10

High-Temperature Interactions among Minerals Occurring in Coal

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Minerals known to be present in the low temperature ash extracted from coals were heated in a microscope heating stage from 25° to about 1400°C. Mineral types were arranged in homogeneous fields where two fields shared a linear boundary or three fields were in contact at a point. Because of the known reactivity of calcite and pyrite, all specimens contained this pair. Clay minerals, kaolinite, illite and montmorillonite were used as the third component. Reaction temperature between calcite and pyrite is lowered by the presence of clays. Iron was observed to migrate into the clay domain after the formation of pyrrhotite from pyrite and oldhamite was observed forming between the domain of lime formed from calcite and the pyrrhotite.

Mineral impurities in coal are known to be primary contributors to the slagging and fouling of utility boilers, fly ash and bottom ash production as well as atmospheric pollution. They also produce undesirable effects in some parts of hydrogenation processes such as liquifaction and gasification (1,2,3). Despite a long history of investigation prompted by these observations, many questions remain unanswered.

Simple empirical relationships between fusion temperature of the furnace deposits and the mineralogy of coals have been proposed (4,5,6). More recently attempts have concentrated on a physico-chemical view of the problem comparing ash fusion temperatures with phase relations in three-component chemical systems (7,8). This method of attack has yielded some significant results, but at least some researchers (8) have questioned this approach, which is based

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on the assumption that these processes occur under conditions of equilibrium.

The aim of the research described here is to observe interactions between minerals known to occur in coals in the most direct fashion possible and in the simplest conditions consistent with causing the reactions to occur. It is considered that observation of simple mixtures of minerals observed to enter into reaction may make possible a better accounting of the processes by which slag and fouling deposits form in furnaces.

Experimental Methods

Isolation and Identification of Coal Minerals. Two coal samples, collected from different coal basins in the United States (see Table I), were subjected to low-temperature ashing as described by Gluskoter (9). This process avoids destruction of the minerals while oxidizing the organic portion of the coal. This ashing procedure occurs at a much lower temperature than that of the American Society for Testing and Materials (ASTM) method it is given the name of "low-temperature ashing" and generally abbreviated LTA. In formation of a mineral concentrate by LTA, a few changes are anticipated; some clays are reversibly dehydrated, and hydrated surfaces are reduced to the hemihydrate form (for instance gypsum is converted to bassanite). Because these changes are known in advance, due allowance can be made for them.

Table I. Coal Samples, Localities of Origin, and Analyses (all samples run-of-mine)

Seam: Illinois #6
Locality: St. Clair County, Illinois

Analysis:	9 mesh x 0 Raw	9 x 32 mesh Float	9 x 32 mesh Sink
Moisture (%):	5.31	5.44	2.55
Ash, ASTM (%):	32.86	7.10	68.05
Pyritic Sulfur (%):	2.46	0.76	5.08
Total Sulfur (%):	4.57	4.57	5.94
Heating Value (BTU/lb.):	9,039	13,248	3,574

Seam: Upper Freeport
Locality: Grant County, West Virginia

Analysis:	9 mesh x 0 Raw	9 x 32 mesh Float	9 x 32 mesh Sink
Moisture (%):	0.30	0.68	0.93
Ash, ASTM (%):	35.90	7.26	72.10
Pyritic Sulfur (%):	1.58	0.27	2.62
Total Sulfur (%):	2.18	1.06	3.00
Heating Value (BTU/lb.):	9,695	13,365	3,086

Mineral constituents of the LTA concentrates were identified by x-ray diffraction techniques. Illite, kaolinite, quartz and pyrite are ubiquitous in the mineral suites; calcite occurs in most concentrates. Many other minerals have been identified in coals but were not observed in these specimens.

Heating-Stage Microscopic Observations. Following the characterization of the mineral suites by x-ray diffraction techniques, each LTA concentrate was heated in a heating stage mounted on a microscope fitted for observation in vertically incident light. Concentrates examined in this way and the product phases are found in Table II.

Table II. LTA Samples and Heating Products

LTA Sample	T_{max} (°C)	Phases Identified
Upper Freeport raw	560	quartz, illite, pyrrhotite
	1410	quartz, mullite[a]
Upper Freeport 1.40 float	1031	quartz[b]
	1250	quartz[b]
Upper Freeport 1.40 sink	635	quartz, illite, pyrrhotite
	1150	quartz, pyrrhotite, illite[c]
Illinois #6 raw	880[d]	quartz, illite, pyrrhotite, oldhamite(?)
Illinois #6 1.40 float	625	quartz, illite, pyrrhotite, troilite(?)
	1370	quartz, pyrrhotite
Illinois #6 1.40 sink	920	quartz, illite, pyrrhotite, oldhamite
	1334	quartz, pyrrhotite, oldhamite

[a] XRD peaks occurred at the correct diffraction angles for mullite but were too weak to permit accurate intensity comparisons.

[b] The overall pattern was similar to the one for the illite-kaolinite pair heated to 1410°C, except that stronger peaks for quartz were found in the LTA XRD pattern.

[c] Peaks were detected at some of the diffraction angles for illite, but the intensities were not comparable with standard patterns; it is possible that these were relict peaks of illite as it began to alter.

[d] Another sample of Illinois #6 raw LTA was heated to 1421°C; it formed a hard, dark-colored glass at about 1400°C; this material could not be removed from the heating-stage crucible.

The heating stage is limited to inert atmosphere or vacuum operation. Therefore, reactions sensitive to atmospheric conditions, such as partial pressure of oxygen, cannot be studied. Furthermore, the extremely small particle size of the sample resulted in inability to observe changes occurring below the mount surface and to resolve the specific minerals entering into a reaction at any point in the run.

These difficulties were addressed by obtaining samples of the minerals identified in the LTA concentrate before heating, grinding them to approximately the same size consist as the concentrate, and mounting them in separate domains in the heating stage crucible. The geometry of these mounts is shown in Fig. 1.

Experiments with Known Minerals

Experiments with Individual Minerals. Single mineral mounts in the heating-stage crucible yielded the expected products, that is, pyrite yielded pyrrhotite and troilite, calcite gave lime and carbon dioxide, and clays reacted under high temperature conditions to yield a silicate glass.

Experiments with Pairs and Triplets of Known Minerals. In these experiments, known minerals were ground and placed in the heating-stage crucible in separate domains as pairs or triplets of minerals. The pairs and triplets were heated and the behavior at their boundaries observed. Table III lists the minerals used in pair mounts and the reaction products obtained by heating.

Because the most reactive phases found in the experiments with pairs of minerals were clays, calcite, and pyrite, these were prepared in triplet mounts. In trials using either montmorillonite or illite with calcite and pyrite, a liquid formed at the mutual boundary of the latter pair at 600-650°C. Pyrite and calcite had, of course, previously reacted and this liquid therefore occurred between the product phases pyrrhotite and lime. Subsequent x-ray analysis showed the presence of pyrrhotite, lime, and oldhamite. In both instances, the temperature of this reaction was lower than that obtained in the pair mount of calcite and pyrite, 1140°C. When kaolinite was in the mount with calcite and pyrite, the same reaction occurred at 750-760°C. Though the mechanism by which the clays reduce the reaction temperature is not yet understood, the differences in reaction temperature with and without clay is considered significant.

The most obvious change in the clays themselves during these experiments was a darkening beginning with pyrite decomposition. This was more marked in the case of illite and montmorillonite. It is considered that in all these cases, the clay mineral structure was destroyed and possibly formed a silicate glass, much like those found in furnace slags but having, perhaps, less oxygen.

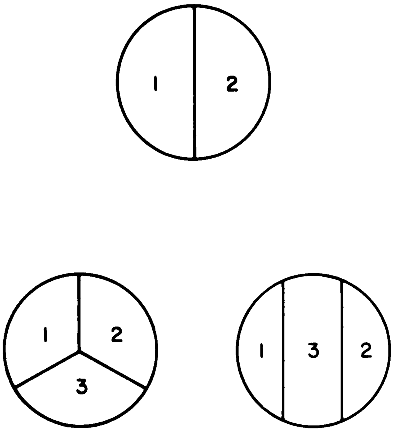

Figure 1. Geometric arrangement of mineral pairs and triplets used in the heating stage experiments and supporting experiments. In all triplet mounts, position 3 was occupied by a clay mineral.

Table III. Mineral Pairs and Heating Products

Mineral Pair	T_{max} (°C)	Products Identified[a]
Calcite-illite	1310	lime (CaO)
Calcite-kaolinite	1322	lime (CaO)
Calcite-montmorillonite	1285	(indeterminate)[b]
Calcite-pyrite	1253	lime, pyrrhotite ($Fe_{1-x}S$), oldhamite (CaS)
Calcite-quartz	1467	quartz (SiO_2), lime (CaO)
Illite-kaolinite	1410	mullite ($Al_6Si_2O_{13}$)
Illite-montmorillonite	662	(indeterminate)[b]
Illite-montmorillonite	1212	(indeterminate)[b]
Illite-pyrite	1519	pyrrhotite, troilite (FeS)
Illite-quartz	1450	quartz
Kaolinite-montmorillonite	1403	mullite (poorly-crystalline)[c]
Kaolinite-pyrite	1445	mullite
Kaolinite-quartz	1220	quartz
Montmorillonite-pyrite	1053	(indeterminate)[b]
Montmorillonite-quartz	1492	quartz
Pyrite-quartz	1571	quartz

[a] Only those products are listed which could be positively identified by XRD; no attempt is made here to deduce the composition of amorphous products.

[b] XRD patterns for these heating products did not match any standard pattern closely; attempts to match with computer routines produced results of low reliability.

[c] "Poorly crystalline" means that diffraction maxima were found corresponding to the indicated phase, but peaks were not sharp and did not have the correct relative intensities in all cases.

Supporting Experiments. To examine the effect of oxidizing and reducing atmosphere on these materials, graphite crucibles 10mm in diameter and 2mm deep were packed in the manner described above and heated in a furnace fitted to permit introduction of specified gases during heating. After heating, the samples were examined by scanning electron microscopy and energy dispersive x-ray spectroscopy (SEM/EDS) (Figure 2). Samples treated in this way are listed in Table IV.

In all these cases where pyrite was used with a clay, iron was found to have migrated from the iron sulfide into region that was originally clay. Elemental mapping showed the presence of iron to have completely pervaded the region formerly occupied by clay. In all mounts containing calcite and pyrite, the calcium and sulfur peaks were present in the region originally occupied by calcite and sometimes found in the region that had been pyrite-filled.

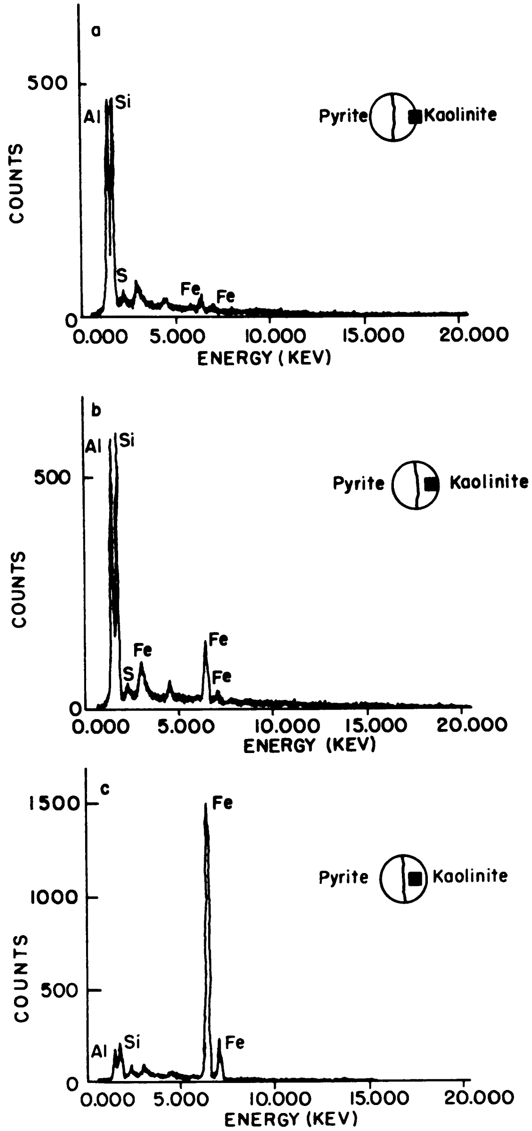

Figure 2. Energy-dispersive spectra from a pyrite-kaolinite mount heated to 1200°C. Locations of the spectra with respect to the sample are indicated by the small squares in the circles.

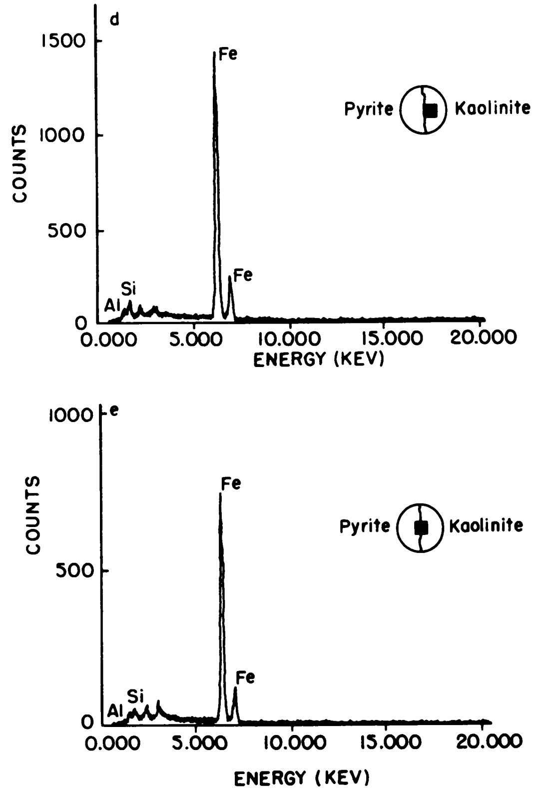

Figure 2. Continued.

Table IV. Subjects of Supporting Experiments

Assemblage	Atmosphere	T (°C)	Duration (min)
Calcite-kaolinite	inert	1400	60
Calcite-quartz	inert	1400	60
Pyrite-quartz	oxidizing	1200	30
Pyrite-quartz	reducing	1200	30
Pyrite-calcite	reducing	1200	30
Pyrite-kaolinite	oxidizing	1200	30
Pyrite-kaolinite	reducing	1200	30
Pyrite-montmorillonite	inert	800	15
Pyrite-montmorillonite	reducing	800	15
Py.-calc.-kao.	reducing	1200	30
Py.-calc.-mont.	inert	800	15
Py.-calc.-mont.	reducing	800	15

Note: The indicated temperature was the steady-state temperature for the trial. The indicated duration was the period of time for which that steady-state temperature was maintained.

Discussion and Conclusions

It is apparent that the phenomena described here are not complete processes terminating in equilibrium assemblages. The times of reaction are too short for many of the products of silicates such as clays and quartz to come to thermodynamic equilibrium at the new temperature. That this is indeed the case in operation of power-plant boilers is obvious from the consideration of the amount of glass found in furnace slags and fly-ash.

Illite and montmorillonite are similar in structure and differ slightly from kaolinite in this regard. The first two are composed of two silicon-oxygen layers per octahedral layer containing iron, magnesium and aluminum and in kaolinite the ratio of tetrahedral and octahedral layers is 1. In clays thermal modification occurs at lower temperature than silica because the bonds formed between the Al, Fe, and Mg atoms and oxygen are weaker than the Si-O bonds. Clays, therefore, are expected to be more reactive than the silica crystals. There is evidence of drastic structural modifications, if not vitrification, in the clay mineral domains during thermal treatment and that iron enters the region. Further inquiries are in progress to answer these questions.

Calcite appears largely inert at temperatures approaching 600°C in the presence of some of the clay minerals and inert until about 900°C in their absence. The cause of this fluxing is not well understood at this time, but investigations are planned to explain this behavior. At whatever temperature, the reaction observed is the decomposition of calcite to lime (CaO) and carbon dioxide. The extent to which carbon dioxide influences further reaction is not known but must be considered as an important step in a complete explanation.

Like calcite, pyrite is quite reactive and its thermal behavior is influenced by the presence of clay minerals. The initial reaction temperature of pyrite alone or in the presence of calcite alone is to produce pyrrhotite, ($Fe_{1-x}S$) and troilite (FeS). The loss of sulfur is obvious and continues over an appreciable temperature range.

The most important reaction products are those of the iron enrichment of the clay mineral residues, probably a precursor of the iron oxide and glass mixtures commonly observed in slags and fly-ashes, and the formation of the sulfide of calcium, oldhamite. Oldhamite is observed in all experiments where calcite and pyrite interact, whereas anhydrite is observed only where they have reacted in the presence of an oxygen-rich atmosphere. This behavior suggests that oldhamite, formed in the reducing part of a flame, is a necessary precursor to the formation of anhydrite.

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