

FUNDAMENTAL STUDY OF LOW-NO<sub>x</sub>  
COMBUSTION FLY ASH UTILIZATION

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## **ABSTRACT**

The objective of the current work was to investigate the oxidation reactivity of fly ash carbons, using thermogravimetric analysis techniques. Good measures of the oxidation reactivity of fly ash carbon were the critical temperature ( $T_{cr}$ ) and the late burnout temperature ( $T_{late}$ ). The lower the critical temperature of the fly ash carbon, the more reactive the sample. By contrast, the higher  $T_{late}$ , the less reactive the fly ash carbon. The difference between  $T_{cr}$  and  $T_{late}$  provided information about the reactivity distribution and was mainly dependent on fly ash carbon content (Loss-On-Ignition - LOI). Fly ash carbons having different origins, some from lower rank coals and some from higher rank coals had slightly different reactivities. Class C fly ash carbons from low rank coals were more reactive than the typical class F fly ash carbons from higher rank coals. The reactivity parameters did not, however, provide any additional ability to predict the suitability of a given ash for use in concrete.

## INTRODUCTION

Unfortunately it is practically impossible to avoid loss of carbon in the fly ash produced from any commercial coal combustor. The content of carbon in ash generally became higher after so called “low-air” burner retrofits. In current commercial practice, this carbon loss is of concern mainly because of its effects on ash reuse, as opposed to fuel heating value loss. The more we know about the fly ash carbons, the easier it will be build up models for determining acceptable carbon levels in fly ash.

The fly ash carbon content and its nature determine the suitability of a particular ash for its utilization in concrete applications. The inorganic part of coal fly ashes has been reported as being mostly non-active inert in concrete mixtures though this fraction contains minerals of value as pozzolans. The main focus of our work has been the carbons, which originate from the organic fraction of coal. These carbons strongly influence the important air entrainment property in concretes. Our previous work showed that the amount of carbon (LOI) was not the only parameter that determined the suitability of fly ash for concrete mixture. In addition, the accessibility, surface area and polarity of the fly ash carbon all played key roles.

A measurable fly ash carbon characteristic is its oxidation reactivity. There is no obvious direct tie between the carbon oxidation reactivity and suitability of the fly ash as a pozzolanic agent. It is, however, the case that high carbon content can rule out use of certain pozzolanic ashes, for reasons of poor air entrainment. Moreover, since the absolute amount of carbon has proven inadequate as a predictor, other simply measured predictors have become of greater interest. In this study, we sought to establish whether fly ash carbon oxidation reactivity could predict its suitability in terms of air entrainment. The existence of an extensive sample bank of commercial fly ash samples provided a unique opportunity to study the reactivity characteristics of unburned carbon in ash.

## EXPERIMENTAL

Over 50 fly ashes from different commercial boilers, located throughout the US, were examined. These fly ashes had LOI values in the range from 0.2 wt % to 66 wt %. Both class C and class F fly ashes were represented in the sample bank.

A TA Instrument 951 Thermogravimetric Analyzer (TGA) was used for thermogravimetric examination of the fly ash samples under low temperature air oxidation conditions. The mass loss associated with oxidative loss of carbon was tracked as a function of temperature and time. In order to keep mass and heat transfer conditions approximately the same in different experiments, more or less constant volumes of fly ash sample were used on the sample pan. The sample mass was about 20 mg for most experiments and decreased to 8-9 mg for high carbon content samples (LOI 66 wt %).

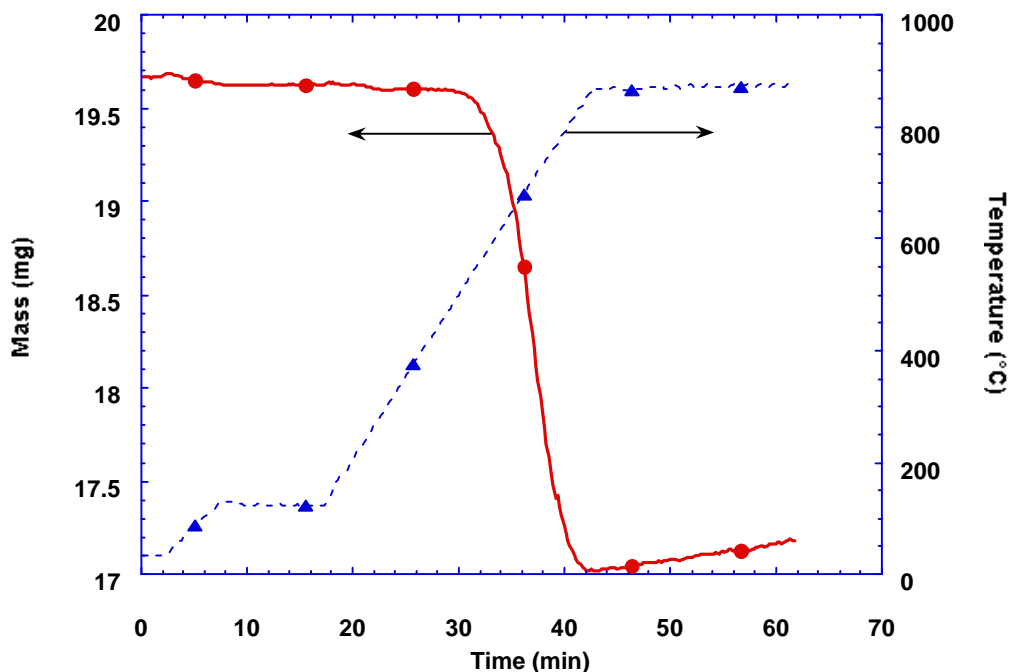
Thermogravimetric analysis requires care in the positioning of the sample temperature measurement thermocouple above the sample pan. This requirement stems from the quite high (up to 50 degrees) radial and axial temperature differences which may exist in the TGA furnace. Small thermocouple positioning differences can significantly affect the temperature readings. In order to get consistent results care was taken before each run to install the thermocouple as close as possible to the sample pan. After a set of four tests with different fly ash samples, a calibration test was performed to establish reproducibility. Two calibration materials, a selected fly ash and calcium oxalate hydrate ( $\text{CaC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ ) were used in order to check the performance of the thermocouple and TGA balance. The results of typical calibration tests are given in Table 1. In the case of the fly ash standard, the critical and late temperatures should all be constant. Likewise, the three decomposition temperatures for the calcium oxalate hydrate should all be the same. The above results suggest that the temperature measurements have an uncertainty of just few degrees at low temperatures, increasing to 16°C at the highest temperatures. Generally speaking, it is unwise to ascribe too much significance to differences of  $\pm 10^\circ\text{C}$  in  $T_{\text{cr}}$  or  $T_{\text{late}}$  values, based upon single experiments. In many cases, replicate experiments were performed. In this case, differences of a few degrees in mean values of  $T_{\text{cr}}$  and  $T_{\text{late}}$

could be significant. In this study, no use needed to be made of results involving only small differences in  $T_{cr}$  and  $T_{late}$ .

**Table 1. Calibration tests for TGA reproducibility.**

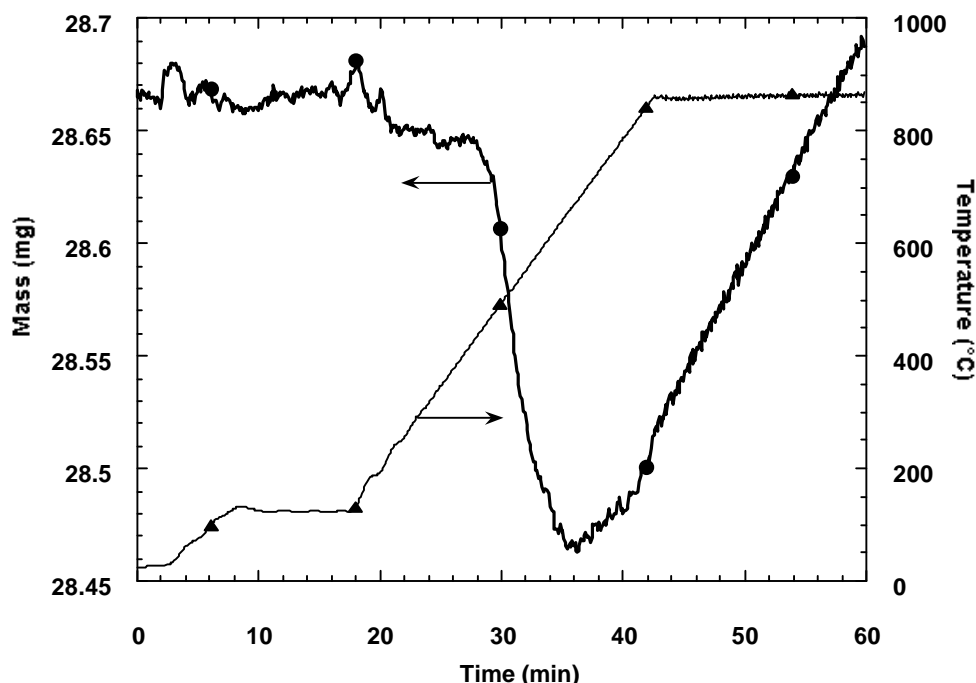
<b>Sample</b>	<b>Critical temperature (°C)</b>	<b>Late temperature (°C)</b>	
<b>Test Fly Ash - run 1</b>	591	798	
<b>Test Fly Ash – run 2</b>	591	790	
<b>Test Fly Ash – run 3</b>	602	782	
<b>Test Fly Ash – run 4</b>	596	789	
	<b>Temperature H<sub>2</sub>O max peak (°C)</b>	<b>Temperature CO max peak (°C)</b>	<b>Temperature CO<sub>2</sub> max peak (°C)</b>
<b>CaC<sub>2</sub>O<sub>4</sub>·xH<sub>2</sub>O</b>	155	471	695
<b>CaC<sub>2</sub>O<sub>4</sub>·xH<sub>2</sub>O</b>	157	475	704
<b>CaC<sub>2</sub>O<sub>4</sub>·xH<sub>2</sub>O</b>	158	472	699

Figure 1A shows a typical temperature profile and the weight loss curve for a class F fly ash with an LOI value 14.6 wt percent. The data set on Figure 1A is from the fly ash 3 in our sample bank. The expected loss of carbon mass is seen to start at a temperature just below 600 °C, and concludes at near 800 °C. The mass gain at the end of the experiment is presumably not associated with processes involving the carbon, which should all be burned off by that point. It probably reflects, instead, a small amount of oxidation of the inorganic species present in fly ash. This sort of oxidation naturally defines some uncertainty in LOI determination. In this particular case, the uncertainty is around 0.5 wt %, for a sample with a nominal LOI of 14.6 wt %.



**Figure 1A. Typical TGA weight loss and temperature curves for class F fly ash carbon reactivity characterization.**

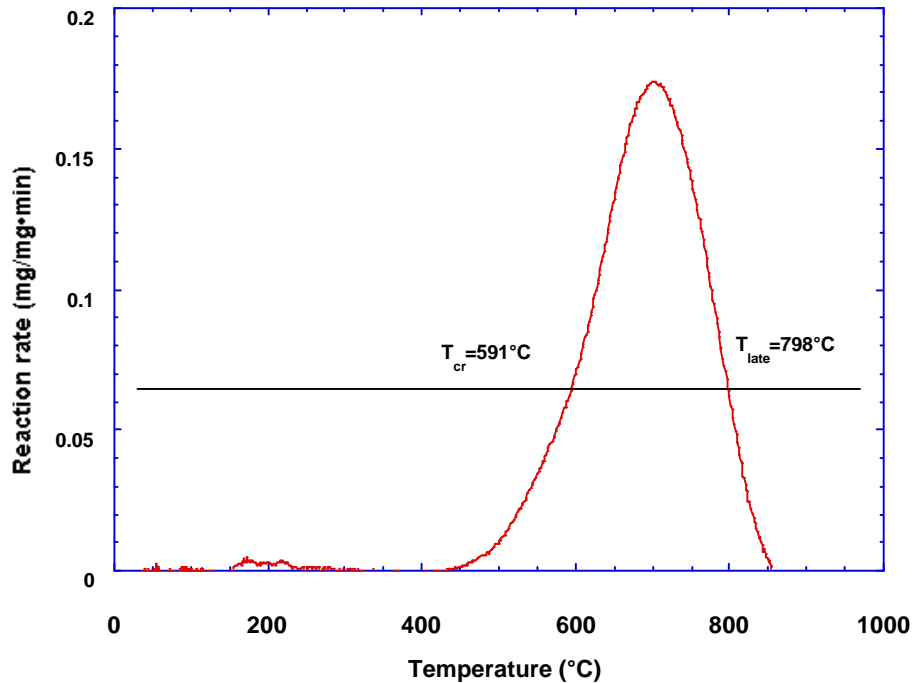
Figure 1B (next page) shows a typical temperature profile and the weight loss curve for class C fly ash with an LOI value 0.92 wt percent. The signal is considerably noisier than that observed for the class F ash. Note that this is a result of use of a much finer mass scale in the case of the class C ash, due to this sample's much lower LOI. The absolute increase in mass following carbon loss is actually quite similar for both class F and class C samples. The results on the Figure 1B are shown for fly ash sample 66. The uncertainty in LOI for this class C fly ash sample was around 0.29 wt percent.



**Figure 1B. Typical TGA weight loss and temperature curves for class C fly ash carbon reactivity characterization.**

The critical temperature ( $T_{cr}$ ) has been defined as a measure of the reactivity of carbons<sup>1,2</sup>. The measurement of  $T_{cr}$  involves a particular weight loss criterion, under conditions presumed to be under intrinsic chemical rate control. In this characterization the sample is heated at constant rate of 30°K/min. A constant airflow (approximately 300 cc/min of air in our case) is fed into the TGA reactor during heating. The reaction is that between carbon and oxygen from air, leading burn-off of carbon, as CO<sub>2</sub> and CO evolve. The reaction rate of course begins at zero and increases with temperature. The temperature at which the reaction rate reaches 0.065 mg/mg·min (based on original carbon content in the fly ash) is taken as the “critical temperature”,  $T_{cr}$ , an indication of carbon oxidation reactivity<sup>1,2</sup>. The critical rate of the weight loss 0.065 mg/mg·min is low enough to be in the kinetic regime and high enough to be easily measurable. The lower the critical temperature, the more reactive the carbon.

Figure 2A shows a derivative of the mass loss rate data of Figure 1A, and shows the identification of the critical value of rate together with  $T_{cr}$ . From the rate data on Figure 1A first the derivative was taken. In order to get a smooth reaction rate curve the differentiated data curve was smoothed. In addition to  $T_{cr}$ , a second related reactivity parameter,  $T_{late}$  has been defined in Figure 2A. This parameter indicates the temperature at which the rate reaches 0.065 mg/mg·min during the final phases of burnout. The presumption is that the higher the value of  $T_{late}$  the lower the reactivity of the residual carbon.

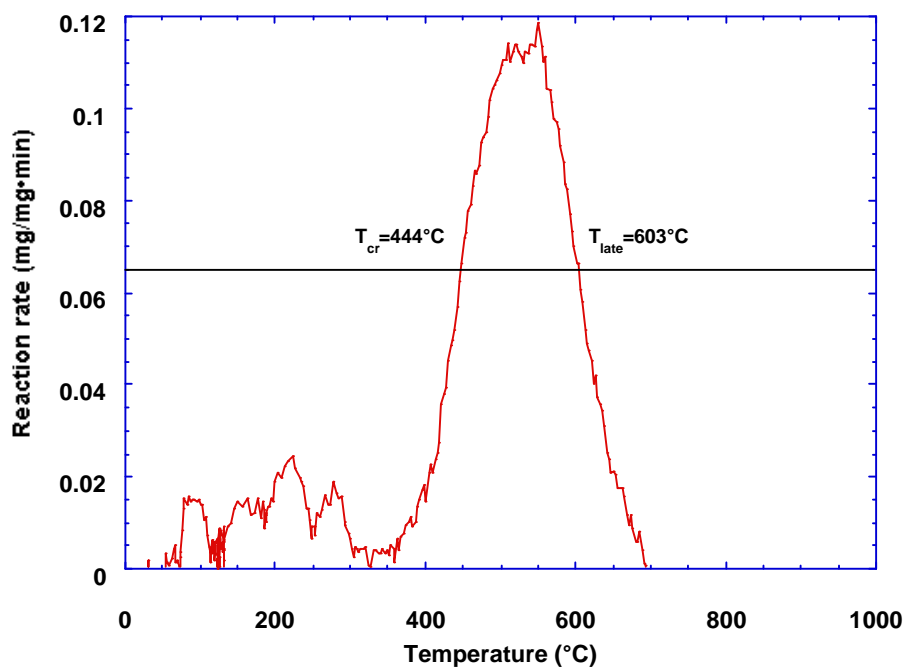


**Figure 2A. Derivative of the mass loss rate as a function of temperature for the class F fly ash carbon, with LOI 14.6 wt percent.**

Figure 2B (next page) shows the mass loss rate as a function of temperature for the class C fly ash carbon with an LOI of 0.92 wt percent. As Figure 2B shows, the reaction rate curve is more “noisy” compared to the class F fly ash reaction rate curve (Figure 2A). The class C fly ash carbon burn-off rate curve is affected more strongly by the noise



inherent in the mass signal, due to the need to perform the measurements at higher sensitivity. Nevertheless,  $T_{cr}$  and  $T_{late}$  can be clearly identified.

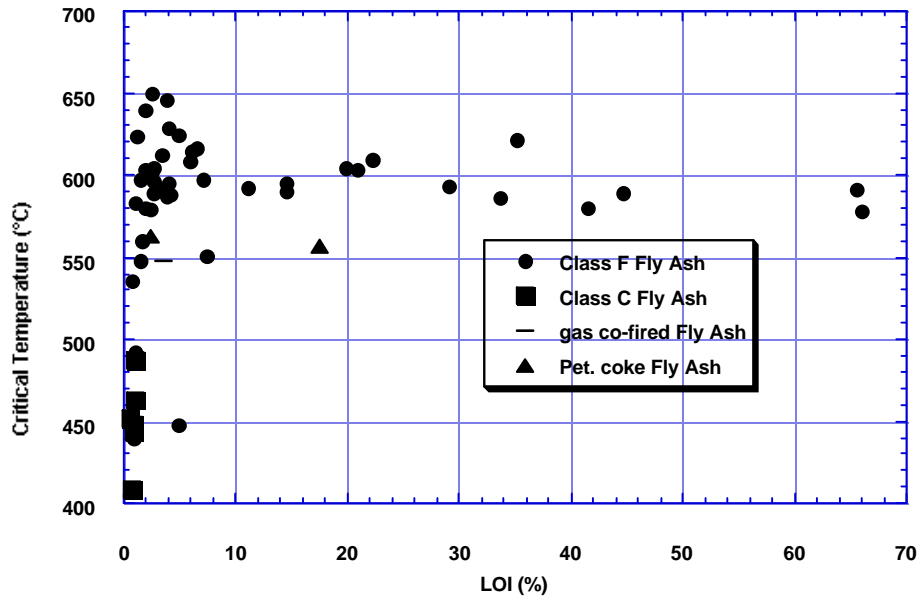


**Figure 2B. Derivative of the mass loss rate as a function of temperature for the class C fly ash carbon with an LOI of 0.92 wt percent.**

## RESULTS AND DISCUSSION

Depending on the amount, the nature and the origin of the carbon in the fly ashes the critical and late temperatures varied over quite a wide range. The results of the oxidation reactivity experiments are shown in Table 2. In many cases, the values are means from several runs.

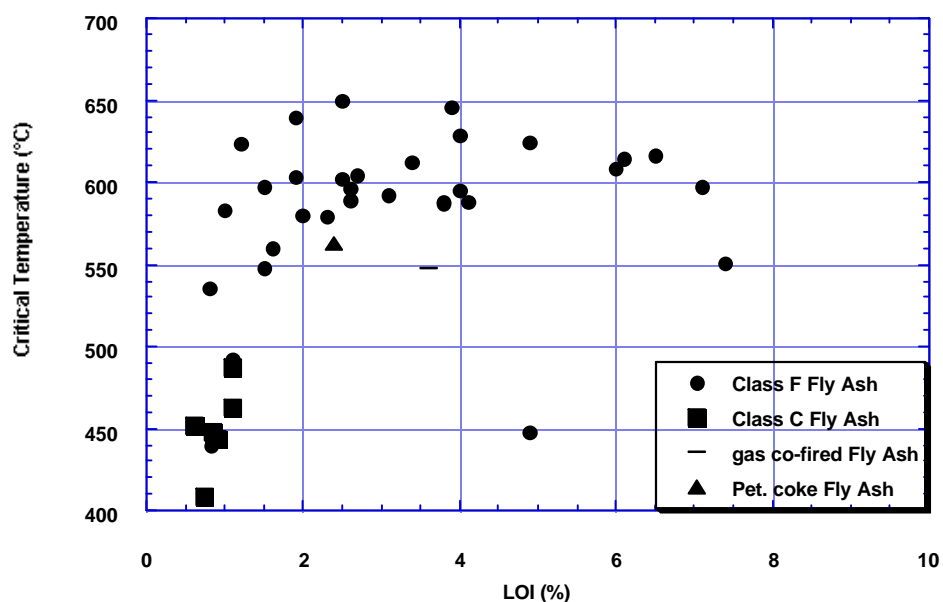
Figure 3 gives a plot of the reactivity  $T_{cr}$  of the fly ash carbons as a function of LOI. As may be seen from Figure 3, the critical temperatures of the class F fly ash carbons did not vary very much in the range of LOI from 10 to 70 wt percent. The  $T_{cr}$  values varied between 580° and 620°C for these higher LOI fly ash carbons. Fly ashes with LOI under 10% had a tendency to exhibit somewhat greater variation in  $T_{cr}$ , and many had considerably lower values of  $T_{cr}$ . The differences between class C and class F ashes is the most likely explanation for the large variation in  $T_{cr}$  at low LOI. This is especially apparent in Figure 4.



**Table 2. Oxidation reactivity results for fly ash carbons.**

<b>Fly Ash</b>	<b>LOI</b>	<b>Type</b>	<b>T<sub>cr</sub></b>	<b>T<sub>late</sub></b>	<b>Surface Area</b>	<b>Specific Foam Index</b>
	<b>wt %</b>		<b>(°C)</b>	<b>(°C)</b>	<b>m<sup>2</sup>/g-carbon</b>	<b>ml Dar II/g-carbon</b>
1	6.5	class F	616	806	41.4	1.637
2	3.1	class F	592	773	58.9	0.951
3	14.6	class F	595	794	67.6	1.666
4	14.6	class F	590	787	64	1.604
5	1.9	class F	640	773	51	0.348
6	3.4	class F	612	783	55	1.945
7	2.6	class F	596	796	67.8	1.009
8	3.8	class F	588	768	62.1	1.162
9	66	class F	578	787	64.5	1.941
10	2.6	class F	589	766	64.2	0.994
11	2.5	class F	602	760	62.5	1.505
12	2.3	class F	579	767	74.3	1.427
13	3.8	class F	587	769	65.5	1.034
16	1.5	class F	548	716	124	8.812
19	3.6	gas co-fired	548	721	107.1	1.815
20	2	class F	580	725	67	0.582
21	6.1	class F	614	790	50.6	2.475
22	33.6	class F	586	784	50.4	1.788
23	65.5	class F	591	795	52.9	1.847
24	2.7	class F	604	793	40.1	0.476
25	2.5	class F	650	777	37.4	0.335
26	4	class F	628	806	31.3	0.66
28	2.4	Petroleum coke	563	702	18.3	0
29	1.5	class F	597	746	67.1	0.86
30	35.1	class F	621	826	41.3	2.082
32	44.7	class F	589	786	46.4	1.681
33	29.1	class F	593	795	41	1.482
34	4.9	class F	624	808	48.9	1.203
35	17.5	Petroleum coke	557	718	4	0
37	4.9	class F	448	567	38.3	0.807
39	0.82	class F	440	720	310.6	6.18
40	1.1	class C	487	683	280.2	0.508
41	1.1	class C	463	570	308.3	0.495

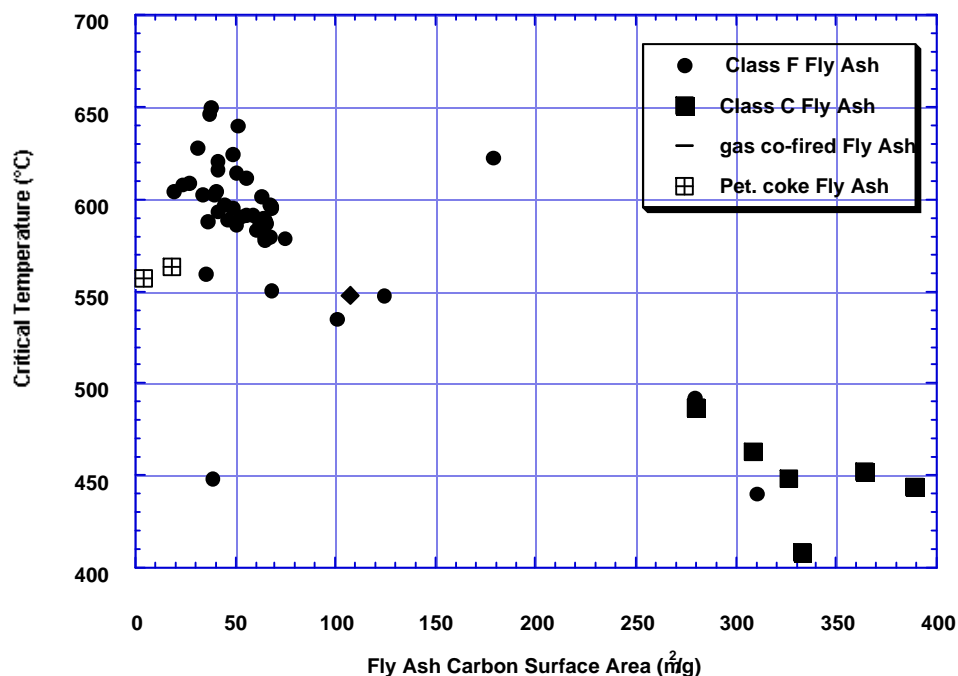
43	0.61	class C	452	738	363.8	0
45	0.74	class C	408	728	333.1	0
46	11.1	class F	592	795	55.1	1.674
47	41.5	class F	580	784	64.7	1.987
49	19.9	class F	604	796	19	0.927
50	22.2	class F	609	801	26.7	1.251
51	20.9	class F	603	798	39.8	1.646
52	1.1	class F	492	641	279.1	8.426
53	4	class F	595	714	48.8	1.621
54	4.1	class F	588	718	35.7	0.968
56	1.2	class F	623	690	178.7	4.120
57	0.8	class F	535	690	100.8	0.000
58	1.9	class F	603	756	33.9	0.000
59	1	class F	583	721	60.1	1.014
60	6	class F	608	784	23.7	0.505
61	1.6	class F	560	707	35	4.352
62	3.9	class F	646	808	37.3	1.796
63	7.1	class F	597	766	44.2	0.430
64	7.4	class F	551	747	68	1.778
66	0.92	class C	444	603	388.9	4.396
68	0.84	class C	448	605	325.9	3.390



**Figure 4. Expanded plot of the critical temperatures as a function of LOI.**

Class C fly ashes of low LOI were generally more reactive than the Class F ash carbons of comparable LOI. Critical temperatures for Class C ash carbons were in the range from 410°to 490°C. The higher reactivity of Class C ash carbons could be understood in terms of the origin of the fly ash carbon. Class C Fly ash carbons mostly come from low rank coals, which give chars that are more reactive than chars from high rank coals which give class F ashes. This is the reason why the LOI of class C fly ashes did not exceed 1.1 % in our sample bank. The higher reactivity of class C vs. class F carbons could have its origin in the different nature of the starting organic matter of the two classes. In addition the catalytic effects of the fly ash minerals could influence reactivity of the fly ash carbons. Class C fly ashes having high CaO content have a natural source of oxidation catalyst, which is not present in the same quantities in Class F fly ash. The catalytic effects of alkalis could also play a role.

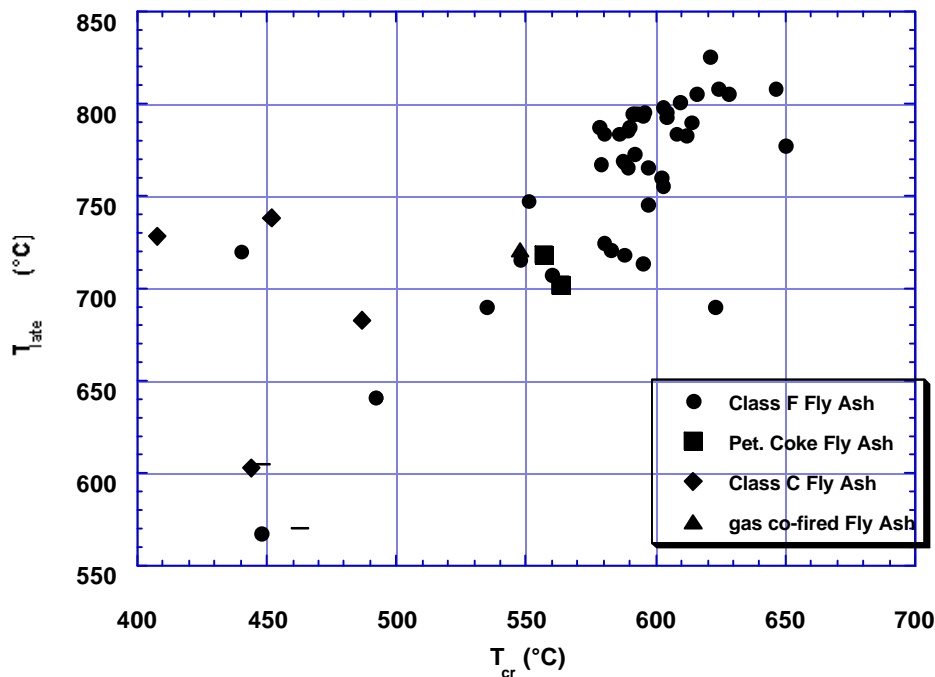
It is logical to expect a correlation of reactivity with char surface area. Figure 5 shows the reactivity of the fly ash carbons as a function of surface area.



**Figure 5. Fly ash carbon reactivity as a function of carbon surface area.**

The correlation between surface area and reactivity appears at first glance to be quite good. The higher reactivity carbons had higher available surface. There are enough exceptions to raise concerns about a correlation. There are a few class F fly ash carbons, which were “unusual”, which were prepared under unusual conditions. These samples demonstrate that it is naive to accept a simple correlation at face value. It should be noted that class C fly ash carbons in Figure 5 were generally located at the bottom-right corner of the figure, indicating their high surface area and high reactivity, while class F ashes clustered at the upper left. Within either group, a good correlation with surface area is not as apparent, though a weak trend is seen. These facts suggest that the apparent correlation of surface area with reactivity may not be indicative of cause and effect, but rather, indicate a secondary correlation of both parameters through coal rank.

Figure 6 shows late temperature,  $T_{late}$ , as a function of critical temperature for the same set of samples discussed above.

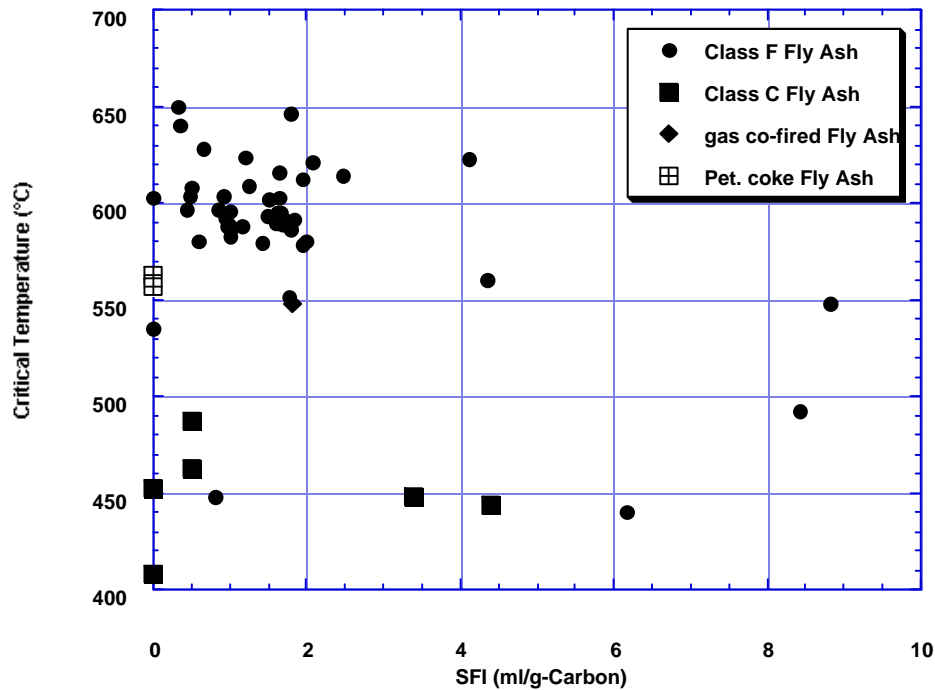


**Figure 6. Fly ash carbon late temperature as a function of critical temperature.**

This plot provides information about the width of the reaction rate distribution curve. The bigger the difference between  $T_{cr}$  and  $T_{late}$ , the wider the reaction rate distribution characterizing the carbon. Most of the class F fly ashes showed both high late temperature and high critical temperature indicating that reaction rate curve was of constant width. Class C fly ash carbons did not show a consistent correlation between critical temperature and late temperature. In this case, the reactivity distribution in the carbon was quite broad. It could be argued that the key parameter for the correlation between  $T_{cr}$  and  $T_{late}$  was the fly ash carbon content, as it was low LOI class C and class F ashes that showed the poorest correlation. Of course at very low values of LOI (roughly less than 0.7 wt %), the reaction rate did not reach the 0.065 mg/mg-min criterion and critical temperature was impossible to determine. As the LOI increased the reaction rate

curve spread out both vertically and horizontally. Further increase on LOI led to a narrowing of the reactivity profile.

Figure 7 shows the correlation between fly ash carbon reactivity and the measure of its air entraining agent (AEA) adsorption activity (Specific Foam Index, SFI).



**Figure 7. Fly ash critical temperature as a function of its specific foam index.**

As can be seen from the plot above there was no apparent relationship between reactivity and specific foam index. Quite a number of class F fly ash carbon samples clustered at the upper left corner of the plot. Class C fly ash carbons showed somewhat different behavior. Some of the class C fly ash carbons were quite reactive and active at the same time, while others were reactive but not active. Class C ashes are known to exhibit a wide range of behavior in practical situations, and the specific foam index parallels this. This clearly indicates that no correlation exists between reactivity and AEA activity, and reactivity tests will be of little value for characterizing suitability for concrete.



## CONCLUSIONS

Fly ash carbon reactivity was investigated using a simple TGA analysis. The critical temperature defined at a reaction rate of 0.065 mg/mg·min was used as measure of the fly ash carbon oxidation reactivity.

Fly ash carbon reactivity was quite invariant with fly ash carbon content in the range from 10 to 70 wt % of LOI. This is because virtually all of these samples were derived from coals giving class F ashes (i.e., high rank coals). Fly ashes with smaller content of carbon (below 2 wt %) showed somewhat higher reactivity. Class C fly ash carbons with relatively low LOI were most reactive, which is consistent with their lower LOI value (more reactive chars burn out to low LOI values).

An apparent correlation existed between fly ash carbon surface area and fly ash carbon reactivity. Relatively high surface area (100-300 m<sup>2</sup>/g-carbon) in a fly ash carbon was a good indicator that the sample was also quite reactive. Class C fly ashes in our sample bank were all highly reactive and had high available surface area. It is likely, however, that the correlation was not indicative of causation. High surface area does not necessarily assure high reactivity, nor vice versa. Rather, it is just generally the case that class C ashes are characterized by both high surface area and high reactivity and class F ashes by lower surface area and relatively lower reactivity.

No correlation could be found between reactivity and activity towards AEA adsorption.

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2. Wojtowicz, M.A., Basilakis, R., Serio, M.A., Char-Oxidation Reactivity at Early and Late Stages of Burn-off, Proceedings Carbon '99, American Carbon Society, p230, July 1999.