particles adhere to the surface of the larger particles. Cross sectioning of the resulting fly ash particles indicates primarily the presence of homogeneous particles.

At lower temperatures, cenosphere particles are found with unburned carbon located in the interior.

Registry No. Na, 7440-23-5; S, 7704-34-9; $SiO_2$, 7631-86-9; C, 7440-44-0; $Na_2SO_4$, 7757-82-6; $Na_2Si_2O_5$, 13870-28-5; poly(furfuryl alcohol) (homopolymer), 25212-86-6; sodium silicate, 1344-09-8.

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# Mechanisms and Kinetics of Rapid, Elevated Pressure Pyrolysis of Illinois No. 6 Bituminous Coal

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An investigation was conducted of the effects of pressure on rapid pyrolysis behavior of a caking coal, using a high-pressure entrained-flow reactor ($10^3$–$10^4$ K/s heating rate) under applied pressures of 100, 309, and 530 psig of $N_2$, with residence times of up to 1.7 s, supplemented by collateral experiments at ambient pressure. Cracking reactions begin at an earlier stage as applied pressure increases, and the time over which cracking reactions occur decreases with increasing pressure. The tar becomes more aromatic and less substituted with increasing residence time. The product gas distribution is strongly dependent on pressure and residence time. The aromatic structures in the char become more condensed at higher applied pressures. Kinetic models for devolatilization and swelling during pyrolysis were developed, and the apparent first-order rate constants were calculated. Applied pressure influences the devolatilization rate and swelling rate differently.

## Introduction

Pyrolysis is the first and most important step in virtually every coal utilization process and influences the course of any subsequent reactions such as combustion, gasification, or liquefaction. Due to the heterogeneous nature of coal and the complexity of the processes involved in pyrolysis, attempts to develop a comprehensive mathematical model for describing the kinetics of pyrolysis often meet with limited success. These difficulties have been thoroughly discussed in several excellent reviews.[1-3] However, like all chemical processes, the pyrolysis reactions are dependent on the nature of the reactant (i.e., coal) and the reaction conditions. The structure and reactivity of the resultant char are largely consequences of the pyrolysis behavior. Coal pyrolysis phenomena are strongly rank dependent because of the differences in coal structures of different ranks. Compared to bituminous coals, the lower rank coals have more oxygen functional groups, and therefore oxygenated species such as CO, $CO_2$, and $H_2O$ are the principal pyrolysis products for lignites, while hydrocarbon gases and tars are the major volatile yields for bituminous coals.[4] Bituminous coal tars are more aromatic and thermally stable than those of lignites.[2] It has been postulated that the chemical properties of coal are determined by a relatively small number of functional groups common to all coals and that coals differ by their content of these functional groups.[5] When all experimental conditions are held constant except for coal type, the kinetics of evolution of individual species from decomposition of functional groups are relatively insensitive (i.e., within an order or magnitude) to coal rank.[5] This observation led to the development of the functional group (FG) model which used rank-independent kinetics to describe evolution of individual species during coal pyrolysis.[6]

A traditional approach to the kinetics of pyrolysis has been the assumption of a first-order decomposition occurring uniformly throughout the particle, so that the rate of volatile release is given by

$$dV/dt = k(V^* - V)$$

where $V$ is the cumulative volatile yield up to reaction time $t$ and $V^*$ is the effective volatile content of the coal. The definition of $V^*$ is ambiguous, and many approaches have been suggested for estimating its value.[7-9] There is also

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