A Novel Method for Determining the Adsorptive Capacity of Carbon Containing Fly Ash

WORLD OF COAL ASH
May 2015
Nashville, TN

Rafic Minkara, PhD, P.E.
Vice President

Co-Authors:
Nortey Yeboah, PhD, Research Engineer
Richard Nordman, Mechanical Engineer
Doug Rhodes, Facility Manager
Jennifer Kelly, Research Chemist
Mass loss in an ash sample heated to 750°C

Mass loss can be due to:

- Ignition of unburned coal
- Ignition of activated carbon
- Loss of CO₂ from carbonates
- Dehydration of sulfates (Ca, Na, ...)

Loss on Ignition

It’s main purpose is to determine the unburned carbon content and its potential impact on air entrainment in concrete.
Carbon impact on air entrainment in concrete is determined by its adsorption capacity (a function of specific surface area and pore size) and NOT its mass (measured as LOI or carbon content).

The ash industry adopted the foam index test to overcome the LOI test deficiency.
**Foam Index**

**Very simple test**

One of the 10+ versions:
- 200 ml of water + 40 gms ash in blender.
- Air Entrainment Agent (AEA) preferred in the market.
- Mason jar & manual mixing are also used.

**Procedure**
- Count the AEA drops.
- Add AEA by the drop using a syringe (or a dropper).
- Mix for 10 seconds.
- Watch for foam development on the surface of slurry.

Repeat steps until a solid layer of air bubbles is formed.
There is no industry standard foam index test.

The procedure has a lot of “slack”.

The AEA’s used are industrial chemicals and not analytical grade.

Drops are counted until end point is achieved.
Reagent delivery mass spread (8 technicians)

Mass of Drops (g) vs Number of drops

Overestimated Foam Index
Large variability in results from 5 operators on identical split samples.

5 fly ash samples (low to high PAC contents)
Activated Carbon Industry Tests. Are they good surrogate for AEA’s?

Methylene Blue adsorption:
- The MB molecular size and structure is different than AEA’s molecules and will give artificially high adsorption values.
- Methylene blue reagent is not friendly (suspected mutagen).

Iodine Number:
- Iodine is a small (<6 Å) diatomic molecule with a MW of 106 g/gmol. Much smaller than AEA’s long chain molecules.
- Iodine may also dissociate in solution and exists as a charged ion with significantly smaller size and with the ability to bond onto functional groups on the AC’s surface.

The adsorption relationship of Iodine on Activated Carbon versus AEA on Activated Carbon are drastically different and would not be linear in behavior.
Before the Foam Index end point:
All added AEA is adsorbed onto the carbon
i.e., AEA is not “in solution”

At the Foam Index end point:
The excess AEA “grabs” air bubbles
i.e., AEA is in solution and can be recovered

How do we measure “excess” AEA in solution?
Conjugated double bonds of a molecule cause the compound to have a color – fruits, dyes, glow in the dark, etc.

Molecules with few conjugated double bonds (such as surfactants and AEA’s) absorb and emit light in the ultraviolet region.

Fluorescence spectroscopy

Patent Pending
AEA’s fluoresce when excited by UV light. The emitted light is not visible but can be detected with optical sensors.
The fluorescence intensity is proportional to the concentration of the compound. This fluorescence method can be used to determine low concentrations of surfactants (AEA's) in water.
Air Entrainment Agents are mixtures of compounds.

AEA’s are industrial chemicals. Some are byproducts from other processes.

AES’s are not available in analytical grade.

Also, the various AEA’s have different optimum fluorescence wave lengths.

Let’s select a surrogate surfactant that can be used as standard reagent for AEA’s.
Non-ionic Surfactant Analytical Reagent

Linear correlation between fluorescence intensity and concentration

Based on this scan:
Excitation @ 260-280 nm
Emission @ 300 – 370 nm

Patent Pending
Two methods to determine Adsorption Capacity of Ash

Single Point Isotherm
- Mix ash in water with known surfactant concentration
- Filter the ash to determine residual concentration

Breakthrough Analysis
- Mix ash with pure water
- Incrementally add surfactant
- Test residual concentration after each addition to determine breakthrough point

Patent Pending
Lab Scale Set-up
Good correlation between adsorbed surfactant and BET specific surface area

Based on 10 ash samples w/ unburned or activated carbons:
Carbon contents ranged from 0.02% to 6.8%
Foam Index ranged from 3 to 76 (MBVR)
A closer look at Breakthrough Point

Breakthrough is the Foam Index point.
Semi-Automated Analyzer for Quality Assurance and Research
Additional Options

This ash sample processing cell can also be used to monitor other ash quality issues such as: ammonia & trona:

- Na byproducts can be detected using conductivity
- Ammonia can be detected using an ion selective probe

Patent Pending
LOI is not appropriate to assess PAC impact. Foam Index is subjective/not easily standardized.

**SUMMARY**

New method/instrument:
- Well understood adsorption and fluorescence principles
- Easy to standardize
- Single point isotherm or breakthrough analysis
- Lab instrument for QA or research
- Semi-automated for site QA
- Fully automated for QC in conjunction with RestoreAir
- Calibrated to calculate traditional Foam Index number

Patent Pending
COMMENTS/QUESTIONS?

Rafic Minkara, PhD., PE  
Vice President – Research & Development  
Headwaters Resources Inc  
rminkara@headwaters.com  
Cell: 770-330-0689

Materials Testing and Research Facility  
2650 Old State Highway 113  
Taylorsville, GA 30178  
Phone: 770-684-0102

Co-Authors:  
Nortey Yeboah, PhD, Research Engineer  
Richard Nordman, Mechanical Engineer  
Jennifer Kelly, Research Chemist  
Doug Rhodes, Facility Manager