

emissive factors less than 0.3 (9). Figure 3 compares the combustion reactivities of the suite of residual carbon samples to those of various laboratory-generated chars in the early-to-intermediate stages of combustion (20 - 60% char carbon conversion). To facilitate direct comparison, char combustion rates are presented at a common oxygen concentration of 6% and a gas temperature of 1500 K. The laboratory char data in Fig. 3 includes a set of previously published oxidation rates for a suite of ten U.S. coals of various rank (4). Char reactivity is seen to be a strong function of rank, represented here by the dry, ash-free carbon content of the parent coal. At any given rank the residual carbon samples are much less reactive than the laboratory chars by factors of 2 to 7. Also, in each case where chars were available from the same parent coal, the residual carbon samples are seen to be much less reactive (see Fig. 2). The residual carbon materials were also found to be significantly less reactive than the laboratory-generated chars in 7% oxygen at 500 - 700 °C, as determined by thermal gravimetric analysis.

**Physicochemical properties:** Carbon dioxide surface areas of the residual carbon sample investigated here range from 93 to 188 m<sup>2</sup>/g-organic-matter (on a dry, ash-free basis) and are roughly comparable to the areas of laboratory chars in the early and middle stages of combustion (8). The residual carbon samples have hydrogen to carbon ratios of 0.2 and 1.2 wt-% and oxygen to carbon ratios of 2 - 6 wt-%, also comparable to those of a variety of laboratory-generated chars in the intermediate stages of combustion (8).

**Carbon structure:** Fig. 4 shows two selected micrographs (HRTEMs); one of Illinois #6 char in the intermediate stages of combustion, after 72 msec residence time and a carbon conversion of approximately 45%, and one of Illinois #6 residual carbon. The images represent typical structures based on examination of at least ten fields for each sample. Individual graphitic layers are easily discernible in the images, often in parallel groupings with the nominal interlayer spacing characteristic of graphitic carbon, 0.34 nm. Curved structures are present in both images, as has been observed for other carbon materials (11). Indeed, there is evidence that curved structures are thermodynamically favored for graphitic carbon units below a certain size — flat graphitic layers of small size would necessarily possess high-energy dangling bonds at the edges (11). Fig. 4 clearly shows that the residual carbon samples possess a higher degree of crystalline order than the laboratory-generated chars at 72 msec residence time. The residual carbon sample in Fig. 4b shows numerous crystallites with stacking depths of 3 - 5 nm, or approximately 10 graphitic layers, and dimensions parallel to the basal planes of up to 10 nm.

#### DISCUSSION AND CONCLUSIONS

Despite the complexity of the boiler environment and the wide variety of boiler operating conditions and fuels examined here, the residual carbon samples, as a class of materials, exhibit consistent and unique properties. Particularly noteworthy is their low combustion reactivity relative to laboratory-generated chars in the early-to-intermediate stages of combustion. Here we attempt to relate the low reactivities to some measurable physicochemical property or properties of the residual carbon samples. In general, the high-temperature reactivity of a carbon material to oxygen is determined by 1) the amount of internal surface area available for reaction, 2) the pore structure which provides access to the particle interior, 3) the degree of encapsulation of carbon by mineral matter, 4) the intrinsic reactivity of the internal surfaces, governed by the chemistry and crystalline structure of the organic matrix and by the catalytic action, if any, of inorganic impurities [12]. The material characterizations performed provide some information on each of these factors and suggest that factor 4 is the likely explanation for the low reactivity of residual carbon.

High resolution TEM shows that residual carbon can possess a much higher degree of crystalline order than the laboratory-generated chars. The observed increase in order is likely the result of thermally induced lattice rearrangement (pregraphitization), possibly promoted by the oxidative removal of carbon. The importance of pregraphitization or "thermal annealing" on char reactivity has been noted by a number of researchers [13,14]. A recent study [15] has shown that a similar degree of turbostratic crystalline order is developed in coal chars over the course of 100 msec of combustion at particle temperatures of 1800 K. Pregraphitization and oxidation have similar time constants and thus occur to a large extent simultaneously under the conditions relevant to pulverized coal combustion. Because increased crystalline order in carbons is generally accompanied by a loss of reactivity due to a reduction in the number of reactive edge sites and basal plane defects, the low combustion reactivity of the residual carbon samples is not surprising.

Finally, we should consider what the residual carbon properties and reactivities may tell us about the combustion process in pulverized coal fired boilers. The boiler environment appears to induce significant crystalline order in chars, thereby reducing their oxidation reactivity relative to the chars formed in the laboratory. The primary differences between the two environments are (1) the much longer residence times in the boiler (approx. 1 sec vs. 70 msec), which leads both to more severe heat treatment and much higher extents of oxidation (> 99% vs. 20-60%) and (2) differences in peak particle temperature (1800 - 2400 K in boilers [16] vs. 1800 - 1900 K in the laboratory). The reactivity differences may also be influenced by differences in particle heating rates, although these are believed to be roughly similar in the two environments. The bulk of the residual carbon has been severely heat treated and oxidized — it is not a fraction of the feed that has bypassed high temperature regions due to poor mixing. Recent studies [8] have shown that subjecting the laboratory chars to further combustion to high conversions (> 80%), leads to loss of reactivity and near-extinction of the oxidation reaction. Low reactivities have thus been observed for highly reacted, highly heat-treated residues from both laboratory and commercial-scale combustors. This result implies that char combustion cannot be accurately modeled assuming a reactivity that is

phenomenon affecting the latter stages of combustion, and accounting for deactivation may be key to making more accurate predictions of unburned carbon levels in fly ash.

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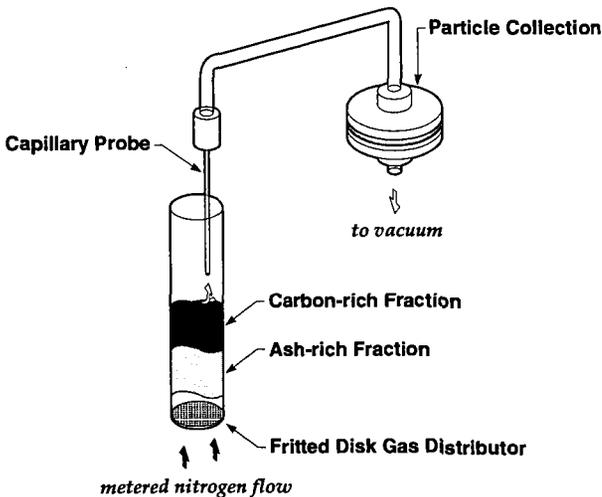


Figure 1. Residual carbon extraction by incipient fluidization.

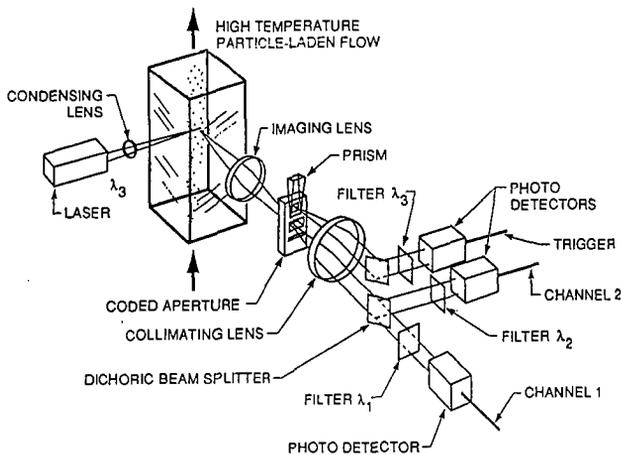


Fig. 2 The laminar flow reactor and optical diagnostic used for in situ measurement of particle size, temperature, velocity, and emissive factor.

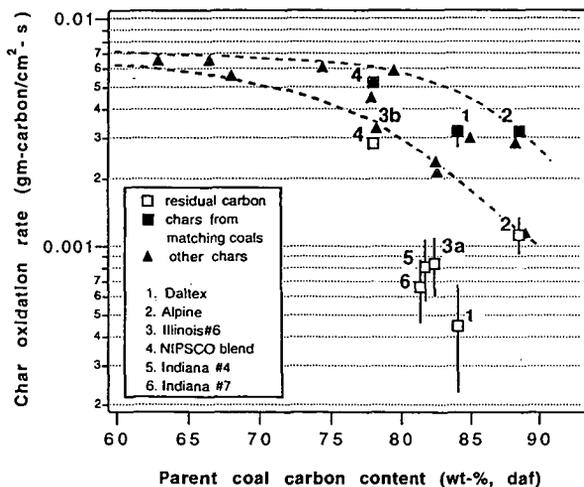
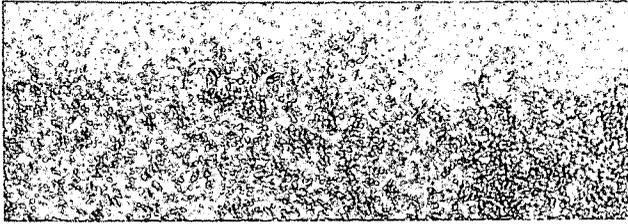


Figure 3 Combustion rates of various chars and residual carbon samples as a function of the carbon content of the parent coal. Gas temperature 1500 K; oxygen concentration 6 mol-%. Dashed curves indicate the range of reactivities observed for laboratory-generated chars at low-to-intermediate carbon conversion. Samples 3a and 3b both originate from Illinois #6 coals, but from two separate sources.

a.



b.



Figure 4 High-resolution transmission electron fringe images of Illinois #6 chars with different combustion histories. a) char samples from Sandia's high-temperature entrained flow reactor after 72 msec of combustion in 12 mole-% oxygen, b) residual carbon from commercial-scale pulverized-coal fired boiler. Magnification 2,000,000x.