# Introductory Chapter: Coal Fly Ash and Its Application for Remediation of Acid Mine Drainage

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## 1. Introduction

The coal mining and other metal extraction industry contributes significantly to the country's economy through export markets of the processed minerals in addition to creation of thousands of jobs in the mining industry. For example, in South Africa, 98% of the country's electricity supply is from coal combustion. Coal mining and coal combustion for electricity generation leaves in its wake various types of waste streams such as acid leachate generating coal discards, acid generating mine tailings, and acid mine drainage (AMD) in mine voids and huge volumes of coal fly ash (CFA) in power utilities. Environmental regulations require these waste streams to be managed and remediated to reduce any negative impact on the environment. Of most concern and increasing interest is the prevention and control of acid mine drainage (AMD) and its treatment. Acid mine drainage has the potential to impact negatively on aquatic ecosystems and groundwater availability in particular. Acid mine drainage (AMD) is generally regarded as the principal environmental problem caused by the mining of the sulfide ore deposits. In coal combustion in power utilities, huge volumes of coal fly ash (CFA) are produced annually and this is normally stockpiled on land as ash heaps that require management due to possible negative environmental impacts such as generation of leachates with high concentration of toxic metal and non-metal species which could affect the quality of surface and groundwater resources in addition to the generation of particulate pollution.

## 2. Acid mine drainage generation and negative environmental impacts

Acid mine drainage is generated when sulfide minerals in the mined rock or overburden are exposed to oxygen and water during the mining process. These sulfide minerals include but not limited to pyrite ($FeS_2$), its dimorph marcasite, and pyrrhotite ($Fe_{1-x}S$). These sulfide

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minerals undergo bacterially catalyzed oxidation reactions which generated acidity and increased Fe, sulfate, and other toxic metal species concentration in recipient water bodies such as groundwater in mine voids [1] (Eq. (1))

$$FeS_2(s) + 3.75\,O_2 + 3.5\,H_2O \rightarrow Fe\,(OH)_3(s) + 2\,SO_4^{2-} + 4\,H^+ \quad (1)$$

AMD is extremely acidic (as low as pH 2.0) and enriched with iron, manganese, aluminum, sulfate, and metal species such as lead, mercury, cadmium, and zinc depending on the geology of the mined rock [2]. During active mining operations, the groundwater is normally pumped out to maintain water table below mining levels but once mining stops pumping stops and the mine voids fill with acid mine drainage and eventually decant to the surface. This mine water requires management, which involves storage and treatment to the specific country's disposal guidelines before disposal to surface water bodies.

Influx of acid mine drainage (AMD) into streams can degrade both aquatic habitat and water quality, often producing an environment devoid of most aquatic life. The extent of impact on aquatic ecosystems depends on a variety of factors which includes frequency of influx, volume, and chemistry of the AMD, and the buffering capacity of the receiving aquatic ecosystem [3]. Drainage from underground mines, surface mines, and refuse piles is the oldest and most chronic industrial pollution associated with coal mining. Various impacts of AMD include quality impacts on groundwater, corrosion of water supply infrastructure, and other manmade structures such as pipes, bridges, dams, and pumps. Acid mine drainage can also be toxic to vegetation; however, toxicity depends on discharged volume, pH, total acidity, and concentration of dissolved chemical species. pH is the most critical with respect to aquatic life. Smothering of stream beds from precipitated metal compounds is a common phenomenon in AMD-impacted streams [4, 5]. Acid mine drainage can also cause reduction in diversity and total number of micro-invertebrates and changes in community structure.

## 3. Coal fly ash generation and its physicochemical properties

Coal fly ash (CFA) is a by-product obtained during the combustion of coal in coal-burning power generation plants. As demand for cheaper electricity increases, huge volumes of coal fly ash will be generated that will require disposal and management. The worldwide annual production of CFA stands at 780 Mt [6] while 415 Mt or 53% is beneficially utilized, but utilization varies across countries. Japan has the highest utilization rate at 96.4%, Europe 90.9%, China 67%, and Middle East and Africa 10.6% [6]. The rest of the CFA is stockpiled on land or slurried to ash dams [7, 8]. South African Bureau of Standards (SABS) [9] defines fly ash as the powdery residue obtained by separation of the solids from the flue gases of furnaces fired with pulverized coal. Coal fly ash consists of many small (0.01–100 μm diameter) glass-like particles of a generally spherical character. The fineness of fly ash particles depends largely on the combustion temperature, the grinding size of introduced coal, and whether the resultant particle is spherical or irregular. The physicochemical and mineralogical properties of CFA depend on the composition of the parent coal, the conditions during coal combustion (temperature, air/fuel ratio, coal pulverization size, and rate of combustion), the efficiency of emission control devices, the storage and handling of the by-products, and the climate [10, 11].

Coal fly ash tends to accumulate toxic chemical species at high temperatures involved during its generation [10, 12] and is considered an environmental hazard in some countries. Anionic species ($Cl^-$, $SO_4^{2-}$), oxy-anionic species (Se, As, Mo, B, and Cr), and cationic species (Al, Fe, Na, K, Ca, Sr, Ba, Zn, Cu, Cd, and Mg) are leached from the ash heaps by the wastewater derived from the ash slurry or by subsequent infiltration by rain upon disposal [8, 10, 13]. This may be of environmental concern due to possible contamination of surface and groundwater in disposal sites and limits beneficial application of CFA. The pH of a fly ash suspension, for example, in water can vary depending on the S content of the parent coal [14]. Fly ashes derived from anthracite coals are generally high in S and produce acidic fly ashes while fly ashes derived from lignite coals are low in S but high in Ca and produce alkaline ashes [15, 16]. South African coal is sub-bituminous and generates fly ash that is characterized by low Fe content. The aqueous extracts of this high Ca coal fly ash are strongly alkaline (pH 12–12.5) due to the free lime content [2, 17]. Mineralogical analysis indicates coal fly ash to be mainly aluminosilicate which forms the basis of its utilization in the synthesis of geopolymers [18], zeolitic adsorbents for water treatment [19]. X-ray diffraction also indicates that CFA has free lime content ranging from 1 to 40% depending on the coal source [6]. This free lime content is the basis of fly ash utilization in acid mine drainage treatment [2] and remediation of acidic mine spoils and control of acid mine drainage generation in sulfidic mine tailings [11].

## 4. Acid mine drainage treatment using coal fly ash

Acid mine drainage is characterized by high acidity (pH 2–4) and often contains high concentrations of chemical species such as Fe, Mn, and Al and anionic species such as $SO_4$ in addition to elements like Zn, Co, Pb, Cr, and Cu, in trace concentrations which necessitate these waters to be treated before release. Management of mine water pollution demands a range of active and passive remediation engineering technologies to minimize its impact on ground and surface waters which can incur significant expense [20]. Consequently, mining companies are in constant search for innovative and economically viable treatment technologies. Traditionally, the remediation of AMD has been carried out through a range of active and passive technologies. Active treatment technologies involve the use of alkaline reagents such as limestone and lime [21, 22], and magnesite [23]. Some of the limitations of limestone treatment processes include armoring of limestone particles by amorphous ferric hydroxide precipitates which reduces the efficiency of treatment process and attains a maximum pH of 7 which leaves species such as Mg in solution [24]. A limitation of lime is its high cost [24]. Passive treatment systems involve a combination of alkaline reagents and utilization of natural biochemical processes in artificially constructed wetlands, ponds, and alkaline-generating drains [25–27]. Innovative acid mine drainage treatment using unconventional alkaline agents such as slag has been evaluated [28, 29]. The steel slags on contact with the AMD increased the pH to circumneutral levels and reduced the levels of most major inorganic contaminants such as

Al, Fe, Ti, Ni, Be, and Cu. However, the slag was observed to leach chemical species in the reaction mixture leading to an increased concentration of Ba, V, Mn, Cr, As, Ag, and Se in the leachates. This would be a major drawback of employing the steel slags in AMD treatment due to the secondary contamination of the product water.

Several research studies have reported on the application of coal fly ash for the amendment of acidic coal mine spoils [30] and of acidic soils [31]. These applications were motivated by the alkaline nature of the coal fly ash. Other researchers have reported on the ability of the coal fly ash to remove metal species from aqueous solutions [32–34].

Due to the pressure on the mining companies to reduce the cost of acid mine drainage treatment, they are constantly looking for cheaper treatment agents for AMD. On the other hand, most coal combustion power utilities are constantly looking for large volumes of beneficial coal fly ash generated by their coal combustion process. In most instances, the coal mines generating AMD are located close to the power utilities producing coal fly ash. This has motivated researchers to look at the possibility of utilization of coal fly ash as liming agent for AMD. Coal fly ash contains free lime content that can be used in the neutralization of AMD leading to an increase of pH and precipitation of the metal ion contaminants as insoluble hydroxides, oxyhydroxides, or oxyhydroxysulfates [17, 35].

Coal fly ash has also been beneficiated into zeolitic materials that are used as adsorbents for metal species in AMD effluents. These zeolites possess adsorptive properties and provide a combination of ion exchange and molecular sieve properties [36, 37]. Results of the treatment of AMD with CFA zeolitic product indicated an increased pH and a decreased metal concentration. These materials have advantage over traditional liming materials such as lime or limestone since they are cheaply produced and contribute to sustainable management of coal fly ash.

Although coal fly ash will continue to attract researchers working on cheaper options for the treatment of AMD in both active and passive systems, it is important to note some of the shortcomings and strengths of its application for AMD effluent treatment. Several authors [2, 17, 35] observe that coal fly ash can effectively increase the pH of AMD and decrease its metal species concentration leading to much cleaner product water. The process was observed to be effective for the treatment of acidic AMD [2]. However, the application of CFA for AMD treatment leads to the release of Na, Cl, K, Mg, B, Sr, Ba, and Mo leading to an increased salinity of product water. The chemistry of the coal fly ash and AMD being treated will be a significant determinant factor on the success of the treatment process in addition to the contact time employed. The authors further observed that the treatment process will be combination specific, meaning that different CFA:AMD combination ratios will give product water with varying quality.

## 5. Conclusions

Coal fly ash can be used effectively to treat AMD. However, the process has its strengths and weaknesses. The treatment technology will be dependent on the chemical properties of the coal fly ash and the AMD effluents being treatment. This means that the treatment process has to be optimized for each coal fly ash/AMD combination for effective results. The product water in this treatment process will require secondary treatment such as reverse osmosis to remove the increased salinity of the product water. Most countries have environmental legislation that classify coal fly ash as a hazardous material, hence reducing its development and utilization as a beneficial material. However, there is still a lot to be learned in terms of the application of coal fly ash and its products for remediation of acid mine waters.

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