

CURRENT RESEARCH ON THE INORGANIC CONSTITUENTS
IN NORTH DAKOTA LIGNITES AND SOME
EFFECTS ON UTILIZATION

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Introduction

Although coal is often considered to be simply an organic rock, most coals contain appreciable quantities of inorganic materials. With the resurgence of interest in coal utilization and conversion processes in recent years has come an increased appreciation for the need to understand both the mineralogical characteristics and the chemical behavior of the inorganic constituents of coal. The recent coal literature contains numerous discussions of the importance of knowing the character, distribution, and behavior of the inorganic species; these discussions span the whole spectrum of coal technology-- preparation and storage, combustion, liquefaction, gasification, and environmental studies.

This paper discusses results of laboratory studies on the characterization of inorganic constituents in low-rank coals and on elucidation of the role of these constituents in combustion and conversion processes. The laboratory studies were undertaken in support of pilot plant activities at the Grand Forks Energy Technology Center (GFETC) of the U.S. Department of Energy. Engineering and process-related details of the various projects have appeared in previous publications, which are noted in the reference section.

Inorganic Constituents in Lignite

Samples from two major lignite mines in western North Dakota were obtained (4) and studied by polarized light microscopy, x-ray diffraction, scanning electron microscopy, and electron microprobe analysis. The initial results of the laboratory studies of these two samples show that the inorganic constituents occur as minerals or combined with organic substances; are closely related in origin to the overburden and underclay; and illustrate part of a complex series of events in the geochemical evolution of the lignites. While the systematic variations that are presented are believed to be significant, they are not claimed to be necessarily representative at this point in the study.

The abundant lignite in North Dakota is contained in the upper part of the Fort Union group within the Bullion Creek formation and the overlying Sentinel Butte formation. Recent summaries of the general geology of the lignite-bearing rocks in western North Dakota are available (1-3).

Lignite, lignite overburden, and underclay were collected from measured, vertical sections on the highwalls at the South Beulah mine, Beulah, and the Baukol-Noonan mine, Center (4). Both mines produce lignites from the Sentinel Butte Formation with major production from the 3.8 m Beulah-Zap bed at South Beulah and the 3.5 m Hagel bed at Baukol-Noonan. Inorganic constituents in the two lignites are similar and contain detrital and authigenic minerals, listed in Table 1 and illustrated in Figure 1, as well as organically bound materials. The bulk chemistry of overburden, lignite, and underclay has been obtained by a rapid microprobe method.

At the South Beulah mine, four samples of overburden above the Beulah-Zap bed consist largely of clayey silt grading downward to organic-rich clay. Illite, quartz, and montmorillonite are the major minerals and kaolinite, chlorite, plagioclase, and mica are present in lesser amounts. Calcite is present in the uppermost sample while dolomite occurs in the other three samples; both decrease in abundance downwards. The Beulah underclay contains major illite, kaolinite, and quartz and lesser montmorillonite and calcite.

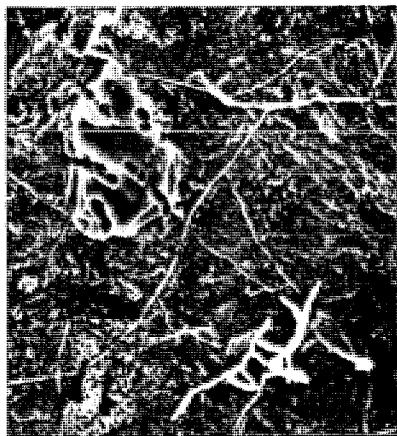
TABLE 1. - Minerals Identified in Two North Dakota Lignites

<u>Common (in approximate order of abundance)</u>	<u>Rare or uncertain</u>
Kaolinite	Montmorillonite?
Quartz	Dolomite?
Pyrite	Barite
Gypsum	Enstatite
Calcite	Corundum
Hematite	Ca, Mg Aluminosilicate?
Na Plagioclase	Ca, Na Aluminosilicate?
Alkali Feldspar?	
Chlorite?	
Hornblende	
Augite?	
Illite?	
Biotite?	

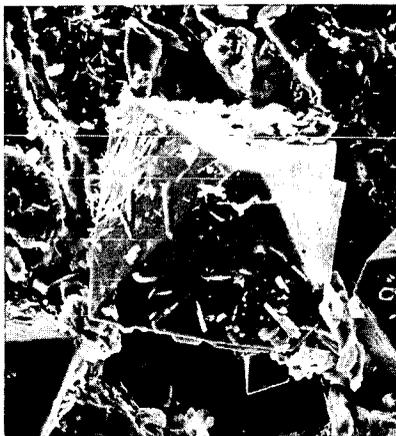
The twelve samples of overburden and the sample of underclay from the Baukol-Noonan mine are mineralogically similar to the Beulah samples. The lower part of the overburden is silty sand and the upper part, clays and silty clays. Overall montmorillonite is somewhat less abundant than at Beulah but is highly variable.

The mineralogical and chemical studies combined with the observation that lignites are aquifers suggest that hydrogeochemical processes have strongly affected the sodium and calcium distribution by removal of calcium by dissolution of carbonate minerals in the lower part of the overburden, concentration of sodium and calcium in the central parts of the lignite seams, and increase in the CaO/Na₂O ratio in the upper parts of the lignite seams (5). Groundwater processes also appear to be a major factor in oxidation and reduction reactions as suggested by sulfide and sulfate distribution in fracture zones at the Baukol-Noonan mine (6). Pyrite development in fractures followed by growth of small gypsum crystals on the pyrite (Figure 1) indicates that groundwater carried and deposited iron and sulfur under reducing conditions, and carried and deposited calcium at a later stage under oxidizing conditions.

The original detrital minerals and organically bound inorganic constituents in lignite have been strongly affected by hydrogeochemical processes in the depositional and post-depositional history of lignite and the associated sediments. Current laboratory studies emphasize cataloging and characterization of inorganic constituents in lignite; establishment of mineralogical and chemical distribution patterns in overburden, lignite, and underclay; and evaluation of the geochemical history of the lignite-bearing sediments.



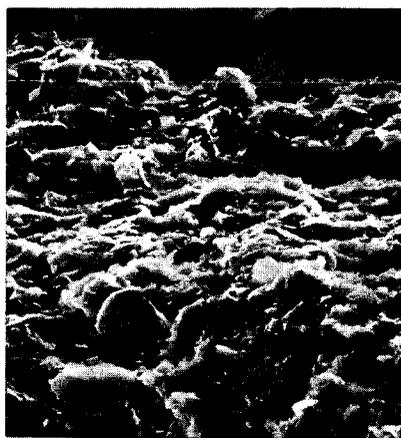
A



B



C



D

Figure 1. Scanning electron microscope photographs of inorganic constituents in lignite-bearing strata. Sentinel Butte Formation, North Dakota.
A. Detrital quartz (?) in ion-etched Beulah lignite. 1540X.
B. Secondary pyrite with gypsum crystals on surface from fracture zone in Baukol-Noonan lignite. 770X.
C. Secondary barite in fracture zone in Baukol-Noonan lignite. 270X.
D. Montmorillonite in overburden at Beulah mine. 1400X.

Gasification

The inorganic constituents of lignite can have several effects in gasification processes. Numerous articles have appeared in the recent literature describing the catalysis of gasification reactions by various inorganic species. Studies at GFETC have focused on the development of an understanding of the relationship between coal ash slag composition and viscosity. These studies have been done in support of the slagging fixed-bed gasification pilot plant at GFETC. Details of the pilot plant project have been given in a series of publications, most recently by Ellman and co-workers (7). Maintaining slag viscosity low enough to allow continuous discharge from the gasifier is crucial to successful operation.

Direct measurement of slag viscosity is a demanding operation, and few laboratories are equipped with suitable high-temperature viscometers. Therefore the development of predictive or correlative techniques for relating viscosity to composition is an important component of gasification research. A previous publication (8) has demonstrated that it is possible to develop empirical equations which give a good fit of experimental viscosity data provided that the equations are developed for, and their use restricted to, slags of a given petrographic classification.

The petrographic normative calculation (9) is a formation used to calculate a set of standard, or normative, mineral species, which then establishes the types of silicate structures to be expected in the slag. The degree of polymerization of silicate species has an important role in determining viscosity behavior (10).

The transformations involved in the formation of slag from the inorganic species in the coal have been partially elucidated in laboratory studies of char and slag samples obtained from the gasifier hearth after a test had been ended and the bed contents quenched. The data presented here were obtained from samples collected from a 1.4 MPa test with Indian Head lignite. Process data from this test, number RA-12, have been published (11).

Discreet slag particles were found in samples collected 0.9 m above the bottom of the bed. The composition at this point was 22% Na_2O , 24% Al_2O_3 , and 53% SiO_2 . This composition lies in the nepheline region of the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ternary (12) and has a melting point of approximately 1200°C. This is consistent with typical temperatures of about 1260°C observed 1.2 m above the hearth bottom. Samples collected at 0.3 and 0.6 m were complex mixtures of silicates and sulfates. Total melting occurred in the bottom-most 0.3 m of the bed, where temperatures exceeding 1700°C have been observed. Some slag components are volatilized in this region, particularly sulfur (approximately 80% is lost), sodium and potassium (30-35%), and phosphorus (25%). Smaller amounts of magnesium, calcium, and silicon are also volatilized.

At 0.1 to 0.3 m above the hearth bottom some reduction of iron compounds to metallic iron occurs. Normally the iron metal drains with the slag and does not appear to interfere with slag flow. However, formation of iron metal removes a potential source of FeO , which is considered to be an excellent slag flux.

The viscosity behavior of the slag with temperature will be determined by its composition; specifically, by the relative amounts of polymer-forming constituents such as SiO_2 and Al_2O_3 and of polymer-breaking species such as Na_2O or CaO . The slag composition is in turn determined by two factors. The composition and nature of the inorganic constituents in the lignite feed broadly determines the relationships between polymer formers and polymer breakers. The thermal and chemical environment established by the gasification and combustion reactions in the gasifier hearth then "fine tune" the slag composition through such processes as volatilization of SO_3 and Na_2O and reduction of Fe_2O_3 to FeO or metal.

Liquefaction

The product distribution from coal liquefaction will vary between a heavy distillate, a light oil, and a gas depending on the extent and method of treatment of the intermediate products. The catalytic effect of naturally occurring inorganic species and minerals on the conversion and product yield is being investigated extensively with Eastern coals and also with low-rank Western subbituminous and lignitic coals. In general certain inorganic constituents of Eastern coals have shown a self-catalyzing effect on the liquefaction yield. High yields have been achieved by adding pyrite, magnetite plus pyrite, sulfur plus magnetite, and coal ash plus sulfur to coals which initially gave a low yield.

The lignites in the Northern Great Plains are distinguished from the higher rank coals by having high moisture, lower sulfur, and high inherent ash content. Most of the alkali and alkaline earth cations exist as humic acid or phenolic salts. These cations are ion exchangeable and are uniformly distributed throughout a coal particle. The majority of the extraneous ash exists as small particles of quartz, pyrite, hematite, and clay. In addition lignites have a large amount of oxygen-containing functional groups. These properties affect the liquefaction behavior of lignite in terms of reactivity, product quality, product yield, catalyst life, and solid residue.

The role of these unique properties of lignite in liquefaction is being investigated in a program at GFETC which seeks to develop a chemical and engineering data base for liquefaction of lignites and subbituminous coals. The programmatic background and process engineering results have been presented in a recent paper by Willson and co-workers (13).

Some of the parameters being studied with the batch autoclave and continuous process unit at GFETC are temperature, pressure, residence time, slurry coal concentrate recycle, solvents, and mineral effects. Extensive research on the effects of individual minerals on the product yield has not been performed thus far. However, a significant increase in the overall product yield was observed when the reaction solids were recycled in the continuous unit. In a recent run using a lignite from the Beulah mine in Mercer County, ND, a deposit formed in the feed slurry and was analyzed for possible minerals and inorganics using a polarizing light microscope and a scanning electron microscope (SEM). Calcium carbonate was initially suspected as a main ingredient in the deposit. However, quartz was the only mineral identified in the product. An elemental analysis of the bulk product using the SEM resulted in a composition not unlike that of the ash in the original coal. Analysis for calcium by atomic absorption also showed no preferential buildup of calcium. Thermogravimetric analysis indicated the presence of some carbonates but no particular cation could be associated with the carbonate. Other workers in liquefaction have reported calcium carbonate deposits when using lignites but thus far no major accumulations have been observed at GFETC. The implications of a low-level carbonate buildup using lignites should be fewer shut downs caused by carbonate plugging.

Combustion

Ash fouling-- the buildup of ash deposits on walls and heat exchange surfaces of boilers-- is a major problem associated with the use of lignite. The causative effects of sodium content in the fouling behavior of low-rank coals has been discussed in previous publications (14-15). Some of the current laboratory research at GFETC relating to ash fouling involves the chemical and physical characterization of ash deposits to develop a better understanding of the mechanisms involved in deposit formation and to predict fuel additives to control fouling.

A typical profile of an ash deposit formed in the 34 kg/hr, PC-fired pilot plant combustor at GFETC is shown in Figure 2 (16). The deposit was collected on an



FIGURE 3. - SEM photomicrograph (3000X) showing particles in the initial stages of attachment.

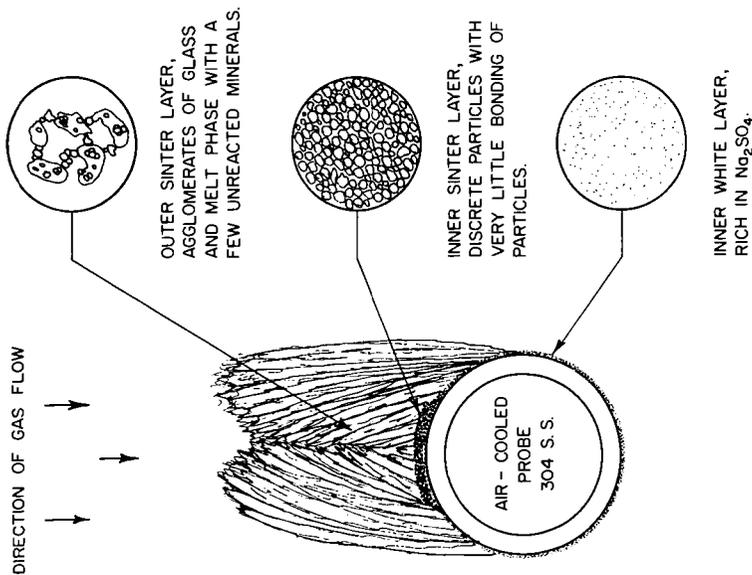


FIGURE 2. - Physical structure of a typical ash deposit formed in the GFEC combustor.

air-cooled probe maintained at 540°C. X-ray diffraction studies have shown that sulfates, mainly Na_2SO_4 and CaSO_4 , predominate near the probe and in the inner sinter layer. The sulfates are present on the surfaces of the ash particles and in the inner white layer immediately surrounding the probe. The melt and reaction of these surface sulfates to form an intermediate $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ eutectic has been proposed (18,19). Figure 3 illustrates the particle-to-particle bonding which occurs upon the melt and reaction of the various sulfates (16).

A second mechanism involving sodium has been observed: the fluxing action of sodium with aluminosilicate (presumably kaolinitic clay) mineral assemblages. Volatilized sodium is believed to react with kaolin particles in the combustion zone to form low-melting (900-1100°C) sodium aluminum silicate compounds. These species react with the molten sulfates in the deposit to form complex melilites $(\text{Na},\text{Ca},\text{K})_2 [(\text{Mg},\text{Fe}^{+2},\text{Fe}^{+3},\text{Al},\text{Si})_3 \text{O}_7]$. X-ray diffraction studies of deposits from the GFETC combustor have shown that melilite formation increases as the distance from the probe increases (16).

The physical strength of the deposits has been observed to increase as a result of continued exposure to SO_2 and SO_3 at high temperatures. This phenomenon is referred to as the sulfating process. X-ray diffraction analysis of deposits obtained from the Hoot Lake Power Company, Fergus Falls, Minnesota, has shown that more anhydrite was present than melilites.

Fouling problems in fluidized bed combustors are not expected to be as severe due to the lower combustion temperatures in FBC's (700-950°C) compared with PC-fired or cyclone combustors (1650°C). Scanning electron microscope studies have been made of bed agglomerates from the GFETC pilot plant FBC from a test burning Beulah lignite with Al_2O_3 bed material, and from the pilot scale FBC of Fluidyne Engineering Corporation of Minneapolis, burning Indian Head lignite with an SiO_2 bed. The agglomerations from the GFETC FBC showed thin films of Na_2SO_4 , CaSO_4 , and $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ surrounding a layer of complex silicates (a typical composition is 11% Na_2O , 9% MgO , 21% Al_2O_3 , 11% CaO , 45% SiO_2) with a core which is predominantly Al_2O_3 . No sulfates were observed in the agglomerations from the Fluidyne combustor (17). A calcium-rich coating surrounded a sodium-rich layer which in turn contained core material that was predominantly SiO_2 and Al_2O_3 .

This preliminary evidence suggests that agglomerates form around particles of bed material via reactions with the inorganic materials in the coal or ash, and may react further with SO_2 or SO_3 . Laboratory investigations of the mechanism of agglomerate formation are expected to provide continuing support to FBC research.

Summary

The results presented here exemplify the types of broad-ranging studies, which, it is hoped, will eventually provide an extensive data base on the origin, distribution, characteristics, and process behavior of the major inorganic species in lignites. For example, the hydrogeochemical history of a lignite deposit and the mineralogy of the overburden and underclay play an important role in determining the amount and distribution of sodium in the lignite. That sodium may then have a detrimental effect on the utilization of the lignite-- by contributing to ash fouling - or it may have a beneficial effect-- by reducing slag viscosity in a slagging gasifier. Continued research will allow coal scientists to follow the fate of the inorganic species from the Paleocene epoch to tomorrow's synfuels technology.

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