

Abstract

Declining supplies of fly ash have generated interest in potential beneficial use of previously geologically-disposed, reclaimed fly ash. However, it is important to determine if weathering elements (e.g., wind, rain, etc.) have significantly changed the ash properties over time. Precipitation of tertiary mineral phases can occur in the ponds and can hinder beneficial use as well as impede water flow through the ash, complicating the process of dewatering. The work performed in this study identified if organic carbon is affected by weathering and any possible tertiary mineral in samples of reclaimed fly ash and compared them to fresh fly ash. Results show that the carbon content in the reclaimed ashes was unaffected by weathering and is most accurately measured using a TOC analyzer or TGA in an oxidizing atmosphere. Reclaimed ashes were depleted in soluble salts compared to fresh fly ash, most likely attributed to weathering processes. Calcium, barium and iron sulfates are the most readily identifiable tertiary mineral phases. The precipitation of new minerals may reduce the overall pore volume of the ash, constrict water flow, and prohibit beneficial use of reclaimed ashes; however, further testing is needed.

Background & Motivation

The inorganic and organic mineral phases may have changed over time due to exposure to weathering elements. The inorganic phases can be categorized temporally based on their origin (Figure 1). Precipitation of tertiary phases into the pore spaces of the ash bind particles together, creating large, agglomerated particles (Figure 2). This process can block pore networks in the particles and reduce water flow through the ash, complicating the process of dewatering. If the pond cannot easily be dewatered, the ash cannot easily be mined for beneficial use. A thorough characterization of the reclaimed fly ash is necessary to determine how tertiary phases may have changed the physical and chemical structure of the ash. The organic (carbon) and inorganic mineral content of reclaimed ash must also be analyzed to determine if the ash can be beneficially used in concrete applications. The concrete sector is currently one of the largest beneficial use sectors for fly ash, so it is important to determine if reclaimed ash is suitable.

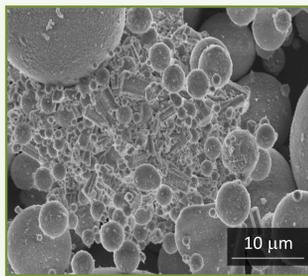


FIGURE 2. Large, unidentified conglomerate phase in the fly ash

Materials & Methods

Ten samples of reclaimed coal ash, labeled PW1-10, were taken from an ash pond in Georgia in Spring 2016. Samples were taken from the ash delta, at a depth of 0.5 ft. A sample of fresh fly ash at Plant PW was analyzed as a control. Five samples of reclaimed coal ash, labeled PM1-5, were taken from a second ash plant in Georgia in Summer 2014. Samples were taken at depths between 0.5-5 ft bgs, and samples are estimated to be less than 10 years old. Samples that were a combination of fly ash and bottom ash (PW1-6, PW10) were sieved across a No. 200 sieve to remove the bottom ash. X-ray fluorescence and SEM electron dispersive spectroscopy (EDS) were used to identify inorganic minerals in the samples. Carbon content was measured using a loss-on-ignition (LOI) procedure, a thermogravimetry analyzer (TGA), and a total organic carbon (TOC) analyzer.

Results I: Mineral Phases

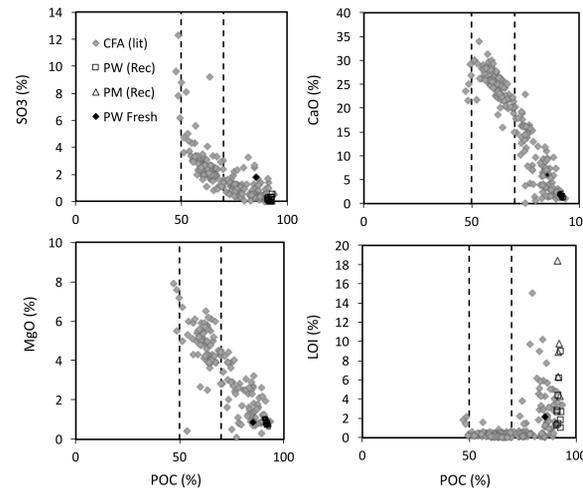


FIGURE 5. Comparison of ten PW reclaimed fly ash samples, five PM reclaimed fly ash sample, and one fresh PW sample to a literature database of fly ash for certain oxides and loss-on-ignition (LOI) versus primary oxide content ($SiO_2 + Al_2O_3 + Fe_2O_3$)

Samples were compared to a literature database of Class C and Class F fly ashes and classified as Class F fly ashes based on their chemical oxide contents. However, PM samples had an organic carbon content (recorded as LOI) above the 6% maximum for the ASTM Concrete Standard C618.

Reclaimed ashes were depleted in calcium, sodium, and sulfur oxides compared to the fresh ash. The relative abundance of non water-soluble phases produced an artificially inflated primary oxide content (POC) in the reclaimed ash, compared to fresh ash.

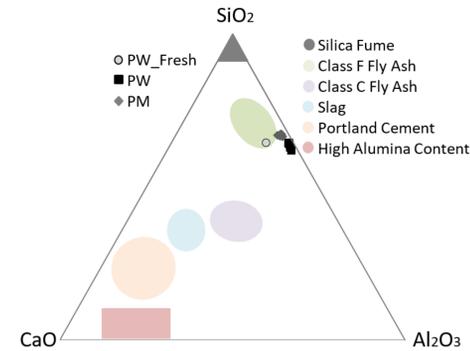


FIGURE 6. Ternary diagram showing relative percentages of SiO_2 , CaO and Al_2O_3 in reclaimed ash samples, compared to a fresh fly ash sample

The fresh fly ash sample is classified as a Class F fly ash on a ternary diagram for supplementary cementitious materials, but reclaimed samples were just outside the typical range because the calcium content was depleted.

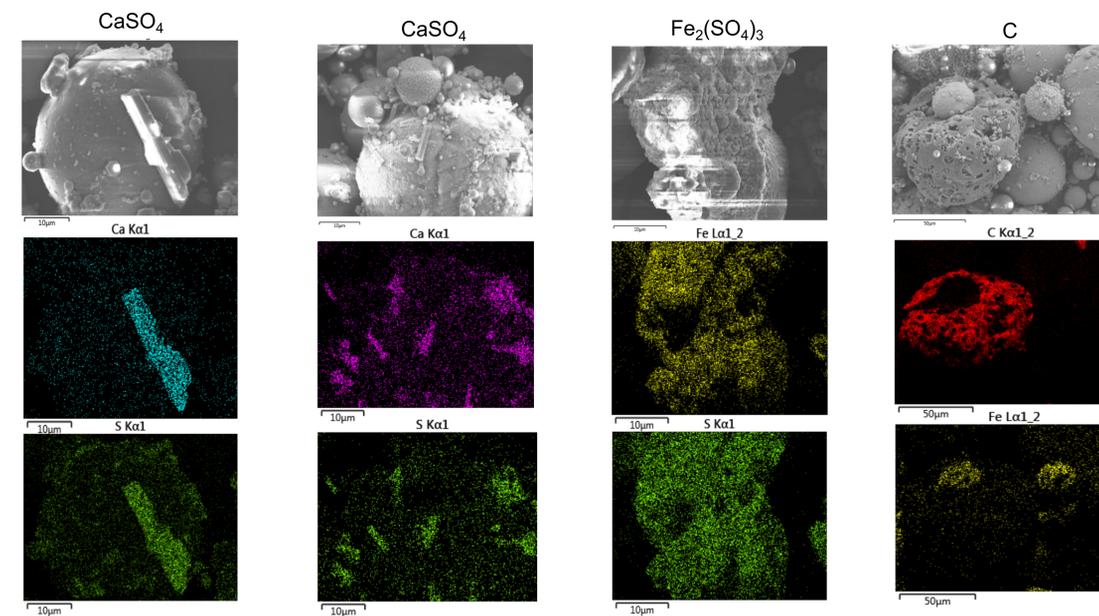


FIGURE 7. SEM EDS images highlighting different structures in the fly ash and matching them to various mineral phases

Calcium sulfate as a distinct mineral phase. This phase is most likely a secondary phase, anhydrite, formed during combustion.

Calcium sulfate as a deposited phase on an aluminosilicate glass sphere. This is most likely a tertiary phase, formed during weathering.

Iron sulfate acting as a tertiary phase binding agent. The precipitation of ferric sulfate compounds in the pore spaces creates large ash conglomerates.

The carbon phase is clearly confirmed as the large, highly porous, honeycombed morphologies in the ash.

Results II: Carbon

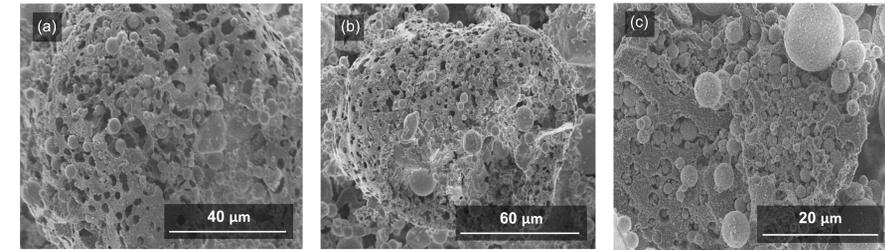


FIGURE 8. SEM images of organic carbon particles in samples: (a) PW_Fresh, (b) PM2, and (c) PW3

The carbon in the reclaimed fly ashes was almost exclusively large, smooth-surfaced, porous organic carbons whose pores contained small glassy cenospheres. There was no difference in carbon structure between the reclaimed and fresh samples. The organic carbon structure is preserved after weathering in an ash pond.

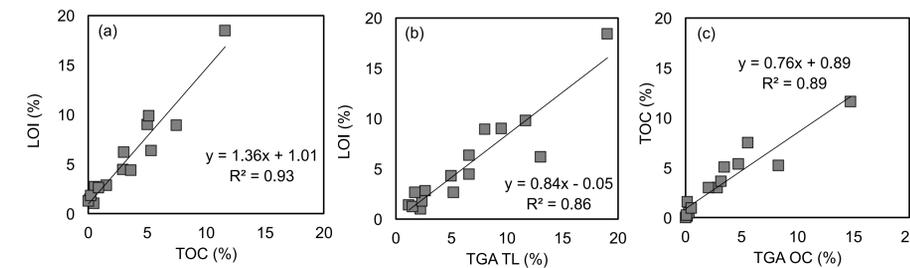


FIGURE 9. Comparison of measurements for total mass loss in reclaimed ash samples (assumed to be primarily due to combustion of carbon), including: (a) loss on ignition (LOI) vs. total organic carbon content (TOC), (b) LOI vs. thermogravimetry total mass loss (TGA TL), and (c) TOC vs. organic carbon content measured by TGA (TGA OC)

The LOI measurement was similar to the total mass loss measured by TGA (TGA TL). Both the LOI and TGA TL measurements potentially include mass loss due to gypsum dehydration and the decomposition of portlandite ($Ca(OH)_2$) to lime (CaO). These measurements consistently overestimate the organic carbon content in the ash. However, the total organic carbon content was similar to the TGA OC measurement. Using either a TOC analyzer or TGA in an oxidizing atmosphere provides the most accurate representation of the true organic carbon content in a sample of reclaimed fly ash.

Conclusion

Fifteen reclaimed fly ash samples were compared to a sample of fresh fly ash to determine how weathering may have influenced the chemical and physical properties of the ash. This study focused particularly on the formation of tertiary mineral phases after ponding and any alterations in the organic carbon in the fly ash due to weathering. Calcium, barium, and iron sulfates were the most readily identifiable tertiary mineral phases in the reclaimed ash. Iron sulfates, in particular, acted as binder phases, creating large particle agglomerates. The precipitation of sulfates into the ash pore spaces may impede water flow through the ash, so it is important to identify these phases. The organic matter (carbon) in the fly ash was present as large, highly porous particles, which were structurally unaffected by weathering. The best method for determining the organic matter content in the fly ash was found to be using a TOC analyzer or using thermogravimetry in an oxidizing atmosphere.