

## MINERAL TRANSFORMATIONS DURING ASHING AND SLAGGING OF SELECTED LOW-RANK COALS

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### Introduction

Inorganic species are incorporated in low-rank coals in many ways: as ion-exchangeable cations, as coordination complexes, and as a diverse array of discrete minerals. In some cases an element will be present in more than one form; potassium, for example, occurs both as an exchangeable cation and in association with clay minerals. The variation in association of inorganics among the multiple modes of occurrence results in a very complex series of reactions and mineral transformations when low-rank coals are ashed or slagged. The behavior or the inorganic components can be at least as important to effective operation as the behavior of the carbonaceous portion in low-rank coal utilization processes. The determination of the extent of the changes in bulk composition and in mineral phases during controlled laboratory ashing is very important in developing an understanding of ash or slag behavior during coal processing and how such changes are related to process conditions.

In the past, mineralogical determinations using ash formed at the standard temperature of 750°C identified minerals which were not originally present in the raw coal but which were artifacts of the ashing procedure. This was due to the alteration of minerals by oxidation, dehydration and other processes at high temperatures. Recent studies by Miller et al (1), Frazer and Belcher (2), and O'Gorman and Walker (3) have concentrated on relating raw coal mineralogy to ash mineralogy generated at low temperatures. Low-temperature ashing (LTA) theoretically would enable one to obtain the true mineralogical composition of a coal since little mineral alteration occurs up to 125°C. Mitchell and Gluskoter (4) expanded this concept to study low to high temperature mineral transformations in ash of subbituminous and bituminous coals. With few exceptions the application of LTA in ash mineralogy studies has been primarily associated with subbituminous and bituminous coals (5). In fact, Miller et al (1) and Frazer and Belcher (2) state that LTA may be unsuitable for obtaining the original mineralogy in lignites without appropriate pretreatment. This is due to the high organic oxygen content with associated inorganic exchangeable cations characteristic of lignites. The presence of organically-bonded inorganics drastically increases the ashing time thereby increasing the chances of mineral alteration by oxidation. In addition, the release of organically-bound cations and organic sulfur in contact with mineral matter can alter the original coal mineralogy with an extended period of low-temperature ashing.

The purpose of this study is to identify mineral transformations in low to high temperature ashes (125°, 750°, and 1000°C) and slags (1300°C) characteristic of lignites. The processes responsible for certain mineral transformation are also examined.

Twelve low-rank coals were selected from the northern Great Plains and Gulf Coast. Nine North Dakota lignites, two Gulf Coast (Texas and Alabama) lignites, and one subbituminous coal from Montana were studied (Table I).

### Experimental

The mineral matter composition of each coal sample was determined directly by X-ray diffraction (XRD) of low temperature ash (LTA). A LFE Model 504 four-chamber oxygen

Table I. Location and Inorganic Analyses (XRF) of Coals Studied. All Coals are Lignites Except for Absaloka Subbituminous

Coal Name	Locality	Major and Minor Elements (Percent)									
		Si	Al	Fe	Mg*	Ca	Na*	S	K	Tl	Ba*
+ Absaloka	Big Horn Co., Montana	< 3.5	1.61	2.58	0.08	0.37	0.33	3.92	0.12	0.06	0.03
Beulah Low Sodium	Mercer Co., North Dakota	0.90	0.54	1.02	1.18	1.57	0.14	2.01	0.09	0.05	0.02
Beulah High Sodium	Mercer Co., North Dakota	0.35	0.29	0.52	0.67	1.81	0.46	0.75	ND	0.06	0.04
Center	Oliver Co., North Dakota	0.66	0.44	0.89	0.94	1.70	0.40	0.65	0.08	0.32	0.04
Choctaw	Choctaw, Alabama	1.06	0.49	1.87	0.56	0.84	0.09	2.50	0.10	0.04	ND
Falkirk	McLean Co., North Dakota	0.86	0.50	0.48	0.91	2.60	0.01	0.55	0.15	0.04	0.02
Gascayne Blue	Bowman Co., North Dakota	1.09	0.73	0.25	0.38	2.28	0.27	0.93	0.14	0.05	0.13
Gascayne Red	Bowman Co., North Dakota	2.86	0.87	0.39	0.59	1.74	0.13	1.12	0.13	0.12	0.06
Indian Head	Mercer Co., North Dakota	0.71	0.49	0.68	0.97	1.56	0.62	0.44	0.12	0.04	0.05
Pike	Pike County, Alabama	1.11	0.66	0.36	0.11	1.77	NA	2.28	0.10	0.65	NA
San Miguel	Atascosa Co., Texas	3.58	1.06	0.47	ND	1.20	0.60	1.88	0.35	0.08	NA
Velva	McHenry Co., North Dakota	0.56	0.33	0.26	0.11	0.98	0.09	NA	0.05	0.02	0.03

\*Concentrations measured by neutron activation analyses (NAA).

+Absaloka coal analysis completely by NAA.

NA (Not Available) ND (Not Detected)

plasma low temperature asher was used. The ashing procedures used were modified after Miller and Givens' (6) technique for low temperature ashing of subbituminous and bituminous coals. One set of samples was ion-exchanged in 1N ammonium acetate at 70°C for 24 hours and freeze-dried prior to low temperature ashing. This procedure was repeated three times to ensure removal of ion-exchangeable cations. Another, but untreated, sample set was also ashed. Preliminary comparison of sample sets showed the exchanged samples to have reduced ashing time and identical mineralogy except for the presence of bassanite in non-exchanged samples. This difference will be discussed later.

Modifications in operating procedures are as follows: an RF Power of approximately 150W and an oxygen flow of 100cc/min at 2 psi were maintained along with a chamber pressure of 1mm Hg. Samples were stirred once every 2 hours during the first eight hours and every eight hours during the remaining ashing time.

Samples were also ashed at 750°C in accordance with ASTM procedure D3174-73 and will be referred to as ASTM samples (7). Samples were then ashed at 1000°C following the same procedure for 750°C coal ashing and will be referred to as HTA (high temperature ash) samples. Finally raw coal samples were heated to 1300°C forming slag. All slag samples were air quenched.

Mineralogical composition of ash samples was analyzed by XRD. X-ray fluorescence (XRF) analysis was also used for bulk ash analysis. Raw coal analysis was performed by XRF and neutron activation (NAA). XRF elemental analyses of raw coal samples are listed in Table I.

## Results and Discussion

Mineralogical phases formed at different temperatures for each coal sample are summarized in Table II. The major mineral phases detected by XRD in LTA samples are quartz, pyrite, bassanite, kaolinite and plagioclase. The processes responsible for mineral transformations include oxidation, vaporization, sulfur fixation, dehydration, solid-state interactions, and recrystallization. The temperatures at which specific transformations occur are based on previous experimental work by Mitchell and Gluskoter (4) and published chemical data in the Handbook of Chemistry and Physics (8). In addition to mineral-mineral interactions it is believed that reactions between minerals and exchangeable cations occur (9).

Pyrite ( $\text{FeS}_2$ ) is present in all LTA samples. While Miller et al (1) stated that pyrite may be oxidized with increased low temperature ashing time in lignites no evidence of oxidized forms of iron was seen by XRD. This may be attributed to the pretreatment of samples with ammonium acetate, thereby reducing ashing times as much as 50%. In ASTM samples pyrite is oxidized to hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). According to Miller and Gluskoter (4), pyrite oxidizes at 500°C. With the oxidation of pyrite to iron oxide rather than iron sulfate, pyritic sulfur is released. The formation of sodium and calcium sulfates, detected in ASTM ash, may be associated with the release of pyritic sulfur. The source of such sulfates may be the interaction of pyritic sulfur released during pyrite oxidation with carbonates as well as with organically-bound calcium and sodium.

Bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) is present in some of the sample LTAs. Bassanite most likely forms from the dehydration of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) at 65°C. Gypsum was detected by scanning electron microscopy (SEM) in raw coal samples. Another source of calcium or sodium sulfate may be the fixation of organic sulfur by organically-bound calcium or sodium cations (9, 10). In this case, bassanite is simply an artifact of the low temperature ashing procedure. This phenomenon is typical of coals having abundant alkali cations associated with carboxyl groups. Continued increases in ashing temperature results in complete dehydration of bassanite to anhydrite ( $\text{CaSO}_4$ ) at 400°C. Anhydrite is a major mineral phase in ASTM and HTA samples and is present in most slags.

Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) is present in only LTA samples. Kaolinite dehydration occurs approximately from 400° to 525°C (4). With removal of water by dehydration, the kaolinite structure collapses, retaining some degree of order forming

Table 11. Mineralogical Composition of Ash and Slag Samples Determined by XRD\*

Sample	LTA (~125°C)	ASTM (750°C)	HTA (1000°C)	Slag(1300°C)
Absaloka	Quartz Pyrite Kaolinite Plagioclase Bassanite	Quartz Anhydrite Hematite	Anhydrite Magnetite Hematite Quartz Melilite Plagioclase Nepheline	Plagioclase Hematite Magnetite Quartz
Beulah-Low Sodium	Quartz Pyrite Kaolinite Bassanite	Quartz Hematite Magnetite Anhydrite	Anhydrite Pyroxene Magnetite Hauyne Hematite Quartz	Anhydrite Pyroxene Magnetite
Beulah-High Sodium	Quartz Bassanite Kaolinite Pyrite	Anhydrite Hematite Magnetite Quartz Melilite Hauyne	Anhydrite Melilite Magnetite Hematite Hauyne Quartz Corundum	Melilite Hauyne Nepheline Magnetite Quartz Corundum
Center	Quartz Bassanite Pyrite Kaolinite	Anhydrite Hematite Quartz	Anhydrite Hauyne Pyroxene Melilite Hematite Quartz	
Choctaw	Quartz Pyrite Kaolinite Bassanite Plagioclase	Anhydrite Quartz Hematite Magnetite Plagioclase Pyroxene	Anhydrite Hematite Quartz Magnetite Plagioclase	
Falkirk	Quartz Kaolinite Pyrite	Anhydrite Quartz Hematite Magnetite Melilite (trace)	Anhydrite Quartz Melilite Hematite Magnetite Hauyne	Melilite (Akermanite) Anhydrite Pyroxene Hematite
Gascoyne Blue- High Sodium	Quartz Kaolinite Pyrite Calcite Sodium Sulfate (trace)	Anhydrite Quartz Hematite Magnetite Nosean Melilite	Anhydrite Melilite Hauyne Quartz	Anhydrite Pyroxene Spinel Melilite Magnetite

Table II. Mineralogical Composition of Ash and Slag Samples Determined by XRD\*--  
Continued

Sample	LTA (~125°C)	ASTM (750°C)	HTA (1000°C)	Slag(1300°C)
Gascoyne Red- Low Sodium	Quartz Kaolinite Pyrite	Quartz Anhydrite Hematite Magnetite	Quartz Anhydrite Pyroxene Hematite Hauyne	(Amorphous)
Indian Head- High Sodium	Quartz Pyrite Kaolinite Bassanite	Anhydrite Quartz Hematite Nosean Melilite Hauyne Sodium Sulfate (?)	Melilite Hematite Anhydrite Hauyne Magnetite Pyroxene	
Pike	Quartz Pyrite Kaolinite	Anhydrite Quartz Pyrite	Anhydrite Hematite Melilite Anorthite Quartz	
San Miguel	Zeolite (Heulandite) Quartz Kaolinite Pyrite Bassanite Plagioclase	Zeolite Anhydrite Hematite Quartz Plagioclase (Anorthite) Melilite	Plagioclase (Anorthite) Hematite Quartz Magnetite Anhydrite	(Amorphous)

\*Minerals listed in decreasing order of peak intensities and occurrence.

metakaolin. No metakaolin was detected by XRD in ASTM samples perhaps due to its poorly defined crystalline structure. However, it is believed that the basic kaolinite components are present in an amorphous form in ASTM ash. With increasing temperature the collapsed kaolinite structure forms corundum ( $\gamma\text{-Al}_2\text{O}_3$ ). While mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and cristobalite ( $\text{SiO}_2$ ) have been reported to form from well-ordered kaolinites in bituminous coals at  $1000^\circ\text{C}$  (4) neither were observed in HTA samples. According to Grim (11), the absence of mullite suggests that the original kaolinitic structure was poorly defined. It has also been suggested by Grim (11) that the presence of impurities in the form of alkali ions, such as in lignites, retards the development of mullites and cristobalite. The mechanism for this is not fully understood.

The collapsed kaolinitic structure acts as a source or framework for several different aluminosilicate complexes formed in HTA and slag samples. Common minerals found are as follows: anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), pyroxenes ( $(\text{Ca},\text{Na})(\text{Mg},\text{Fe},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ ), melilites ( $(\text{Na},\text{Ca})_2(\text{Mg},\text{Fe},\text{Al})(\text{Si},\text{Al})_2\text{O}_7$ ), haüyne ( $(\text{Na},\text{Ca})_{4-8}(\text{AlSiO}_4)(\text{SO}_4)_{1-2}$ ), nosean ( $\text{Na}_3\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$ ) and nepheline ( $(\text{Na},\text{K})\text{AlSiO}_4$ ). At  $1000^\circ\text{C}$  aluminosilicates minerals form from solid-state reactions of kaolinitic material with cations derived from carbonates, oxides, or sulfates. Interstitial substitution of alkali cations occurs within the dehydrated kaolinite structure with increasing temperature due to thermal expansion. In some coals, particularly those high in sodium, these aluminosilicates are also seen in ASTM samples.

At  $1300^\circ\text{C}$  inorganics are in a liquid phase. Upon quenching some sample slags remain amorphous due to rapid cooling thereby inhibiting nucleation of elements preventing the formation of crystalline structures. Other samples recrystallized upon cooling forming previously existing and new aluminosilicate structures. Differences between sample slagging behavior can be traced to silica content of the raw coal. Samples high in silica, such as Gascoyne Red and San Miguel coals, formed amorphous slags upon cooling. Samples having relatively low silica contents such as Absaloka, Beulah High and Low Sodium, Falkirk and Gascoyne Blue coals, formed crystalline slags when cooled. Anhydrite and magnetite are still present at  $1300^\circ\text{C}$ .

Minor amounts of calcite ( $\text{CaCO}_3$ ) were detected in raw coal samples by SEM. XRD failed to detect calcite in LTA samples possibly due to extraction by ammonium acetate or because the amounts of calcite were below detection limits ( $\sim 5\%$ ). For the most part, calcium is supplied to the system by gypsum and organically-bound calcium. As previously discussed, calcium whether in the form of bassanite, calcite, or cations in LTA samples forms anhydrite in ASTM samples. In HTA samples calcium reacts primarily with dehydrated kaolinite forming aluminosilicates discussed under kaolinite reactions.

Quartz ( $\text{SiO}_2$ ) is stable throughout the ash samples at varying temperatures up to  $1000^\circ\text{C}$ . In slag analysis, quartz is not always present in crystalline form but forms an amorphous substance along with other compounds.

With increasing temperature quartz peak intensities in HTA samples decrease or disappear while various aluminosilicate peaks increase in intensity and number. According to Rindt et al (12) localized reducing areas are present within coal particles during combustion. In these areas, reactions between volatilized sodium and quartz occur forming sodium silicates (13). The sodium is fixed and not readily released on further heating.

Figure 1 displays a typical X-ray diffractogram sequence from LTA sample through slagging of the Beulah High Sodium lignite. Predominant peaks are identified according to the mineral phases present. Mineral transformations at higher temperatures are characterized by the presence of numerous aluminosilicate solid-solution series. Often several members of a particular solid-solution series have almost identical diffractogram patterns making identification by XRD difficult. When comparing several of these diffractograms there is little difference between LTA samples while ASTM, HTA, and slag samples are quite different. When comparing mineralogical differences to raw coal elemental compositions of various coals samples containing higher amounts of sodium tend to form aluminosilicates at lower temperatures ( $750^\circ\text{C}$ ) than samples high in calcium. High sodium coals such as Beulah

High Sodium and Gascoyne Blue develop complex silicates in ASTM samples and are known to be high fouling coals. Typical of such alumino-silicates in ASTM, HTA and slag samples are melilites, hauyne, nepheline, nosean and pyroxenes. Commonly these are minerals found in combustion fouling deposits of most lignites.

#### Concluding Remarks

The results of this study reflect the preliminary stage of investigation into the mineral phase transformations seen in low-rank coals. The original mineralogies of coals sampled do not vary a great deal. Quartz, kaolinite, pyrite, and bassanite are found in abundance in each LTA sample. Greater differences between samples are apparent at higher temperatures where complex alumino-silicates predominate. Perhaps this is a reflection of differences not so much in original mineral matter but in the total inorganic composition of the coal, specifically the presence of exchangeable alkali cations. The interactions of such organically-bound cations with crystalline inorganic phases in lignites account for differences in ashing and slagging behavior between coal samples (9).

The processes responsible for most reactions identified are oxidation, dehydration, sulfur fixation, solid-state interactions, vaporization, and recrystallization. Isolating specific reactions occurring in a multi-component system is difficult at best. Understanding the thermodynamics of mineral transformations is a necessity and will be pursued in future study. In addition, future studies isolating mineral pairs to observe phase transformations at various temperatures will support or refute results presented here.

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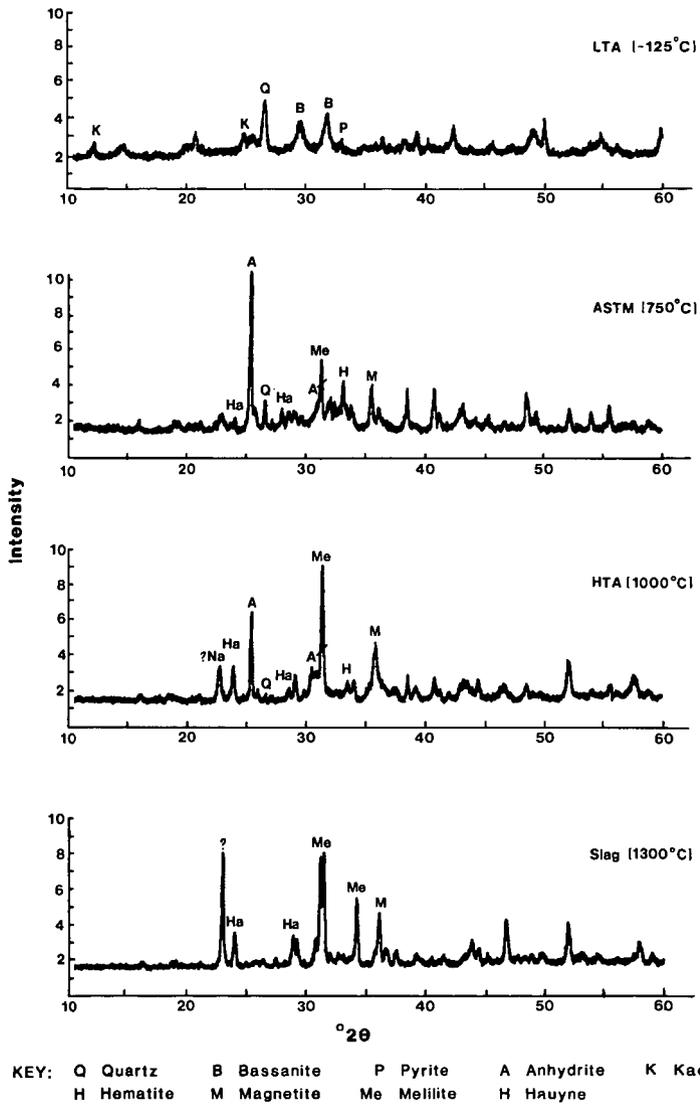


Figure 1. X-ray diffractograms of LTA, ASTM, HTA, and slag samples of Beulah high sodium coal.