FLY ASH - Coal Combustion residue

Fly ash is the finely divided mineral residue resulting from the combustion of ground or powdered coal in electric generating plant (ASTM C 618). Fly ash consists of inorganic matter present in the coal that has been fused during coal combustion. This material is solidified while suspended in the exhaust gases and is collected from the exhaust gases by electrostatic precipitators. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape (Ferguson et. al., 1999). Fly ash particles those are collected in electrostatic precipitators are usually silt size (0.074 - 0.005 mm).

Components of coal ash

- Detrital or authigenic minerals
- 95% of the mineral matter present in coal is composed of clay, pyrite and calcite
- Clay minerals make up 60–80% of the total mineral content of coal
- Type of clay mineral is dependent on environment Kaolinite with fresh water influence
- Illite with overlying marine rocks

Coal combustion

- Finely crushed coal is fed into a combustion chamber where it ignites
- Most of the carbon is burned, the volatiles vaporize and the boiler tubes, filled with water are heated to form steam to drive the turbines
- The inorganic noncombustible material forms coal combustion byproducts

Coal combustion products

- Fly ash (flue gas stream)
- Boiler slag (coats boiler tubes)
- Bottom ash (sand size material+boiler slag)
- FGD sludge (SO2 scrubber)
- Depending on the type of coal, burners, and boiler, 65-85% of the inorganic material is fly ash

Fly ash characteristics

- Molten minerals such as clay, quartz, and feldspar, solidify in the moving air stream, giving approximately 60% of the fly ash particles a spherical shape.

Fly Ash Classification

Fly ash is a pozzolanic material (concrete production) and has been classified into two classes, F and C, based on the chemical composition of the fly ash. According to ASTM C 618, the chemical requirements to classify any fly ash are shown in the following table.
Chemical Requirements for Fly Ash Classification

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fly Ash Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide (SiO$_2$) plus aluminum oxide (Al$_2$O$_3$) plus iron oxide (Fe$_2$O$_3$), min, %</td>
<td>70.0</td>
</tr>
<tr>
<td>Sulfur trioxide (SO$_3$), max, %</td>
<td>5.0</td>
</tr>
<tr>
<td>Moisture Content, max, %</td>
<td>3.0</td>
</tr>
<tr>
<td>Loss on ignition, max, %</td>
<td>6.0*</td>
</tr>
</tbody>
</table>

* The use of class F fly ash containing up to 12% loss of ignition may be approved by the user if acceptable performance results are available.

Class F fly ash is produced from burning anthracite and bituminous coals. This fly ash has siliceous or siliceous and aluminous material, which itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form cementitious compounds (Chu et. al., 1993). Class C fly ash is produced normally from lignite and sub-bituminous coals and usually contains significant amount of Calcium Hydroxide (CaO) or lime (Cockrell et. al., 1970). This class of fly ash, in addition to having pozzolanic properties, also has some cementitious properties (ASTM C 618-99).

Color is one of the important physical properties of fly ash in terms of estimating the lime content qualitatively. It is suggested that lighter color indicate the presence of high calcium oxide and darker colors suggest high organic content (Cockrell et. al., 1970).

Fly Ash Chemistry

Chemical constituents of fly ash mainly depend on the chemical composition of the coal. However, fly ash that are produced from the same source and which have very similar chemical composition, can have significantly different ash mineralogies depending on the coal combustion technology used. Because of this, the ash hydration properties as well as the leaching characteristic can vary significantly between generating facilities.

The amount of crystalline material versus glassy phase material depends largely on the combustion and classification process used at a particular power plant. When the maximum temperature of the combustion process is above approximately 1200°C and the cooling time is short, the ash produced is mostly glassy phase material (McCarthy et. al., 1987). Where boiler design or operation allows a more gradual cooling of the ash particles, crystalline phase calcium compounds are formed.

The relative proportion of the spherical glassy phase and crystalline materials, the size distribution of the ash, the chemical nature of glass phase, the type of crystalline material, and the nature and the percentage of unburned carbon are the factors that can affect the hydration and leaching properties of fly ash (Roy et. al., 1985). The primary factors that influence the mineralogy of a coal fly ash are (Baker, 1987):
1. Chemical composition of the coal

2. Coal combustion process including coal pulvarization, combustion, flue gas clean up, and fly ash collection operations

3. Additives used, including oil additives for flame stabilization and corrosion control additives.

The minerals present in the coal dictates the elemental composition of the fly ash. But the mineralogy and crystallinity of the ash is dictated by the boiler design and operation.

**Hydration of Fly Ash**

Formation of cementitious material by the reaction of free lime (CaO) with the pozzolans (AlO$_3$, SiO$_2$, Fe$_2$O$_3$) in the presence of water is known as hydration. The hydrated calcium silicate gel or calcium aluminate gel (cementitious material) can bind inert material together. For class C fly ash, the calcium oxide (lime) of the fly ash can react with the siliceous and aluminous materials (pozzolans) of the fly ash itself. Since the lime content of class F fly ash is relatively low, addition of lime is necessary for hydration reaction with the pozzolans of the fly ash. For lime stabilization of soils, pozzolanic reactions depend on the siliceous and aluminous materials provided by the soil. The pozzolanic reactions are as follows:

\[
\text{Ca(OH)}_2 \rightarrow \text{Ca}^{++} + 2[\text{OH}]^{-}
\]

\[
\text{Ca}^{++} + 2[\text{OH}]^{-} + \text{SiO}_2 \rightarrow \text{CSH} \quad \text{(silica) (gel)}
\]

\[
\text{Ca}^{++} + 2[\text{OH}]^{-} + \text{Al}_2\text{O}_3 \rightarrow \text{CAH} \quad \text{(alumina) (gel)}
\]

Hydration of tricalcium aluminate in the ash provides one of the primary cementitious products in many ashes. The rapid rate at which hydration of the tricalcium aluminate occurs results in the rapid set of these materials, and is the reason why delays in compaction result in lower strengths of the stabilized materials.

The hydration chemistry of fly ash is very complex in nature. So the stabilization application must be based on the physical properties of the ash treated stabilized soil and cannot be predicted based on the chemical composition of the fly ash.

**Leaching from Fly Ash**

The total metals content for a specific ash source depends on the composition of the coal. The potential for leaching of these metals not only depends on the total metals content but also influenced by the crystallinity of the fly ash, as this would dictate whether the metals are incorporated within the glasseous phase or within crystalline compounds, which will hydrate (ACAA). The metals in the glasseous phase are expected to leach at much lower rate than that from the crystalline phase.

Since the degree of crystallinity is a function of boiler design and remains relatively constant for a given source, leachable materials remain relatively constant for a given ash source. A
number of state regulatory agencies have issued source approval for specific generating facilities after the consistency of these materials had been demonstrated.

For stabilized soil, the leachability of metals not only depends on the property of the fly ash but also the soil that is used for stabilized soil. Some part of these metals leached from the fly ash will be adsorbed on the clay minerals of the soil.

Example of Fly ash (from Western US coal industry) – pattern of use

<table>
<thead>
<tr>
<th>Class C</th>
<th>Class F</th>
</tr>
</thead>
<tbody>
<tr>
<td>42% produced is used-791 thousand mt</td>
<td>51% produced is used-2.3 million mt</td>
</tr>
<tr>
<td>246 thousand mt for concrete products</td>
<td>1.3 million mt for concrete products</td>
</tr>
<tr>
<td>more diversity in uses</td>
<td>Backfill 2nd largest application</td>
</tr>
<tr>
<td>cementing properties are a factor in many of the applications</td>
<td><strong>Cenospheres</strong> - minor use</td>
</tr>
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