

Evolution of the Properties of Organic Matter and Mineral Phases of Reclaimed Coal Fly Ash

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ABSTRACT

Recent trends in the supply of commercial fly ash have generated interest in potential re-use applications for previously geologically-disposed, reclaimed fly ash. However, it is important to determine if aging through the exposure of ash to weathering elements (e.g., wind, rain, etc.) has significantly changed the ash properties over time because ponding in saturated storage conditions can alter the geochemical and hydraulic properties of the fly ash. Processes such as precipitation of tertiary mineral phases can occur in the ponds, and can complicate productive reuse due to issues such as impeding water flow through the ash, complicating the process of dewatering. The work performed in this study identified the organic material changes and possible tertiary mineral precipitates in samples of reclaimed fly ash and compared them to fresh fly ash. Thermogravimetry, X-ray diffraction, total organic carbon analysis, and X-ray fluorescence were used to measure the fly ash chemical constituents. Preliminary results show that the carbon content in these fly ashes was organic carbon, not inorganic carbonates. Also, reclaimed ashes were depleted in soluble salts compared to fresh fly ash, most likely attributed to the weathering processes. There was also visual evidence of new, binding mineral phases which created large particle agglomerates. The precipitation of new minerals may reduce the overall pore volume and constrict water flow, and ash re-use; however, further testing is needed.

Introduction

An upsurge in domestic natural gas usage has contributed to a decrease in fly ash production, driving suppliers to consider beneficial use of alternative ash products. Reclaimed, previously-disposed fly ash is a potential new source of coal fly ash that is being examined for use in concrete applications, including as a supplementary cementitious material (SCM). A particular application as an SCM would be for alkali-silica reaction (ASR) mitigation. However, exposure to weathering and aging agents may have altered the geochemical properties of the ash, rendering it unsuitable for beneficial use in concrete. Deposition of new, hardened mineral phases after ponding may also clog pores spaces in the ash, complicating the process of dewatering the pond and reclaiming the ash. The evolution of organic and inorganic carbon phases and the formation of new mineral phases are of particular importance to determine if reclaimed ash can be economically mined and productively beneficiated.

Carbon in Coal Fly Ash

Unburned carbon content is an important parameter for determining fly ash suitability in concrete because unburned carbon acts as an adsorbent for concrete air-entraining agents (AEA), reducing the effectiveness of the AEA in freeze-thaw crack prevention (Freeman et al. 1997 and references therein). The concrete industry standard for determining unburned carbon content in fly ash is ASTM D7348, which measures mass loss of a sample after it has been combusted under oxidizing conditions in a muffle furnace at 750°C (Method A) or 950°C (Method B) (ASTM 2013). The mass loss is assumed to be due to combustion of unburned carbon and volatilization of organic carbon, but this bulk measurement captures mass loss from inorganic carbonation, dehydration of clay minerals, and decomposition of other volatile mineral phases such as calcium hydroxide (Payá et al. 2002; Styszko-Grochowiak et al. 2004; Vassilev and Vassileva 2007). Additionally, loss on ignition (LOI) provides little to no information about the carbon phases present in the ash. Coal fly ash may contain both inorganic carbonates and organic carbon residues resulting from incomplete coal combustion (Payá et al. 2002; Schure et al. 1985; Villain et al. 2007). The larger-sized, amorphous, organic carbon residues are the most likely phase to interact with air-entraining agents (Freeman et al. 1997; Hill et al. 1997). Determining total organic carbon (TOC) content and inorganic carbon (IC) content separately from LOI is more insightful than relying solely on a bulk mass loss measurement.

Mineral Phases in Coal Fly Ash

Mineral phases in fly ash include both organic chars from incomplete combustion and inorganic aluminosilicate glass, iron, clay and other mineral phases that were inherited from the parent coal (primary) or transformed during high temperature combustion (secondary). The most abundant mineral phase in coal fly ash is glassy aluminosilicates (Vassilev et al. 2003). Major crystalline phases include mullite, hematite, magnetite, and

quartz, though x-ray diffraction (XRD) analyses also indicate the presence of amorphous, reactive silica (Jones et al. 2006; Yeboah et al. 2014). There is a distinct rise in many XRD scans of fly ashes between 2Θ angles of 15° and 40° , commonly referred to as an amorphous hump, which indicates the presence of amorphous silica (Das and Yudhbir 2006; Jones et al. 2006; Musić et al. 2011). Other amorphous and crystalline mineral phases found in coal fly ashes include kaolinite, plagioclase, K-feldspar, corundum and anhydrite (Vassilev et al. 2003). Feldspars, quartz, and corundum are a few primary phases with high melting temperatures that are present in the parent coal and remain in the fly ash after combustion (Vassilev et al. 2003). Secondary minerals that formed during combustion may include iron oxides, anhydrite, mullite, and calcium silicates (Vassilev et al. 2003).

Mineral Phases in Reclaimed Coal Fly Ash

Prolonged exposure to weathering elements and introduction of water to fly ash during transport to final storage facilities allows for the formation of new, tertiary mineral phases that may not be present in freshly-combusted fly ash. Gypsum and other sulfates with bonded water molecules, carbonates, and chlorides are some possible tertiary phases (Vassilev et al. 2003). These phases are often encrusted on fly ash glass phases or occur as discrete particles within the fly ash matrix (Eze et al. 2013; Vassilev et al. 2003). Some of the active calcium phases present in the fresh ash undergo cementation and hardening after water exposure and evaporation, binding ash phases into larger conglomerates (Vassilev and Vassileva 2007). Weathering may also remove soluble salt minerals from the fly ash surface. Soluble alkali-earth oxides including CaO and K₂O may be leached from fresh fly ash after exposure to precipitation, and these compounds are often present in reduced quantities in reclaimed fly ash (Akinyemi et al. 2012).

Materials and Methods

Two samples of reclaimed coal ash, labeled PW1 and PW2, were taken from an ash plant in Georgia in Spring 2016. This plant operates as a natural gas/coal combination plant, and bottom and fly ash are still being produced and disposed on-site in ash ponds. The ashes are hydraulically sluiced to the ash pond and wet deposited. Samples were taken from the ash delta, at a depth of 0.5 ft because there was no standing water, though the samples were still saturated with water. The surficial ash crust was removed before sampling. Samples are a combination of fly ash and bottom ash. A sample of the fresh fly ash directly from the ash silo was also collected at Plant PW and analyzed as a control.

All ash samples were oven-dried overnight at 100°C to remove water. The samples were then ground with mortar and pestle (if necessary) and stored. To isolate

the fly ash particles for analysis, samples were sieved using a No. 200 (75 μ m) sieve. Particles passing the No. 200 sieve were collected and used for analysis. No other alterations of the samples were performed before characterization.

Physical characteristics, including specific surface, specific gravity, loss on ignition (LOI), and grain size distribution, were measured. Specific surface area was measured by N₂ adsorption (ASAP 2020) and the Brunner-Emmett-Teller (BET) theory. Grain size analysis was performed using a Malvern 3000 Hydro EV laser particle size analyzer. Specific gravity was analyzed in a helium atmosphere (Quantachrome ULTRAPYC 1200e), and LOI was determined by heating samples to 750°C in a muffle furnace, according to ASTM D7348, Method A. Organic and inorganic carbon phases were determined using a Shimadzu TOC-V Analyzer fitted with a solid sample module (SSM-5000A). Inorganic and total carbon content were measured, and total organic content (TOC) was determined by subtraction. Visual classification was determined by scanning electron microscope (SEM), using a Hitachi SU8010. Major elemental composition (expressed as oxides) and crystalline surface groups were identified using x-ray fluorescence (XRF) spectrometry (Brucker S8 Tiger) and x-ray diffraction (XRD) (Panalytical Empyrean), respectively.

Results and Discussion

Carbon Phases in Fresh and Reclaimed Fly Ashes

Both fresh and reclaimed fly ash samples had undetectable levels of inorganic carbon and measurable levels of organic carbon, and the organic carbon content was less than the loss-on-ignition. The consistently-higher LOI values were most likely due to the release of volatile material, the dehydration of clay minerals, and the decomposition of carbonates during high heating in a muffle furnace (Table 1) (Vassilev and Vassileva 2007). The high LOI and TOC values in the reclaimed samples corresponded to elevated specific surface areas, but the same trend was not observed in the PW_Fresh sample (Table 1). Higher values of specific surface area due to the porous nature of unburned carbon has been reported by others (Girón et al. 2013; Yeboah et al. 2014). Visual observation from SEM images confirms that the unburned organic carbon phases in all samples are some of the largest, most highly porous discrete particles in the fly ash (Figure 1).

Table 1. Physical Properties of Two Reclaimed Fly Ash Samples, Compared to One Fresh Fly Ash Sample

Sample	Sam W1	F W2	F Fresh	PW
SSA (m ² /g)	.63	.01	7	0.9
G _s ¹	.90	.73	2	2.5
LOI (%)	.65	.79	2	2.1
TOC (%)	.54	.55	1	0.7
D ₅₀ (μm) ²	7.4	3.3	2	18.
C _u ³	.68	.80	0	0.9

¹G_s: specific gravity

²D₅₀: the median particle size, where 50% of particles are smaller

³C_u: coefficient of uniformity = D₆₀/D₁₀

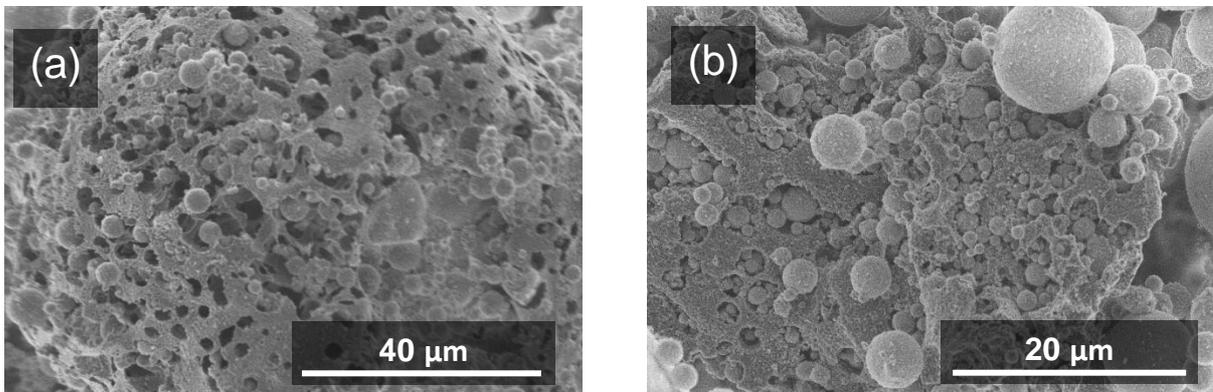


Figure 1. SEM images showing: (a) an unburned carbon particle in a sample of fresh PW fly ash and (b) an unburned carbon sample in a reclaimed PW fly ash sample

Mineral Phases in Fresh and Reclaimed Fly Ashes

Major oxide composition, as determined by XRF, indicates that silica, aluminum, and iron oxides are the most prevalent oxides in all samples. Primary oxide content (POC), as the sum of SiO₂, Al₂O₃, and Fe₂O₃ oxides, is higher in the reclaimed samples than the fresh fly ash, and the calcium, sodium, sulfur, and potassium percentages are lower. The leaching of water-soluble oxides from the disposed ash elevates the relative proportion of the non-soluble, inactive and semi-active primary oxides, which is expressed as an increase in POC (Akinyemi et al. 2012; Vassilev et al. 2003). The

comparatively higher Fe content in the reclaimed samples is also related to this leaching. All samples pass the chemical requirements for a Class F fly ash, according to ASTM C618 (ASTM 2015). Samples were plotted on a ternary diagram, to determine if the relative percentages of calcium, silica and aluminum oxides matched typical pozzolanic or supplementary cementitious materials (SCMs) used in concrete applications (Figure 3). The fresh fly ash has the correct relative proportions to be a Class F fly ash, and the reclaimed ash samples fell just at the border of a Class F fly ash (Figure 3). Some of the chemical and physical changes between the control (fresh) fly ash and the reclaimed ash may be due to changes in combustion conditions and feed coal, as the plant has been commercially operational for over 40 years.

Table 2. Oxide Content of Six Reclaimed Fly Ashes, Expressed as Percentages of Total Oxide Content, Compared to One Fresh Fly Ash Sample, as Analyzed by XRF

Major Oxides	PW1	PW2	PW_Fresh
SiO ₂	37.43	43.73	48.61
Al ₂ O ₃	16.95	19.82	20.69
Fe ₂ O ₃	38.77	27.66	16.01
SO ₃	0.54	0.3	1.78
CaO	1.1	1.83	5.97
Na ₂ O	0.41	0.51	0.94
MgO	0.55	1.01	0.83
K ₂ O	1.82	2.18	2.33
P ₂ O ₅	0.16	0.14	0.12
TiO ₂	0.93	1.08	1.05
SrO	0.07	0.08	0.05
BaO	0.07	0.09	0.05
LOI (%)	2.65	2.79	2.15
POC (%)	98.8	98.43	85.31

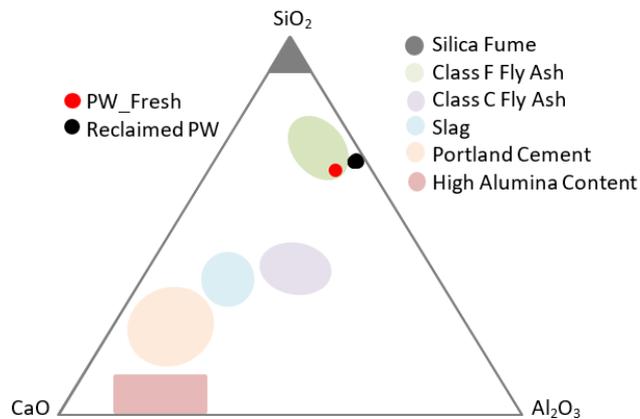


Figure 2. Ternary diagram of silicon dioxide, lime, and aluminum oxide content of PW coal fly ash samples, where oxide contents are normalized with respect to the sum of silicon dioxide, calcium oxide, and aluminum oxide equaling 100%, compared to six standard pozzolanic materials used in concrete applications

Visual observation using SEM highlights the heterogenous nature of mineral phases in fresh and reclaimed fly ashes. Some of the aluminosilicate glassy spheres of the fresh fly ash sample were heavily encrusted with a variety of mineral phases mineral groups, possibly including iron oxides, silicates, and sulfates (Figure 3a). Further research using energy-dispersive X-ray spectroscopy (EDS) will be performed to identify these phases. In the reclaimed ashes, a distinct, needle-like crystalline formation was observed at interfaces between aluminosilicate glassy spheres and a potentially cementitious binding phase (Figure 3b). Vassilev et al. identified similar phases in a Spanish coal fly ash as “needle anhydrite crystals,” although iron oxides sometimes also grow in needle-like structures (Vassilev et al. 2003).

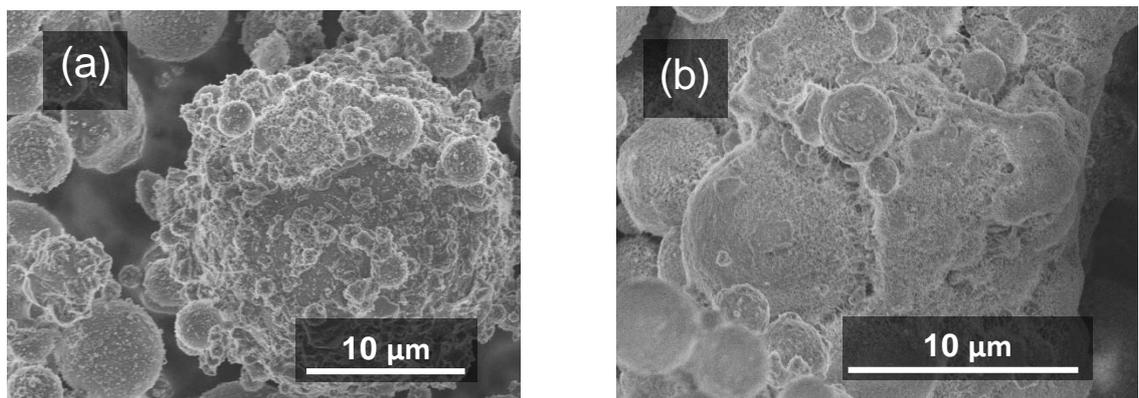


Figure 3. SEM photos of (a) fresh and (b) ponded PW fly ash, showing (a) an encrusted aluminosilicate sphere and (b) a large conglomeration of aluminosilicate spheres with needle-like surficial extrusions

XRD analysis indicates that hematite, magnetite, quartz and mullite are the dominant crystalline forms found in both the fresh and reclaimed ash samples (Figure 4). Portlandite was present in the fresh PW fly ash (specifically at 18 and 34° 2θ) but not found in the reclaimed ash. The distinct amorphous hump between 15 and 40° 2θ indicates the presence of reactive silica.

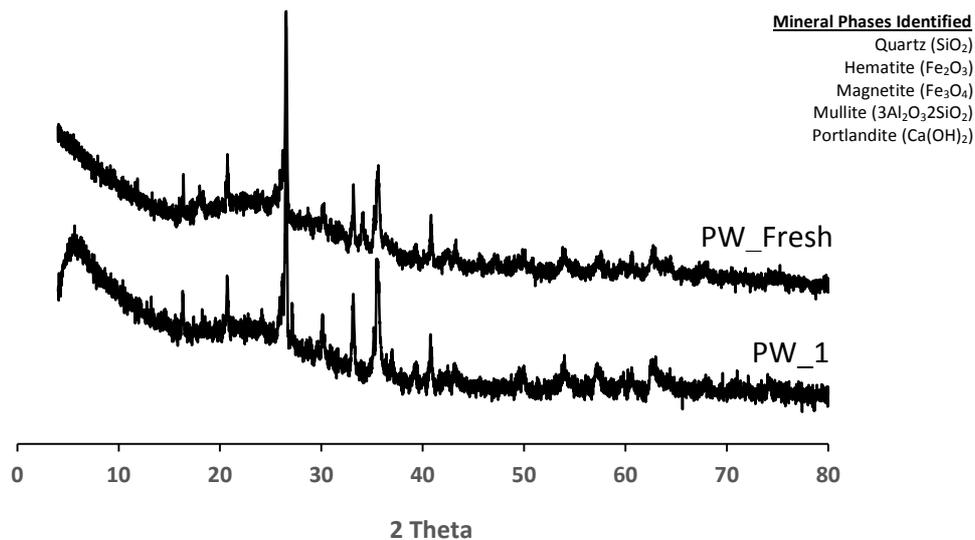


Figure 4. XRD scans of reclaimed and fresh fly ash samples, indicating that quartz, hematite, magnetite and mullite are the major crystalline components in fresh and reclaimed PW fly ashes. The distinct rise between 15 and 30° 2θ also indicates the presence of amorphous, reactive silica.

Conclusion

Carbon phase analysis indicated that all samples had only organic carbon phases and no inorganic carbonates. The LOI was consistently higher than the amount of organic carbon. XRD analysis confirms that no crystalline carbonates were found in any of the samples, though the fresh fly ash sample had portlandite (Ca(OH)₂). Reclaimed ash samples were diminished in soluble salts, indicating that exposure to water will leach soluble salts from fly ash. However, all samples have retained their inactive or semi-active crystalline compounds after weathering, including mullite, hematite, magnetite and quartz. Samples also retained their reactive silica after weathering and are classified as Class F fly ashes according to the chemical requirements of ASTM C618. However, a pozzolanicity test should be performed on these samples to determine if the samples will be reactive when used in concrete. Visual observation indicates that tertiary mineral phases may act as binding agents, producing large agglomerates of aluminosilicate spheres and other phases. Precipitation between particles may clog

available pore spaces in the reclaimed fly ash, reducing the hydraulic conductivity and complicating dewatering. More research is needed to determine exactly how tertiary mineral phases influence in-situ hydraulic properties of reclaimed fly ash.

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