Class C & Class F: How Relevant are They for Predicting Performance?

Richard A. Livingston
Dept. of Materials Science& Engineering
University of Maryland

Anna Maria Workshop XII, November 9, 2011

Acknowledgements

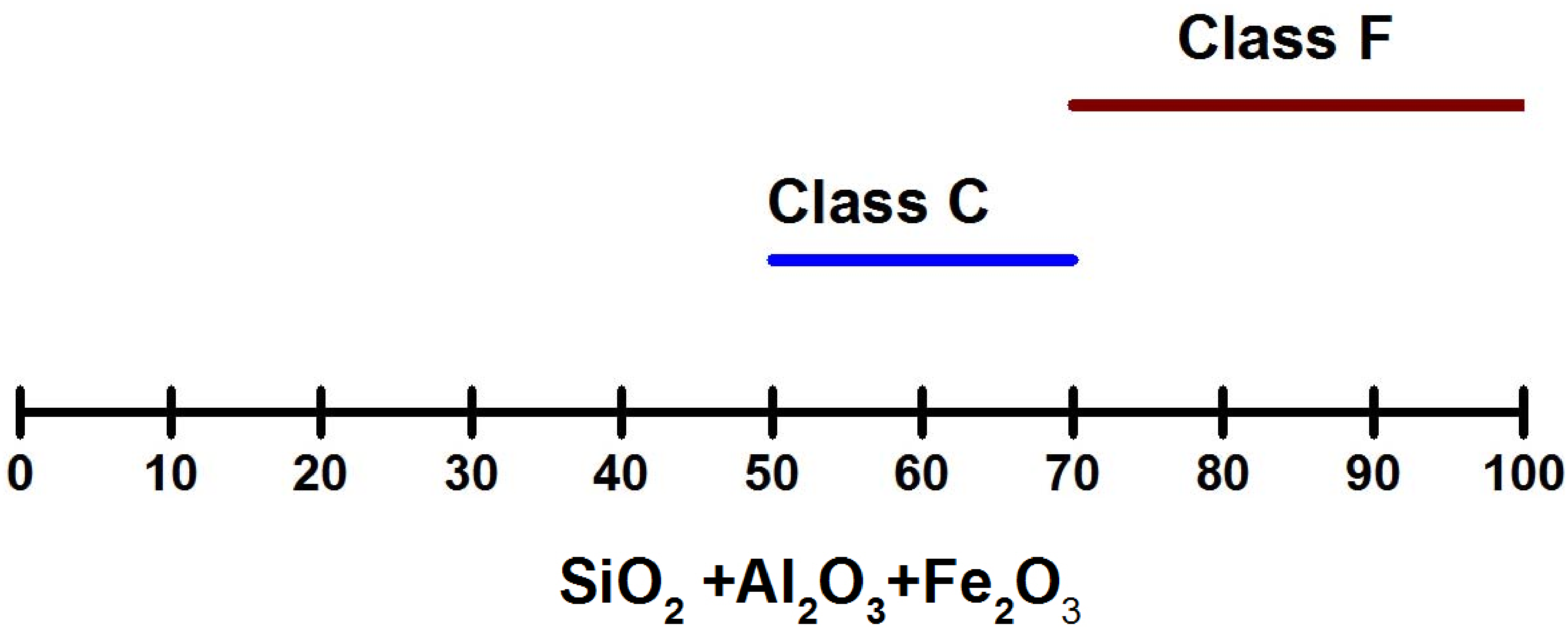
Walairat Bumrongjaroen & Isabelle Muller
Catholic University

Jeff Davis
National Institute of Standard and Technology

Outline

- ASTM C-618
- Fly ash Particle Characterization by ASEM
- Comparison with Class C & F
- Application of Cluster Analysis
- Development of a Performance-Based Reactivity Classification System
- Conclusions

ASTM C- 618



ISSUES

- Selection of oxides
- Selection of limits
- Significance of classes

$SiO_2 + Al_2O_3 + Fe_2O_3$ Reactions

Pozzolanic reaction

$$SiO_4^{4-} + xCa(OH)_2 + \left(y - 2x\right)OH^- + nH_2O \rightarrow Ca_xSi(OH)_y \cdot nH_2O$$

Hydrogarnet Formation

$$2Al(OH)_4^- + 3Ca^{2+} + SiO_4^{4-} \rightarrow Ca_3Al_2Si(OH)_8O_4$$

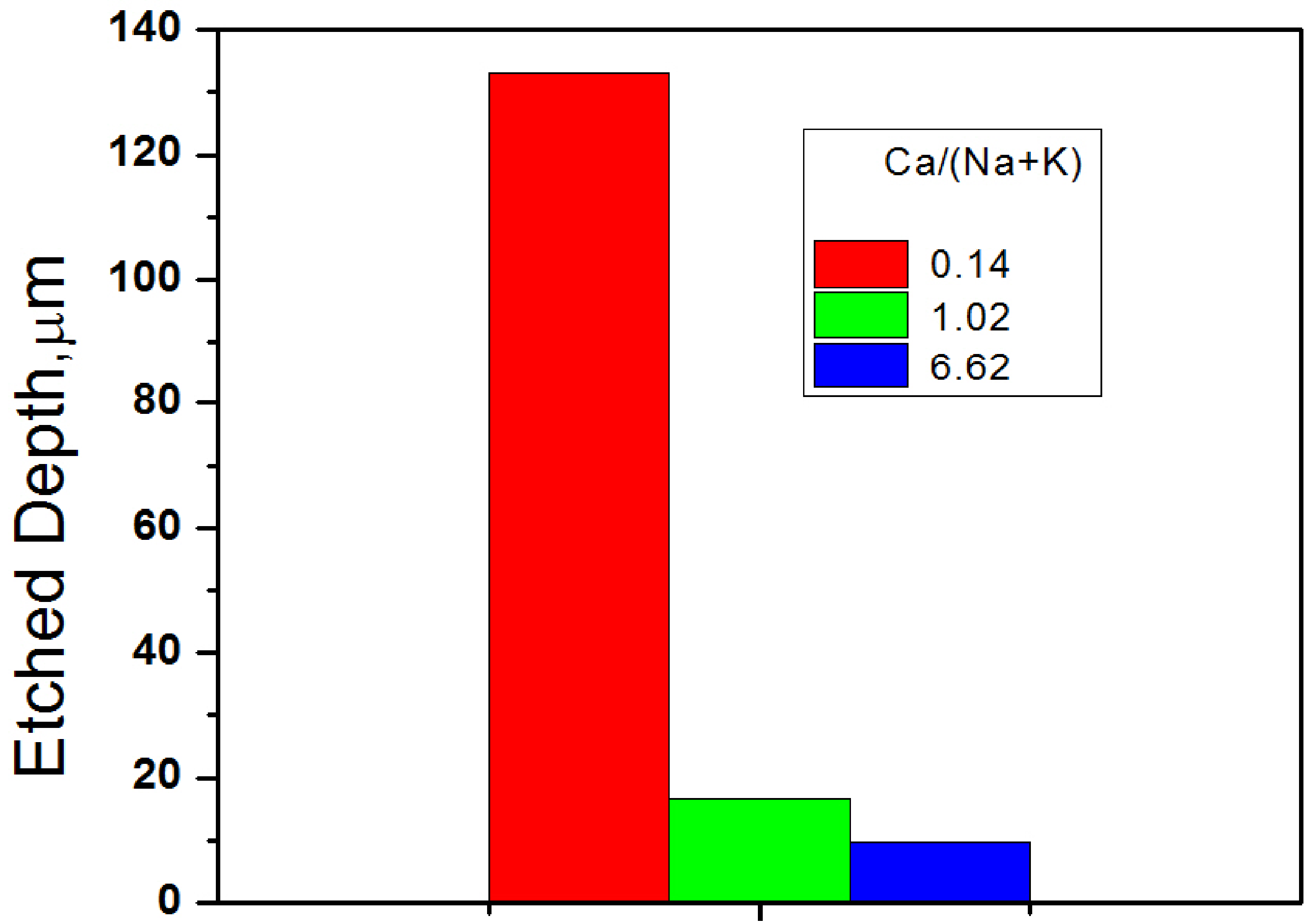
Limonite Formation

$$Fe_2O_3 + H_2O \rightarrow 2FeOOH$$

Calcium Effect

$$SiO_2 + Al_2O_3 + Fe_2O_3 + CaO = 100\%$$

Silica Dissolution, Synthetic Fly Ash Glass in Simulated Porewater, 72 hr



ASTM C-618

- Class F = Bituminous coal fly ash
- Class C = Sub-bituminous coal fly ash

ASTM C-618

- Class F = ~~Bituminous coal fly ash~~
- Class C = ~~Sub-bituminous coal fly ash~~

Bulk XRF Analysis

- Includes both reactive and inert phases
- Does not provide particle size data
- No information on variance of measured values

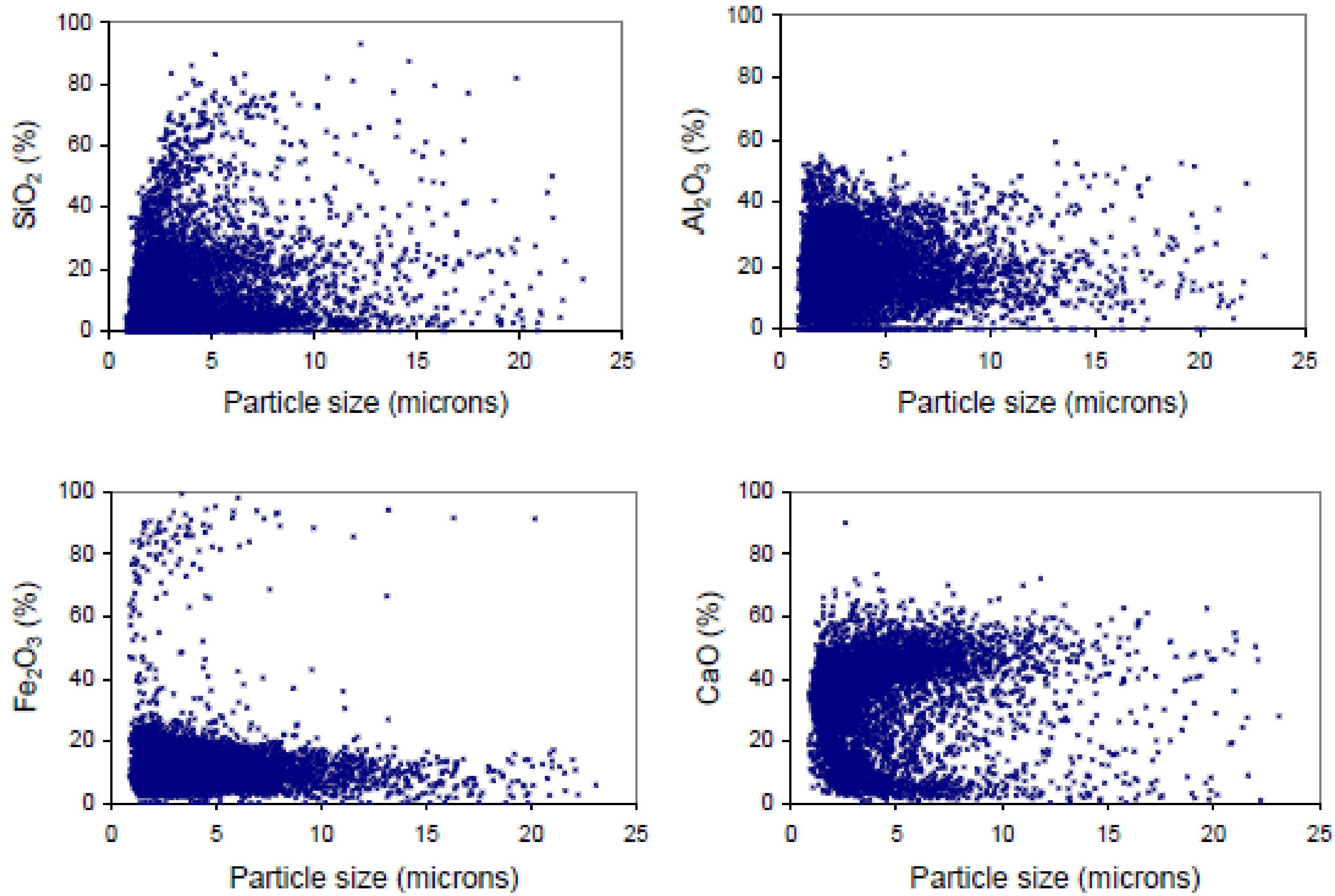
CCSEM (or PSEM or ASEM)

- SEM with Energy Dispersive XRF
- Computer-controlled stage
- Particle analysis software

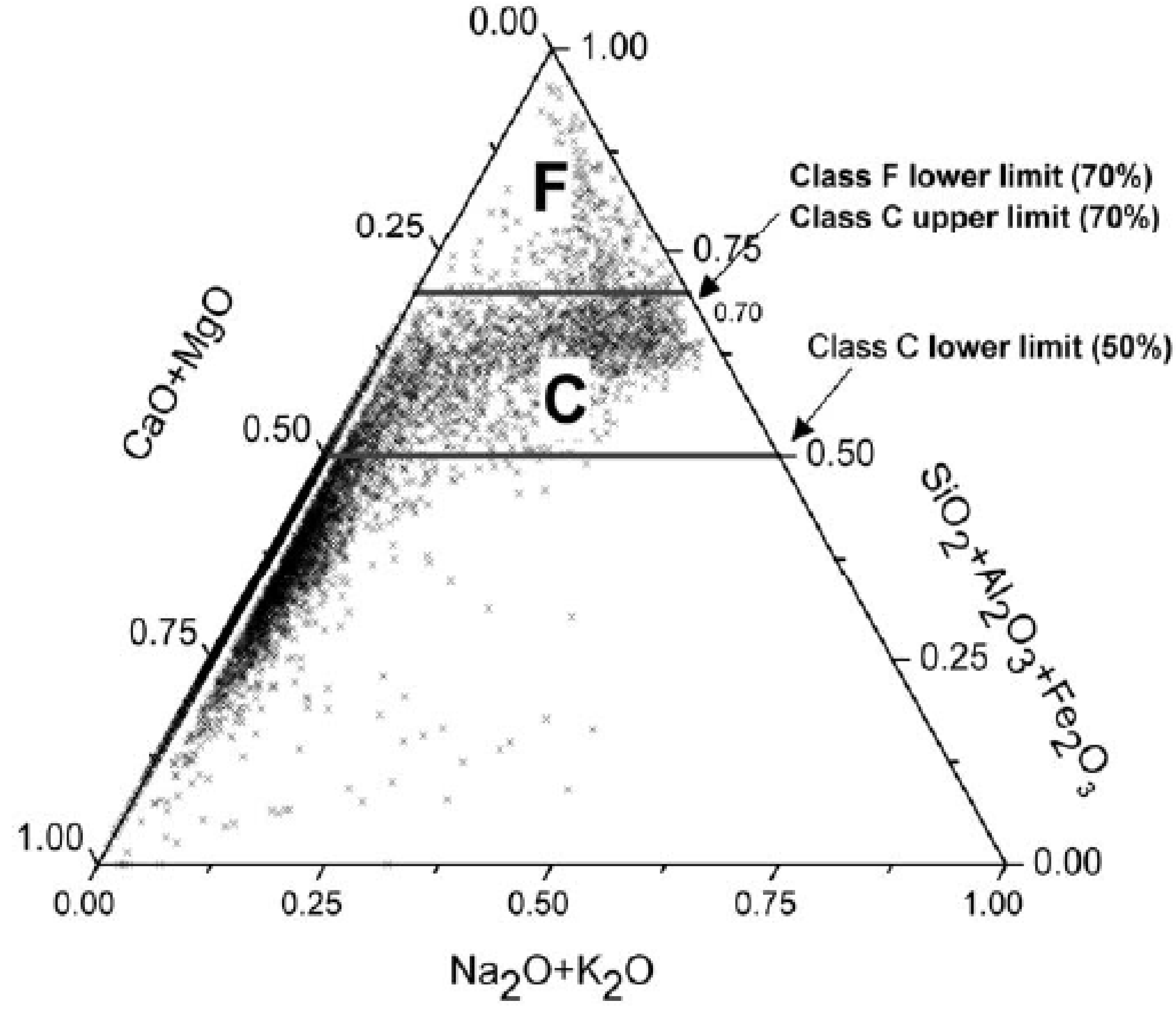
ASEM Data

- ~ 10,000 particles per sample
- 16 elements: Na, Mg, Al, Si, P, S, K, Ca, Fe,
  Ti, Fe, Ni, Zr, Ba, Ce, and Pb
- Glassy particles identified by:
  - Circularity - aspect ratio <1.3
  - Size range 0.20 -25 microns

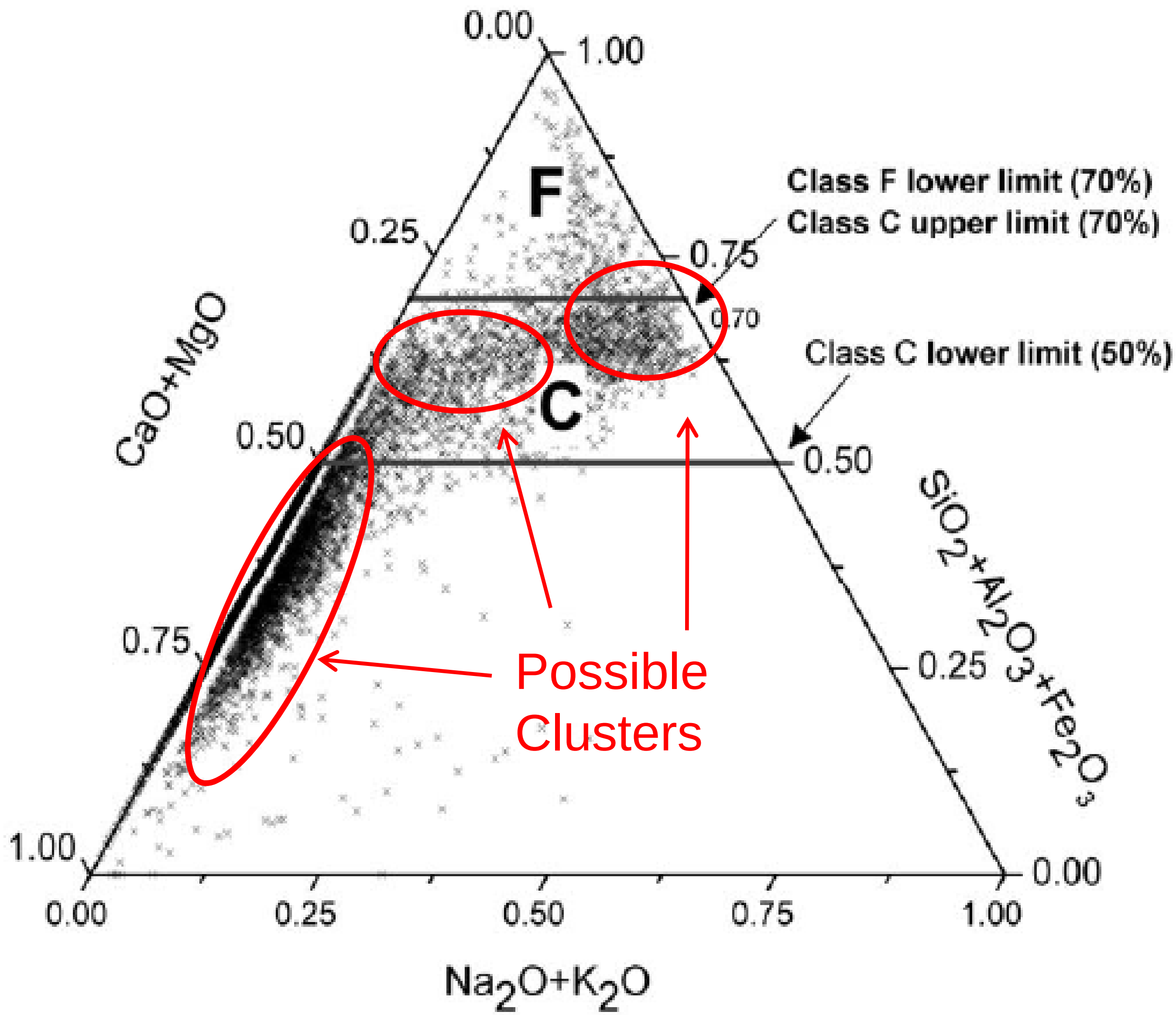
Element vs Particle Size



Coal Creek Fly Ash Particle Analysis



Coal Creek Fly Ash Particle Analysis



K-means algorithm

1) Pick a number (k) of cluster centers
2) Assign every data point to its nearest cluster center based on Euclidian distance
3) Move each cluster center to the mean of its assigned data point
4) Repeat 2-3 until convergence
5) Calculate the fraction of each cluster

Clusters of Coal Creek fly ash particles in glass coordinates

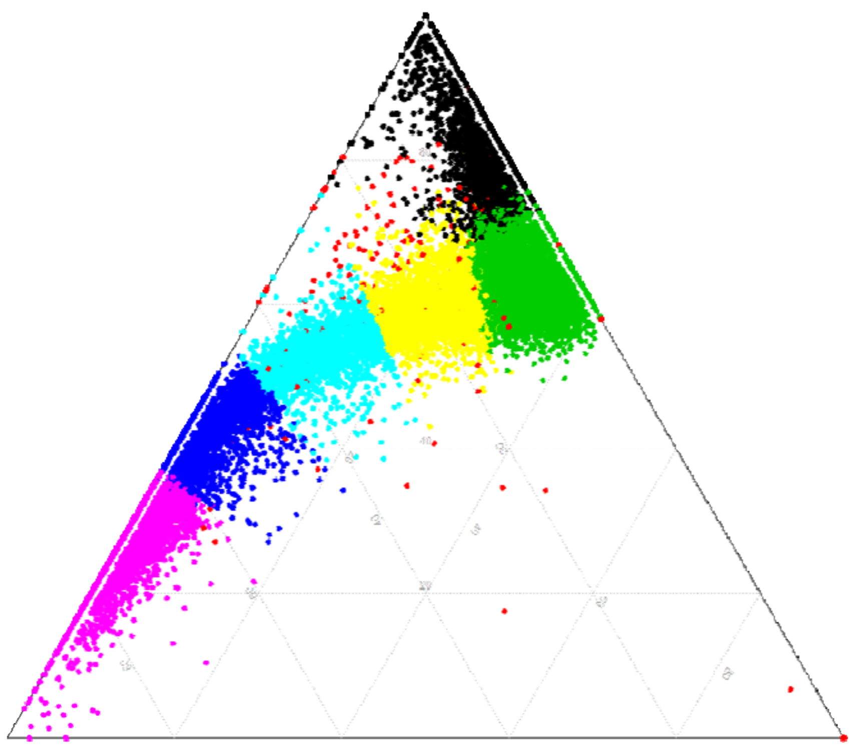


Table 1 Classification of Glassy Phase based on Cluster Analysis of Coal Creek Fly Ash

Cluster No.	Color	Name	Number (%)
1	Black	Si-Al-Fe glass	9.57
2	Red	Trace element	1.00
3	Green	Si-Al-Fe glass	32.67
4	Blue	CAS glass	11.85
5	Cyan	CAS glass	11.93
6	Magenta	Ca rich glass	15.64
7	Yellow	CAS glass	17.34

Proposed Application of Clustered Fly Ash Composition

- Define a set of standard clusters based on statistical analysis of clusters analyzed from variety of actual fly ashes.
- The centroid of each of these standard clusters would be a specific chemical composition defining a standard glass.
- A given fly ash particle data set could then be classified in terms of this set of standard glasses
- The reactivity of each standard glass would be known

Development of a Performance-based Classification System

1. For a total number, N, of glassy particles analyzed by ASEM, each particle would be assigned to a standard glass class, based on its chemical composition. Then for *k* number of standard glass classes:

$$N = \sum_{i=o}^{k} n_i$$

where n_i is the number of particles in the i^{th} class

Approach (con't)

2. To convert them to mass fractions it is necessary to use the individual particle radius and the density of the glass.

$$x_i = \frac{\sum_{j=1}^{n_i} r_j^3 \rho_i}{\sum_{i=1}^{k} \sum_{j=1}^{n_i} r_j^3 \rho_i}$$

where x_{i} is the mass fraction, r_{j} is the radius of the j^{th} particle and ρ_i is the density of the i^{th} standard glass

Conclusions

- ASTM C-618 Classification system does not include all the chemically relevant oxides
- Rationale for Class C and Class F limits is not clear
- ASTM C-618 does not provide a reliable prediction of reactivity
- ASEM provides data on individual fly ash particles and makes it possible to discriminate between reactive and inert phases
- Particle-based data make it possible to identify characteristic clusters of glass particles with similar compositions.
- These clusters can then be used to develop a standard set of fly ash glass compositions.

UNIVERSITY OF MARYLAND

Thank you for your attention

Richard A. Livingston: rliving1@umd.edu