



The surface chemistry of leaching coal fly ash

Ramasubramania Iyer*

Department of Chemical Engineering, University of Queensland, St. Lucia, Qld 4072, Australia

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Abstract

The utilization of coal fly ash in the construction and non-construction areas has seen a rapid growth in the last decade. As production outweighs the utilization of fly ash, its disposal as a dilute or dense slurry is still practiced in coal fired power stations. In this review the surface chemistry of leaching coal fly ash is presented to highlight the role of mass transfer in providing resistance and consequently delayed leaching of elements, when fly ash is disposed or used for value addition. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Surface chemistry; Leaching; Coal fly ash; Disposal; Mass transfer

1. Introduction

The disposal of fly ash as a by-product of incineration of coal, is a more significant problem than ash produced from burning of municipal solid wastes, sugarcane bagasse, rice husks or tea dusts because of its volume. Fly ash finds reuse primarily in cementitious products [1,2], construction areas such as highway road bases [3] grout mixes [4] stabilizing clay based building materials [5]. Utilization of fly ash in materials other than the construction industry has been reviewed by Iyer and Scott [6]. However despite positive uses, the rate of production is greater than the consumption. For the unused fly ash, disposal practice involves holding ponds, lagoons, landfills and slag heaps. There are coal based power plants situated in places where disposal sites are difficult to locate. The limited availability of space and tightening of regulations of leachate water and the subsequent discharge requires prudent management to satisfy regulatory bodies. The surface chemistry of leaching coal fly ash (CFA) during disposal and value addition is presented in this review.

* Tel.: +61-7-33659062; fax: +61-7-33654199.

E-mail address: ramai.i@hotmail.com (R. Iyer).

2. Size dependent leaching properties of fly ash

Coal fly ash is a heterogeneous material, both between particles and within the particle [7]. The formation of inorganic pollutants during coal combustion has been reviewed [8]. A detailed study on the elements versus particle size distribution shows that there is an inverse dependence on concentration with respect to particle size for some elements. Elements were divided into two groups on the basis of their concentration dependence upon particle size, those with no enrichment in the smallest particle size and those which are enriched. Results of the analysis by particle size indicates that the elements Mn, Ba, V, Co, Cr, Ni, Ln, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg and S are usually volatile to a significant extent in the combustion process. The volatility for these elements is inversely proportional to the particle size. Elements Mg, Na, K, Mo, Ce, Rb, Cs and Nb appear to have a smaller fraction volatilized during coal combustion or have significant variations in behavior between plants. Here the volatility is directly proportional to particle size. The measured elements Si, As, Fe, Ca, Sr, La, Sm, Eu, Tb, Py, Yb, Y, Se, Zr, Ta, Na, Th, Ag and Zn are either not volatilized or may show minor trends which is related to geochemistry of the mineral matter. In some cases, the concentration dependence on particle size has yielded surprising results. In one example the concentration of Ca and Sr reach a maximum concentration in a particle size of 5 μm and then decreases with increase in particle size. The volatility of trace elements increased from a larger particle size to a smaller particle size which establishes an inverse relationship of volatility and particle size [9].

It was found that the surface layer of fly ash particles probably only microns in thickness, contains a significant amount of readily leachable material which is deposited during cooling after combustion [10]. A plot of the inverse of particle size ($1/d_{32}$) versus conductivity of the ions in the leached solution shows that the intercept $1/d_{32} = 0$, i.e. infinite particle size, represents the contribution of ions from the bulk of the particle [11]. The increase in conductivity with increasing $1/d_{32}$ is contribution from the shell of the particle. This is presented in Fig. 1. The study was conducted on fly ashes obtained from two coal fired power stations, Curragh and Tarong with a particle size of less than 2 μm . This air-cyclized fraction was analyzed in a Malvern particle size analyzer based on the principles of laser diffraction. Sauter diameter was used to grade the micron size. Tarong fly ash leachate had a

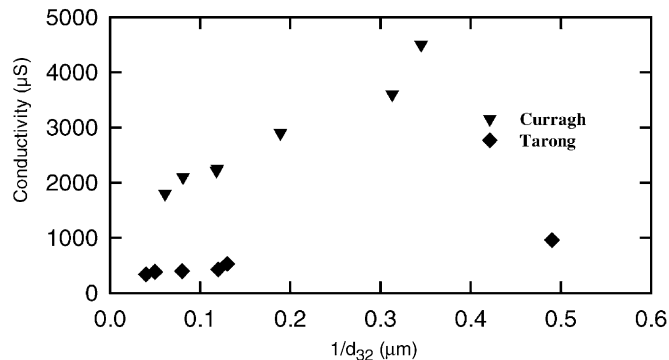


Fig. 1. The increase in conductivity with increasing $1/d_{32}$ [11].

lower ionic strength compared to Curragh fly ash. With the smaller particles the contribution of the surface becomes larger. When fly ash is disposed as a dense slurry, the fine particles ($-10\ \mu\text{m}$) contributes to non-Newtonian behavior of the slurry [12]. The explanation of these leaching mechanisms is presented in Section 4.

3. Leachate chemistry

There are two types of fly ashes produced from coal combustion, types F and C. Type F is produced when anthracite, bituminous or sub-bituminous coal is burnt and is low in lime ($<7\%$) and contains more silica, alumina and iron oxide. Type C comes from lignite coal and contains more lime (18%). The major oxides of types C and F fly ash is as follows (<http://www.cpmash.com/ash/flyash.html>). The minor oxides are not mentioned.

Oxide (%)	Type F	Type C
SiO ₂	49.90	53.79
Al ₂ O ₃	16.25	16.42
Fe ₂ O ₃	22.31	5.00
TiO ₂	1.09	1.55
CaO	4.48	18.00

The fly ashes, Curragh and Tarong mentioned in this review are of the type F. Fly ash has hydrophilic surface and is extremely porous, with particle size the most important characteristic determining reactivity. The smaller particle has a larger specific surface area, making a larger area susceptible to hydrolysis [13]. Studies have shown that only about 1–3% fly ash material is soluble in water with lignite fly ashes having a higher proportion of water soluble constituents [14]. The leaching of major elements from CFA has been extensively reviewed [15]. Analysis of water extracts [16,17] showed that the principal cations in water extracts are calcium and sodium whereas anions are dominated by OH⁻, CO₃ with aqueous extracts of the ash nearly saturated with Ca(OH)₂. The alkalinity and acidity controlled the extractability of elements like As, B, Be, Cd, Cr, Cu, F, Mo, Se, V and Zn. Aqueous extracts of an acidic fly ash contained concentrations of Cd, Co, Cu, Mn, Ni, Zn, As, B, Be, Cd, F, Mo, Se and V [18,19]. Leachate waters can have markedly different compositions, depending on the surface of fly ash, flue gas process conditions design of combustion systems and whether lime or lime stone injection processes were implemented for desulfurization. Total dissolved solid concentrations may vary from hundreds to tens of thousands of milligram/liter. Even a small sample can show marked differences in leachate water chemistry, depending on reaction time and water/solid ratio in batch equilibration's or with column length and flow rate in a dynamic leaching test. The mineral and glass phases that constitute fly ash material are formed over a wide range of temperatures in the furnace environment. All these phases are unstable. They dissolve and then precipitate as stable and less soluble secondary phases. The primary phases even though highly soluble in water especially in dissolve very slowly as they are trapped in the glass and crystalline aluminosilicates. Secondary hydrous aluminosilicate products are shown to be very insoluble [20] and build up on rinds on the surfaces of primary phases. The dissolution of primary phases

is slowed down as the mass transport of ions and water between phases becomes diffusion controlled. Two opposing processes to establish the pH of the leachate has been proposed [21].

- (1) The dissolution and hydrolysis of oxide components such as CaO and MgO contribute to an increase in solution pH



Offset by pH increase caused by basic components, is the dissolution of soluble acids, such as B_2O_3 and salts containing hydrolysable constituents such as $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$.

- (2) There is a slow dissolution of silica from fly ash particles. This reaction is provided at both high and low pH, resulting in the formation of silicic acid.



Sorption studies of arsenate and selenite on three major elements haematite, portlandite and haematite found in fly ash samples showed that when sorption is reversed arsenate is leached at a slower rate than selenite [22]. This explains partly the low availability of arsenic during leaching of fly ash and the consequent delay in detecting arsenic. Readers interested in the standard USEPA tests of toxicity characteristic leaching (TCLP) and extraction procedures should refer to [23].

4. The mechanism of leaching CFA during disposal and value addition

4.1. The leaching of CFA during disposal

There are two methods of disposing fly ash, one as a dilute slurry and the other as a dense slurry. For a dilute slurry disposal system effective water management techniques are required. The dilute slurry disposal even though still in use in several countries has been effectively replaced by a dense slurry disposal system at the Stanwell power station in Queensland, Australia [24]. In this process the ash, rather than being sluiced from hoppers with a stream of water, is added to a stirred tank with continuous water addition to give a slurry with controlled density. This is then pumped continuously by a positive displacement pump through a pipeline to the disposal point. The disposal area is a gentle sloping piece of land which allows the slurry to discharge. The discharge point is moved periodically around the site to build up an even deposit. The disposal in a sloping piece of land takes place till the slurry is immobilized due to evaporation of water.

The disposal of fly ash as a dilute slurry involves the construction of large ash ponds along with the construction of a new power station to receive all ash which will be produced during the life cycle of a power station. The ash is conveyed to these disposal sites by hydraulic conveying as a dilute slurry. The slurry is allowed to settle and the water recycled for further conveying of ash as a dilute slurry. The recycling of water from the settled slurry builds up the concentration of solids in water. The leaching of toxic elements takes place when fly ash is disposed as a dilute slurry. In the field studies of leachability of aged brown CFA [25]

a slurry of coarse ash and bottom ash was pumped to a distance to an ash disposal pond and monitored for a year and it was found that the ash is an unsaturated porous material and the evaporation controls the production of leachate.

Experiments conducted on different CFA/water ratios showed that leaching could be extended up to 140 days [26]. It was concluded that the concentration of ions in leachates is controlled by the solubility of particular minerals and chemical equilibrium models can be used to predict leachate concentration of elements whose dissolution is controlled by reaction kinetics [27]. The leaching of elements from fly ash as a dilute slurry takes an indefinite period to attain steady state. The dissolution of ions from charged fly ash particles as solid liquid mass transfer of ions across the diffuse double layer provides insights into the prolonged delay to achieve a steady state. The novelty of the mass transfer model is that it amounts for the accumulation of ions in the diffuse double layer around the charged fly ash particle. The leached ions traverse two spherical shells surrounding the particle, e.g. the diffuse double layer and bulk convective layer (see Fig. 2) has been experimentally shown by exchange of ions, that the ions namely calcium as $\text{Ca}(\text{OH})_2$ is retained in the diffuse double layer. The retention of ions coupled with the resistance of the diffuse double layer provides an explanation for the delayed achievement of steady state. Calculations of the mass transfer coefficients from the surface of fly ash particle into the diffuse double layer (K_1) and from the diffuse double layer into the bulk convective layer (K_2) indicates that leaching of ions from the surface of fly ash into the diffuse double layer is the rate controlling step. The concentration of calcium within the fly ash particle is uniform till it reaches the surface wherein the surface charge of the fly ash particle alters the rate of leaching [11,28].

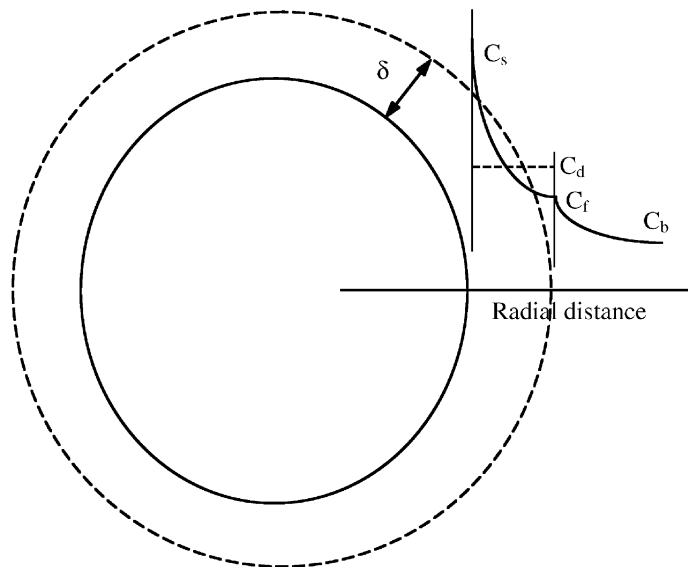


Fig. 2. Mass transfer across the surface of fly ash particle [11]: δ , diffuse double layer on the surface of fly ash particle (nm); C_s , concentration of calcium hydroxide (mg/l) at particle surface; C_d , concentration of calcium hydroxide (mg/l) in the double layer; C_f , concentration of calcium hydroxide (mg/l) at the double layer boundary layer interface; C_b , concentration of calcium hydroxide (mg/l) in the bulk.

The disposal of fly ash as a dense slurry was quantified by correlating surface chemistry to rheological properties. Two fly ashes with the same particle size ($-10\ \mu\text{m}$) but having leachates of different ionic strengths were considered [12]. When dense aqueous slurries of these fines ($-10\ \mu\text{m}$) were subjected to rheological measurement in a rotating viscometer, the two ashes exhibited different packing propensities. To interpret the flow properties, the authors redefined a packing fraction (ϕ_m) to include the volume of the diffuse double layer. The thickness of the diffuse double layer is approximated by the inverse of the Debye Huckel parameter and its value depends on the ionic concentration of the leachate and the temperature. At $25\ ^\circ\text{C}$ in water, the value is given by $\delta = 0.304 \times 10^{-9} I^{-1/2}$, where I is the ionic strength and δ is the diffuse double layer thickness in nanometers. In the study on two fly ashes from Curragh and Tarong power stations it was found that the differences in rheological behavior and variation in ϕ_m is due to the surface chemistry of fine particles. The diffuse double layer was calculated based on the ionic strength of $\text{Ca}(\text{OH})_2$. The two fly ashes produce leachates of different ionic strength and hence generate different thicknesses of the diffuse double layer. Shearing at close packing produces distortion in the diffuse double layer, especially in dilute leachates with thick diffuse double layers. A particle packing model based on fly ash particle as a point in a unit cell was proposed to quantify the distortion of the diffuse double layer, and the subsequent increase in maximum packing fraction (ϕ_m). Fly ash with a thicker double layer (Tarong fly ash) had significant diffuse double layer distortion to have an increase in maximum packing fraction. An increased packing fraction leads to the shear thinning (reduced viscosity) of the slurry for a leachate of low ionic strength. This was correlated by fitting the Krieger–Dougherty equation:

$$\eta_r = \frac{\eta_a}{\eta_0} \left(1 - \frac{\phi}{\phi_m} \right)^{[-\eta]\phi_m}$$

where η_r is the relative viscosity, η_a the apparent viscosity (mPa), η_0 the viscosity of the continuous phase (mPa) and $[\eta]$ is the intrinsic viscosity (2.5 for spherical particles of fly ash).

Two fly ash particles were considered for the distortion of the diffuse double layer in the above model. When distortion is applied to whole matrix of the dense fly ash slurry, this microscopic quantity is shown to have considerable effect on the macroscopic property of flow via the Krieger–Dougherty equation.

4.2. Leaching of CFA for value addition

In the 1980s there was a growing concern over the shortage of aluminum in USA [29,30]. The number of power plants based on coal increased and considerable quantity of fly ash was produced. An alternative method of use of fly ash for recovery of aluminum was initiated. The study of complex treatment of alumina silica containing fly ash by chemical enrichment has been reported [31]. The removal of silica from aluminum containing raw material with high silica content is based on the property of hydroaluminum silicates. Basic silica containing materials undergo intramolecular phase changes by thermal treatment, resulting in the formation of amorphous silica. Leaching the heat treated raw material with sodium hydroxide solution affected dissolution of silica. Al_2O_3 was recovered in the solid

state in the form of alpha or gamma alumina. Silica content in the fly ash was reduced chemically resulting in the utilization of CFA for alumina production. The direct acid leach (DAL) process of electric power station (EPRI) [32,33] has not yet realized its full commercial potential. These chemical processes for recovery of aluminum from fly ash involve high temperature and pressures. This process even though economically inferior to extraction of aluminum from bauxite deposits, has potential as the utilization of fly ash will be preferred to disposal in the future. Further these processes could be a viable proposition for countries without bauxite deposits [34]. The leaching process uses sulfuric acid to the preferred hydrochloric acid as the sulfates formed is used as a chemical agent for *Thiobacillus* bacteria metabolism, during bioleaching processes [35].

The process of leaching of fly ash with 1 N sulfuric acid is described as a heterogeneous non-catalytic chemical reaction that follows the geometry of a shrinking core model [36,37]. With the above outline followed by experiments it was concluded.

- (1) The rate controlling step of aluminum and iron leaching from CFA is the mass transfer at the surface leaching sites and through the leached ash layer.
- (2) The authors found intriguing phenomena of a decrease in aluminum content with an increase in CFA content in the leaching medium which they attribute is due to the precipitation of calcium sulfate at the surface.
- (3) The precipitation of calcium sulfate forms barriers and provides resistance to mass transfer by diffusion and the effect of diffusion length in pores is an additional factor for mass transfer resistance. The addition of calcium chloride reduces the leaching rate as compared to the control, which confirms the formation of calcium sulfate at the surface.
- (4) The above evidence of self-inhibition by calcium sulfate providing the film to resistance was eased by pre-leaching with hydrochloric acid. This step removed a part of the calcium. The kinetics in the second leaching stage with sulfuric acid was therefore enhanced. The overall kinetics of the two step process is reported to be faster as compared to the leaching with sulfuric acid only.
- (5) The leaching process was found to have no effect on the particle size distribution.

5. Discussion

In this review the surface chemistry and mechanism of leaching of CFA has been presented. The leaching of elements, both toxic and non-toxic during disposal has been a focal point of many publications. The delay in achieving a steady state during disposal and the self-inhibition during value addition by leaching with sulfuric acid has interesting conclusions.

The mechanism of leaching during disposal attributes the retention of ions in the diffuse double layer and the subsequent resistance it provides to mass transfer as the key reason for the delayed leaching, whereas the value addition work attributes the precipitation of calcium on the surface sites and their subsequent attachment to the active sites as the cause of self-inhibition and subsequent slow leaching. The investigators use 1 N sulfuric acid for leaching of aluminum from CFA, which will have a large percentage of water. This could lead to the competitive leaching of CFA by water as well as sulfuric acid.

The author of this review, intuitively feels that a diffuse double layer could be formed and calcium from calcium sulfate could be retained in the diffuse double layer apart from the proposition in the value addition model that the surface sites are responsible for holding calcium sulfate. The authors of the self-inhibition model have not presented the surface charge measurements of CFA, both in the dry as well as wet conditions. The measurement of surface charge of the fly ash samples would provide a deeper insight and could lead to coupling the diffuse double layer retention of ions and the self-inhibition approach.

6. Conclusions

- (1) The heterogeneity leading to the wide range of elements leached from CFA is highlighted in this review.
- (2) The particle size distribution being constant after the leaching process proves that the surface of fly ash particle, a few microns in thickness is wholly involved in leaching. Therefore the charge on the surface of fly ash particle and formation of the diffuse double layer plays a significant role in leaching.
- (3) Delayed leaching, the similarity in both the approaches is due to resistance provided by mass transfer at the surface of fly ash.
- (4) The extended steady state, focused on calcium for the disposal model could be extended to other elements and could have implications if fly ash is stored in landfills with low to high moisture content.

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