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Mineral Matter Effects on Char Structural Evolution and Oxidation Kinetics During Coal Char Combustion

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Abstract

We report on recent investigations of the evolution of char structure during carbon burnout and the role of mineral matter in determining this structure. Char samples collected in a carefully controlled laminar, flame-supported entrained flow reactor have been characterized using a number of microscopy tools. Observations of the inorganic structure of chars produced at a variety of combustion conditions are coupled with *in-situ* optical measurements of the char particle population with an eye towards identifying the mechanism of mineral interaction and its effects on carbon burnout kinetics during pulverized coal char combustion. Preliminary results show a surprising amount of inorganic mineral in solid solution with the carbonaceous matrix. This intimate mixing of organic and inorganic constituents may affect reactivity by both blocking oxygen access to active carbon sites and influencing the microscopic carbon structure that evolves during combustion.

Introduction

Although most activities concerning the determination of coal char reactivity have focused on the reactivity of the carbonaceous organic matrix in the char, it is generally acknowledged that mineral matter can also play an important role. Most research efforts concerning mineral matter have focused upon ash formation and deposition with regard to boiler performance issues such as slagging/fouling behavior and its deleterious effect on process efficiency, and the corrosive behavior of specific mineral constituents. Towards that end, there have been numerous investigations of the physical mechanism and associated chemistry of fly ash formation [1,2]. However, the influence of mineral matter on the combustion behavior and reactivity of pulverized coal particles has not received as much attention. Historically, the primary research activities involving mineral matter have concerned the investigations of the catalytic effects of individual species [3,4,5]. Little effort has been devoted towards understanding the effects of mineral matter on the structural evolution and the oxidation rate of the char during combustion.

The distribution of mineral matter within the organic structure influences reactivity by affecting the number of active carbon sites as well as the pore structure that provides oxygen access to these sites. These effects are of particular importance in late-stage carbon burnout, when the char structure consists of small amounts of carbon in a predominately ash framework. The problems associated with carbon burnout in pulverized coal combusters have become more important recently, particularly with the implementation of staged, low-NOx burners, as this technology has lead to unacceptable carbon levels in ash [6]. With new processes, such as coal blending, and the increased use of "non-traditional" coal sources, descriptions of reactivity based on global Arhenius rate parameters may no

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longer adequate for design purposes and attention has necessarily turned towards more fundamental studies of carbonaceous materials from first principles. A necessary corollary to these studies is how the mineral distribution, chemistry, and structure affect both intrinsic carbon kinetics and the global char particle combustion kinetics.

Mineral Matter and Char Reactivity

The understanding of the origin, identity, and structure of most mineral species in coal is relatively advanced. Mineral matter in coal exists as both inherent, organically bound, atomically dispersed impurities and as adventitious mineral matter, which is less intimately associated with the coal and consists of coherent particle grains or layers [7]. The adventitious particles exist as either submicron included particles or larger extraneous mineral particles. [8,9,10,11] The schematic shown in Figure 1 illustrates the different types of mineral matter in coal, as well as some of the important interactions between mineral matter and the organic matrix.
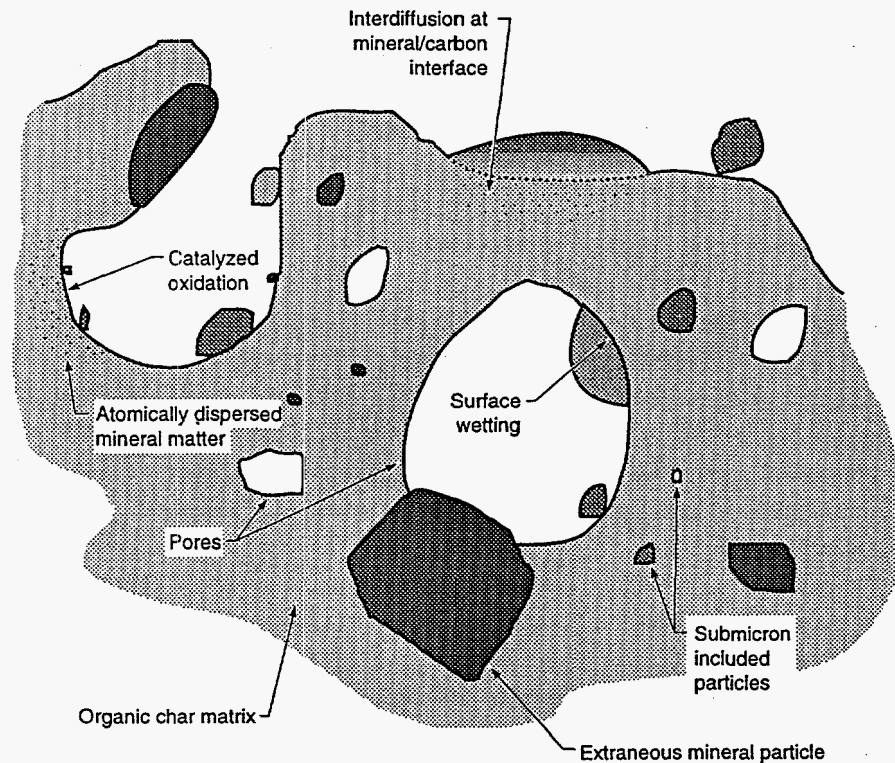

Figure 1   Schematic illustrating some important aspects of mineral matter distribution and mineral/organic interactions in coal char.

There have been a limited number of investigations of the influence of specific mineral species and their mode of occurrence on the evolving char structure during combustion.

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There appears to be some correlation between coal rank and the way in which the mineral matter distributes during char combustion. High-volatile bituminous coals are generally swelling coals, with little evidence of mineral matter segregation at the surface of the resulting char particle. Lignites show no appreciable shape change during combustion, and the surface of the char particle is covered with fine spherical droplets, rich in alkalis such as calcium [9,12,13]. Subbituminous and low-volatile bituminous coals yield structures between these two extremes, with no discernible marker for which type of structure will result for a given coal [9,10,11].

Mineral matter can inhibit combustion in the late stages by several mechanisms. First, an inorganic-rich layer on the char surface can act as a diffusion barrier restricting oxygen transport to the reacting surface. This is often referred to as an "unreacted core" model, where the diffusion through the ash layer can control global reactivity [14]. Second, mineral matter may simply occupy some volume of the particle, reducing carbon mass and carbon surface available per unit volume. This "dilution" effect reduces the global rate of reaction expressed on an external surface area basis. Finally, the inorganic material may directly interfere with the active carbon surface by wetting or encapsulation, totally restricting oxygen access.

Some researchers report that naturally occurring mineral matter has little effect on burning rates during the main portion of the char combustion process [15]. However, Vleeskens and Nandi [16] found a negative correlation between total burnout and coal ash content in drop tube experiments. Some recent work concerning the nature of carbon kinetics at high-carbon conversion strongly implies that ash-forming mineral matter can have significant, first-order effects upon carbon burnout in the later stages of combustion. Single-particle imaging studies of 100-200 µm char particles at a gas temperature of 1250 K provide compelling evidence of mineral effects during char combustion [17]. Results show that char combustion occurs in two stages: first, a rapid high-temperature combustion stage consumes a large fraction of the char carbon and ends with near-extinction (due to a drop in global reactivity), and second, a significantly slower final burnout stage occurs at lower particle temperatures. For most particles the late stages of combustion consist of the removal of the residual carbon from the inorganic ash framework in a very slow process referred to as "ash decarburization."

Recent attempts to model changes in reactivity with burnout have shown that both thermal deactivation of active carbon sites and ash inhibition effects combine to produce the long "tails" observed in carbon burnout curves that extend to high conversion [16]. A Carbon Burnout Kinetic (CBK) [16] model was recently developed to provide a description of the important chemical and physical phenomena in the high-conversion region by combining the single-film model of char oxidation with additional descriptions of thermal annealing, statistical kinetics, statistical densities, and ash inhibition in the late stages of combustion. Although in this work thermal annealing is assumed to be a first-order process in producing long burnout times, broad agreement with experimental observations obtained by Hurt et al [16] cannot be accomplished without the inclusion of an ash effect. Ash inhibition is modeled as an ash film that grows in thickness as combustion proceeds. The film is described using two parameters, a minimum film thickness and a film porosity. The

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predicted location of the near-extinction event is quite sensitive to the value chosen for the minimum film thickness, as this determines when combustion will shift to ash film diffusion control. The mean value of ash porosity which produced the best model fit to the experimental results for all coals investigated was 0.21, including low-volatile bituminous coals where there is no experimental evidence of an ash film. Whereas the existence of an ash film may be important in some coals (particularly those of low rank), and it can be used to fit experimental results, it is clear that it does not always correlate with observed char structures.

Although several observations imply that mineral matter can effect char reactivity, particularly at high extents of burnout, there is no consensus on the nature and extent of the effect. There are a number of individual observations of specific elements involving structure or catalysis. However, many of these results are primarily qualitative in nature. Limited effort has been devoted to integrating the varied observations into a thorough mechanistic picture of the evolution of mineral matter during char combustion. It is the goal of this work to attempt a unification of these individual issues, with a focus on the mechanism and kinetics of mineral interaction during pulverized coal char combustion.

Experimental

Recently, experiments have been performed with Pittsburgh #8 (PSOC1451), a high-volatile A bituminous coal. The elemental and mineral content of this coal is shown in Table 1. Pittsburgh #8 is an Eastern U.S., moderate-sulfur coal with which Sandia has significant experimental experience [19]. Particles in the 75 - 106 μm size range (150-200 mesh) were burned in an entrained flow reactor in a 12 mole-% post-flame oxygen concentration. Three different reactor temperatures, produced by varying the CH_4/H_2 fuel and O_2/N_2 oxidizer flows to the laminar, multi-element diffusion flamelet burner, were used to investigate the effect of temperature on mineral behavior. The gas temperatures in the char combustion stage of the burner (subsequent to devolatilization) for the low, medium, and high temperature environments were 1450-1550 K, 1550-1700 K, and 1700-1850 K, respectively. The reactor is equipped with an optical pyrometer that allows *in situ* measurements of particle size, temperature, and velocity [19]. A set of optical data was acquired for each reactor condition at a number of particle residence times. In addition, char particles were collected for both microscopic and laboratory analysis using a helium-quench, iso-kinetic sampling probe.

The collected coal chars were analyzed using several microscopic techniques. Whole chars were examined using a field-emission scanning electron microscope (FESEM), model JEOL 6400F, equipped with an Oxford Energy Dispersive X-ray Spectroscope (EDS) for chemical speciation. To view char particle cross-sections, the collected char was embedded in an epoxy, metallographically polished, and examined in the FESEM. To prepare samples for high-resolution transmission electron microscope (HRTEM) imaging, the coal chars were ground, placed on a carbon grid, and examined with a Phillips Model CM30 microscope, similarly equipped with an EDS, operating at 300 kV. The particle structure is examined in the vicinity of the optically thin edges of the ground particles.

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Table 1
Elemental and Mineral Content of Pittsburgh #8 (PSOC 1451)

Proximate Analysis (wt-% daf)		Mineral Content (wt-% of ash)	
Carbon	85.14	Si	58.2
Oxygen	5.542	Al	27.7
Hydrogen	8.66	Ti	1.2
Nitrogen	1.79	Fe	7.0
Sulfur	1.73	Ca	2.7
		Mg	0.73
Ash	10.95	K	2.0
		Na	0.34

Results and Discussion

Table 2 summarizes the measured mean particle temperatures, T_p, diameters, D_p, and mass loss, m/m_0 for each reactor temperature condition. Measurements of mean particle temperature and diameter at the earliest sampling height (6.4 cm) are not possible because this reactor location often corresponds to the end of coal devolatilization, and the luminosity produced by volatiles combustion interferes with the optical pyrometer. Note that the temperature decrease as a function of height in the reactor increases with increasing reactor temperature, and is much larger for the high temperature condition. Moreover, the change in char mass loss along the length of the reactor (i.e., char mass divided by initial coal mass, m/m_0, relative to its value at 6.4 cm) is noticeably less for the high-temperature condition than for the other two. This may imply that the rate of carbon burnout in the high-temperature condition is slower than for the others, or simply be a reaffirmation of slower oxidation kinetics at large extents of burnout. To correlate burnout-induced changes in combustion behavior with char and mineral structure, we choose to focus upon the chars collected at 6.35 cm and 25 cm to maximize observable transformations occurring in the char structure during combustion.

Figures 2 shows micrographs of char samples taken at the 6.4 and 25.4 cm heights at the low and high temperature reactor conditions. The chars have a cenosphere structure, with relatively thick, porous walls. The pores increase in size at longer residence times, indicating oxidation within the char structure. At the earliest sampling location, the char shows a large amount of fine precipitate on the surface of the char. This precipitate does not exist on the raw coal particles, and is formed during devolatilization. EDS spectral analysis of the precipitate from the polished sample shows that it is predominately aluminum and silicon, as shown in Figure 3. At longer residence times, under both reactor temperature conditions, the precipitate disappears. We speculate that the material is diffusing into the carbonaceous char matrix as the particle heats up. Interestingly, the surface structure on the nascent chars is not present in a small radius around the surface pores. This phenomenon may be due to a local surface temperature effect near the pore entrances, resulting in higher local temperatures and diffusion into the char matrix. The presence of this surface precipitate may serve to retard oxidation by restricting access to the char surface like an ash film, but since the char is in the early stages of combustion, this

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effect is unlikely. This is not a consideration at later combustion times because the precipitate disappears from the surface.

Table 2
Temperature, Diameter, and Mass Loss of Char Particles

	Reactor Height (cm)	Residence Time (ms)	Gas Temp (K)	Tp (K)	Dp (μm)	m/m_0
Low Temperature Condition	6.4	50	1685			51.9
	12.7	78	1668	1714	114.5	
	19.1	103	1630	1671	103.4	
	25.4	127	1577	1579	97.6	20
Medium Temperature Condition	6.4	47	1682			45.2
	12.7	72	1627	1800	98.1	
	19.1	95	1575	1710	99.7	
	25.4	117	1519	1609	99.2	17.3
High Temperature Condition	6.4	45	1835			32.5
	12.7	68	1767	2021	108.9	
	19.1	89	1694	1829	106.0	
	25.4	109	1623	1665	99.0	16.8

Observations of the polished char cross-sections show the porous nature of the cenospheric char walls in more detail. Again, both the total number of pores and the average pore size increase with increasing residence time. Elemental analysis of the cross-sections show several large included mineral particles that are primarily aluminum and silicon. However, the elemental mapping of the surface also shows a noticeable amount of dispersed mineral matter (approximately 2 to 5%) that appears to be in the char matrix. Small mineral particles are also present within many of the interior pores. These particles, also shown in Figure 3, are primarily composed of aluminum and silicon. This phenomenon is similar to the calcium spheres seen to appear on the surface of lignite char particles [9,13]. The fact that these mineral particles appear on the interior pore surfaces of the Pittsburgh #8 char implies that a significant amount of oxidation is occurring inside the char particle, whereas lignites generally burn in the diffusion-limited regime [19] and therefore will have limited internal oxidation. SEM analysis of both the whole char particles and the cross-sections show little evidence of a macroscopic ash film.

High resolution transmission electron microscopy of the chars show mineral matter, primarily aluminum and silicon, in solid solution within the carbonaceous matrix at levels of approximately 2 to 5 % of the total local mass. This atomically dispersed inorganic does not appear in the raw coal. One possible hypothesis is that the chars containing less mineral matter have burned out first, skewing the observations toward those particles that contain more. However, these solid solutions are present in samples obtained at the earliest sample residence time, just subsequent to devolatilization and before significant char combustion has occurred. It is difficult to imagine that any particles have achieved significant burnout at this location. An alternate hypothesis is that this mineral matter becomes incorporated during combustion by melting and diffusing into the particle. This

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diffusion may occur as the mineral on the surface melts as the char particle heats up, creating a concentration gradient between the surface and the interior of the particle. The presence of iron, a known ash fluxing agent, in significant amounts in this coal may serve to enhance this effect.

Analysis of the area around interior pore surfaces shows that the amount of inorganic matter in solution increases toward the pore wall. Clearly, the area around the pore will be enriched in minerals as the carbon burns out leaving the mineral behind. Indeed, this is how macroscopic ash films, consisting of larger included inorganic particles, are considered to evolve. The larger surface concentration of inorganic matter in solution will act as both a microscopic ash film, blocking oxygen access to active carbon sites, and as a diluent, reducing the available carbon per surface area in the char.

The HRTEM images also show varying amounts of turbostratic crystallinity development within the carbonaceous matrix, as shown in Figure 4. This increase in crystalline order has been previously shown to correspond to a decrease in char reactivity, often termed thermal deactivation [20,21,22]. The chars burned at the low temperature condition show a dramatic change in order between the two collection locations. At high temperature, there is little change between the two samples. In addition, the char collected at 6.4 cm under the high temperature condition looks similar to the char collected at 25.4 cm under the low temperature condition. While the extent of carbon thermal annealing is known to increase with both temperature and residence time [21,23], the presence of inorganic matter in solution in and around this turbostratic structure may affect both the extent of ordering in the carbon matrix and the carbon reactivity directly. This interaction could occur in two ways: individual mineral species may act as a pinning agent, restricting the growth of individual crystallites, or mineral species may act as a catalyst in promoting order. Whereas the second potential influence of mineral matter on carbon ordering would clearly reduce the char reactivity, the net effect of the first postulated influence ("pinning" effect) is unclear, because the same molecular strain from the mineral particle that prevents carbon ordering may also resist penetration of oxygen into the carbon matrix. Our present measurements cannot distinguish between these potential effects of mineral matter on carbon ordering and molecular-level reactivity.

Conclusions

Preliminary results of this study indicate several ways in which inorganic mineral matter can interact with the carbonaceous matrix to effect char reactivity. The most surprising of these is the amount of inorganic mineral matter in solid solution within the carbonaceous matrix. This atomically dispersed inorganic can affect reactivity by both blocking access to carbon active sites and reducing the available carbon per surface area in the char. In addition, the inorganic atoms may possibly be affecting the process of carbon turbostratic crystallite growth and therefore loss of reactivity by thermal annealing. No samples investigated show any evidence of an macroscopic ash film forming at the char surface. However, there is evidence of enrichment of the inorganic in solid solution around individual interior pore surfaces, leading to a microscopic "ash-rich film."

The underlying mechanisms behind many of the experimental observations presented in this paper remain uncertain. Towards that end, experiments are continuing with coals of similar rank and carbon content, but which vary in the extent and specific chemical content of mineral matter. In addition, coals of different rank (e.g. lignites or high-volatile bituminous) will be investigated.

Acknowledgments

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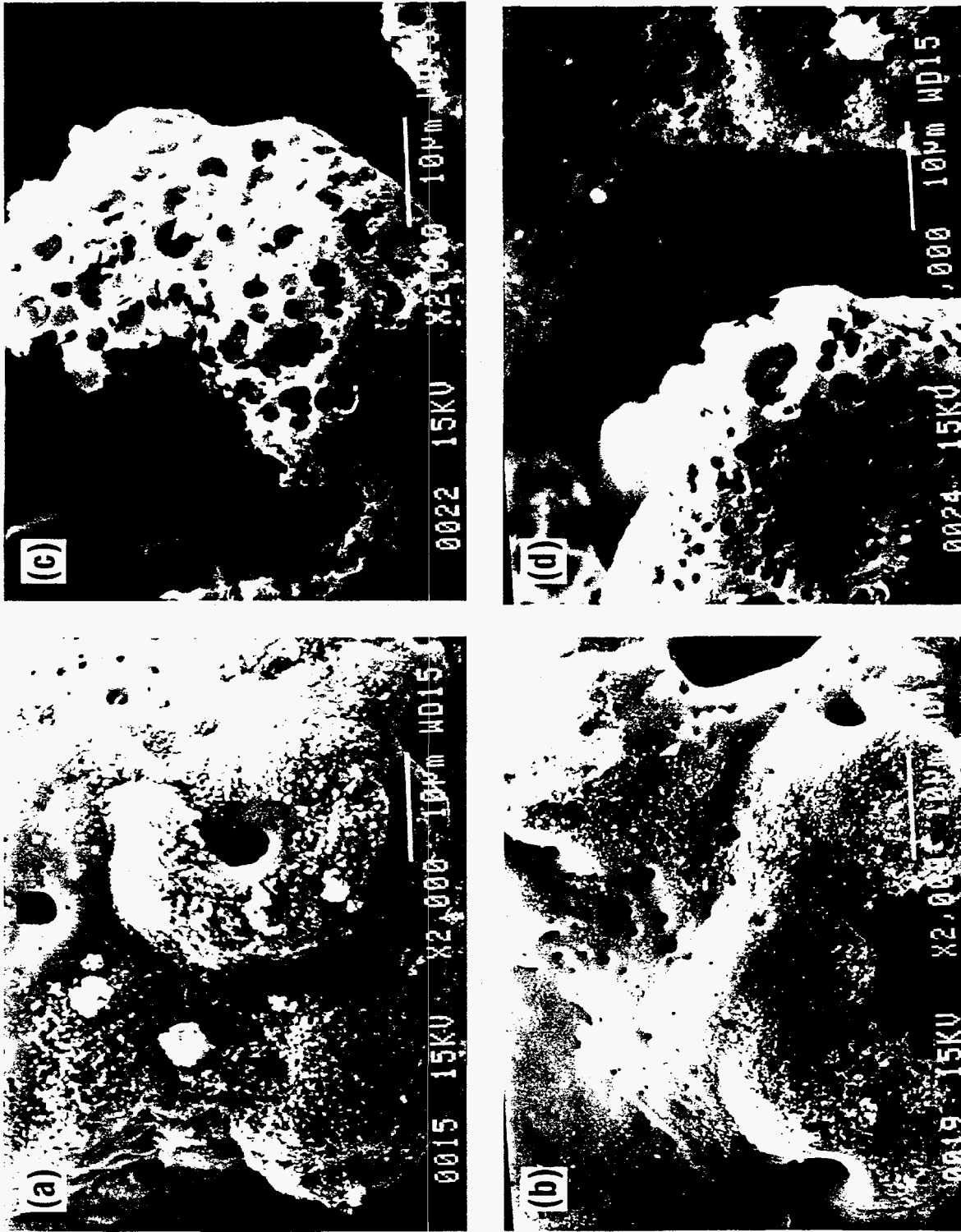
Figure 2. SEM micrographs of partially combusted Pittsburgh #8 char samples for (a) 6.4 cm at the low temperature condition (b) 6.4 cm at the high temperature condition (c) 25.4 cm at the low temperature condition and (d) 25.4 at the medium temperature condition. Photo magnification is 2,000X.
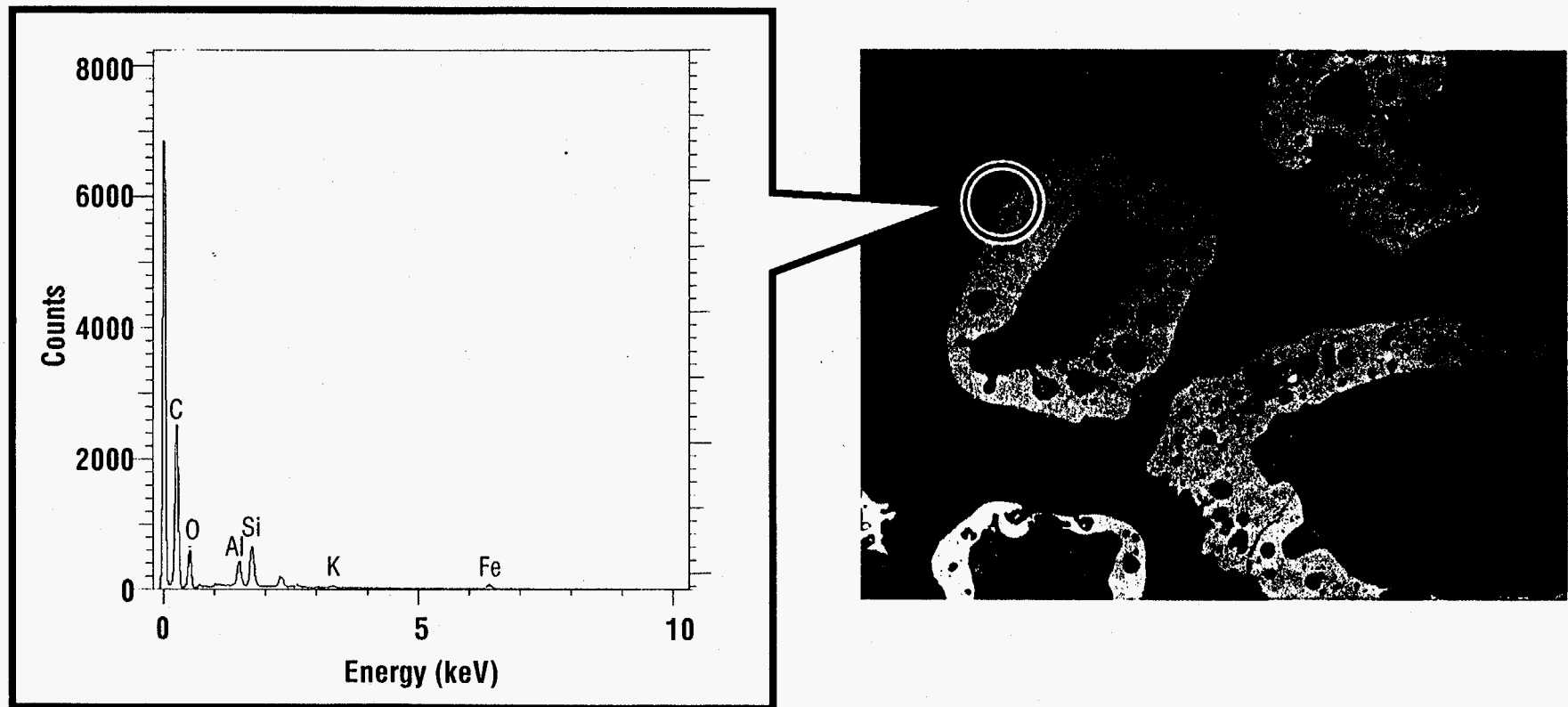
Figure 3. SEM micrograph of a cross-section of a partially combusted Pittsburgh #8 char sample collected at the low temperature reactor condition. An EDS spectra of the fine precipitate (shown in the circled area) indicates that it consists primarily of aluminum and silicon. Some of the small mineral particles inside the pores are also visible.
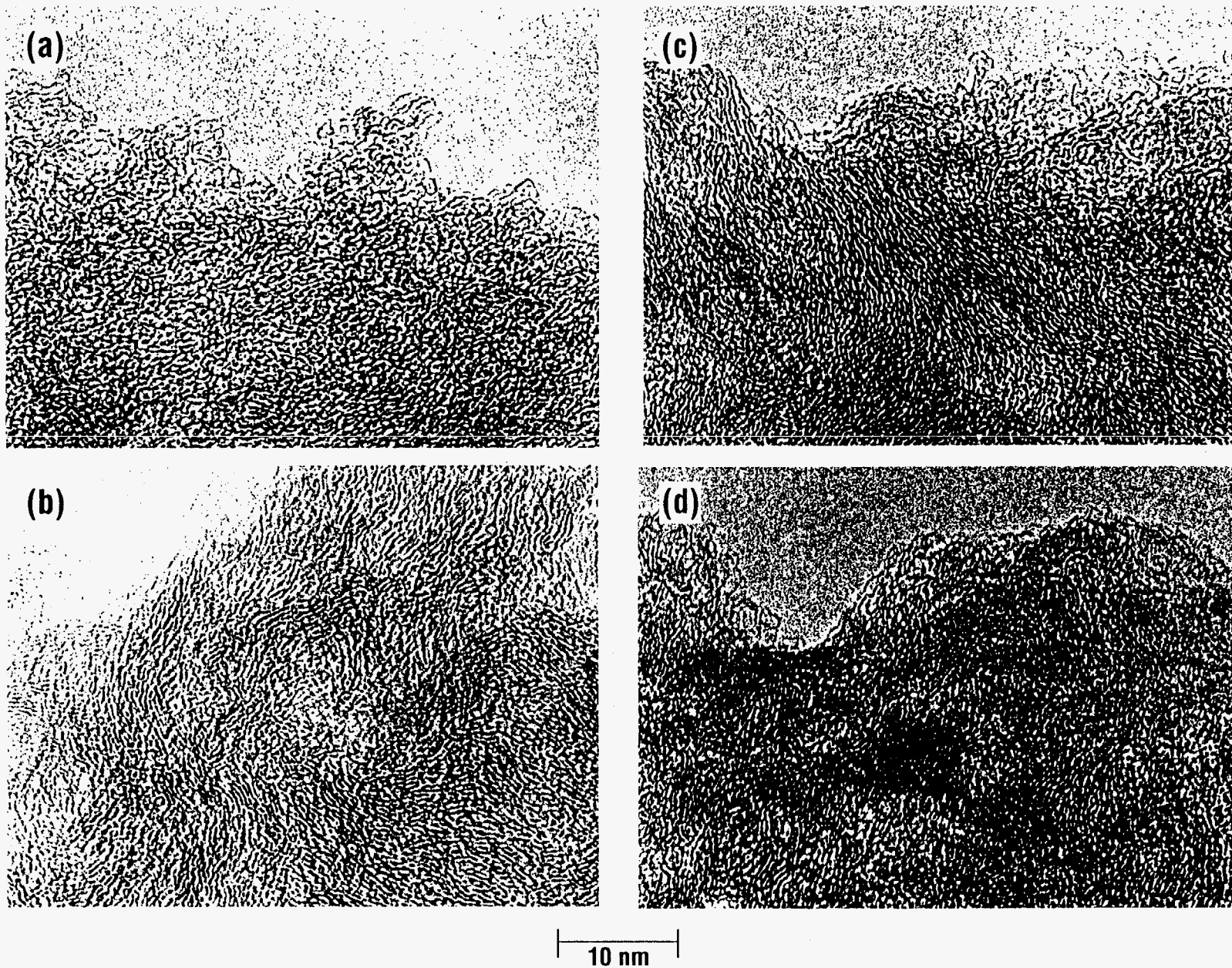
Figure 4. HRTEM fringe images of partially combusted Pittsburgh #8 char samples for (a) 6.4 cm at the low temperature condition (b) 6.4 cm at the high temperature condition (c) 25.4 cm at the low temperature condition and (d) 25.4 cm at the high temperature condition. Photo magnification 2,000,000X.

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