

CHAPTER 2

SORBENTS USED AND THE AIM OF THE STUDY

2.1. Fly ash

2.1.1. Production from the combustion of coal

Large quantities of pulverised coal are burned in coal-fired boilers in many parts of the world to raise steam from water, the steam then being used to drive turbines to produce electricity for domestic and industrial consumption. Fly ash is a by-product of this process of electric power generation.

Coal is formed by the decomposition of plant matter, without free access to air, under the influence of moisture, pressure and temperature (Vorres, 1979; Pettijohn, 1957). It is composed mainly of carbon, hydrogen and oxygen, with nitrogen and sulphur being lesser constituents. These elements account for the organic constituents of coal, mostly polycyclic aromatic hydrocarbons.

In addition, some mineral matter also becomes incorporated into coal during and after peat formation, the initial step of the coalification of plant matter. This includes the clay minerals (e.g. $[Al,Fe,Mg]_6[Si,Al]_4O_{10}[OH]_8$), quartz (SiO_2), feldspars ($KAlSi_3O_8$, $NaAlSi_3O_8$, $CaAl_2Si_2O_8$), garnets ($[[R^{2+}]_3[R^{3+}]_2[SiO_4]_3]$; R= Ca,

Mg, Fe or Mn; R' = Al, Fe, Mn or Cr), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5[\text{OH}]_2$), calcite (CaCO_3) and pyrite (FeS_2) (Spackman et al., 1976; Nowacki, 1980). Smaller and trace amounts of many other elements are also present (Ray and Parker, 1977).

Two types of residual ash primarily result from the incombustible mineral constituents during the burning of coal. These are bottom ash, which is retained in the boiler as fused slag, and the fly ash, which leaves the furnace as dry ash carried in the flue gas (vapour). The bottom ash particles are much coarser than fly ash. The vapour is that part of the coal material which is volatilised during combustion.

The percentage of fly ash produced depends on the type of coal (lignite, anthracite, bituminous or sub-bituminous) and the type of boiler (and method of firing) used. The higher the ash fusion temperature of the coal, the lower the proportion of ash that is melted within the boiler and collects as bottom ash, and the higher the firing temperature in the boiler, the larger the proportion of bottom ash formed (Torrey, 1978). The electric utility industry generally uses three types of boilers, namely, dry-bottom boilers, wet-bottom boilers and cyclone furnaces (Babcock and Wilcox Co., 1978).

After leaving the combustion zone the ash particles are cooled rapidly (1500 °C to 200 °C in 4 seconds reported by Ray and Parker, 1977), leading to the formation of sub-micron particles from the inorganic vapours via nucleation and condensation on

existing particles. Ulrich et al. (1971 & 1976) proposed a mechanism to explain the growth in particle size. Finally, the ash is collected in a particulate control system, usually an electrostatic precipitator or a mechanical collector. The method of collection used also influences the characteristics of the final product.

In the year 2000, ca. 56.6 million metric tons of fly ash was produced in the United States alone (American Coal Ash Association, 2002). The corresponding figure for South Africa was 25 (Eskom 22, Sasol 3) million metric tons, the largest single source being the Lethabo power station near Vereeniging (Kruger, 2002).

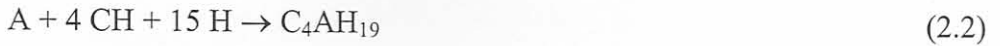
2.1.2. Characterisation

2.1.2.1. Introduction

Fly ash is pozzolanic; that is, a siliceous and aluminous material which possesses little or no cementitious value in itself but will react with lime in the presence of water at ambient temperature to form compounds with cementitious properties (Diamond, 1981).

The hydraulicity that results from pozzolanic reactions is due to the formation of solid and water-insoluble masses consisting of hydrated compounds with C-S-H

bonds, such as tri-calcium silicate hydrate and tetra-calcium aluminate hydrate, from the reactions of reactive silica and alumina with lime (Turriziani, 1964):



Because of the wide range of composition and characteristics of fly ashes, they are classified into two general types: Class F and Class C. Class F fly ash is produced from anthracite or bituminous coal and contains less than ca. 10 % CaO. Class C fly ash is produced from lignite or sub-bituminous coal, may contain as high as 30 or 40 % CaO, and possesses some cementitious properties in addition to being pozzolanic. Characterisation of fly ash requires the knowledge of chemical parameters such as mineralogical and chemical composition, as well as physical parameters such as fineness (granulometry, particle size distribution, and specific surface area) and density.

2.1.2.2. Mineralogical and chemical composition

The mineralogical and chemical composition of a fly ash depends on the characteristics and composition of the coal burned in the power plant. Due to the rapid cooling already mentioned in Section 2.1.1, the main (ca. 50-90 %) phase of fly ash is mineral matter in the form of glassy particles. The minor phase occurs in

the form of crystalline phases, together with particles of carbon resulting from unburned coal. The most common crystalline phases in Class F fly ash is magnetite (Fe_3O_4), hematite (Fe_2O_3), quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), anhydrite (CaSO_4), and free CaO (Ray and Parker, 1977).

Many workers have used X-ray diffraction (XRD) and light microscopic techniques such as Scanning Electron Microscopy (SEM) to identify and determine the quantities of glassy and other phases present in fly ash (Luke, 1961; Adams, 1980; Joshi et al., 1985). Watt and Thorne (1965) found by SEM and XRD examinations that most fly ashes, after extraction with water, contained mainly four crystalline phases: quartz, mullite, hematite, and magnetite. From the analyses for these minerals by X-ray methods and the chemically determined carbon content, the glass content was determined by difference, giving the results in Table 2.1. Then the composition of the glass phase was calculated from oxide chemical analysis, giving the results in Table 2.2.

Table 2.1 Mineralogical analysis of fly ash

Constituent	Quartz	Mullite	Hematite	Magnetite	Carbon	Glass
Mass percentage	2.2	6.5	1.1	0.8	0.9	88

Table 2.2 Calculated mean composition of glassy components of fly ash

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂
Mass percentage	52	27	10	0.8	2.4	1.8	4.6	1.1

The pozzolanicity is due to the glass phase; the crystalline phases influence the amount and composition of the glass phase, but they are not pozzolanic. Carbon is the most important component of ignition loss (LOI, 1000 °C). For cement and concrete applications low carbon content is desirable; this decreases the amount of water required to obtain a paste of normal consistency and produces higher strength concrete.

2.1.2.3. Physical properties

Fly ash consists of fine, powdery particles that are predominantly spherical in nature. The carbonaceous material in fly ash is composed of angular particles. The material usually has a light greyish colour, appearing darker as the Fe₂O₃ (brown) and unburned carbon (black) contents increase. The most important physical parameters that are determined for fly ash are density and fineness.

The mean density of the solid phases can be measured after grinding the ash to high fineness (ca. 1200 m²/kg) to eliminate the bubbles and voids in agglomerates. Such values range from ca. 2.65 to 2.80 g/cm³ (Jarrige, 1971). The bulk density

varies greatly with packing; without close compaction, values as low as 0.54 g/cm^3 have been reported (Berry and Malhotra, 1978).

Three measures of fineness are used, namely, granulometry, particle size distribution and specific surface area (Helmuth, 1987). Granulometry (ASTM 618) involves dry or wet sieve analysis; it measures the percentages retained on various size sieves. For fly ash to be used as a mineral additive in Portland cement concrete, the residue on a $45\text{-}\mu\text{m}$ sieve should not be more than 34 % (ASTM 618-87). For South African fly ashes this is usually less than 12 % (Mantel, 1991). A cumulative particle size distribution curve shows the percentage finer (or coarser) than any particular size over the entire range of sizes. Fly ash particles typically range in size from ca. 2 to over $300 \mu\text{m}$, with mean particle diameters of the order of $20 \mu\text{m}$.

Specific surface area is determined by the Blaine air permeability method (ASTM C204), the BET technique, where nitrogen adsorption isotherms are measured, the Wagner turbidimeter method (ASTM C115), and the hydrometer method (ASTM D422). Unfortunately, these standard methods yield widely different values for the same fly ash sample (Cabrera and Gray, 1973), indicating significant systematic errors. Automated particle size analysis instruments are also available which use

the scattering of a laser beam by the particles to measure parameters such as specific surface area, mean particle diameter, and particle size distribution.

2.1.3. Utilisation

Due to its pozzolanic reactivity with lime (a hydration product of Portland cement), fly ash has been used extensively in the cement and concrete industry, as an admixture, as a raw feed material in the manufacture of Portland cement, and as a component of Portland-pozzolan blended cement. The largest single use of fly ash is as a mineral admixture in Portland cement mortar and concrete. Reasons for fly ash addition include economy and enhancement of certain properties of fresh concrete and hardened concrete, as mentioned later in Section 2.4.

Other important uses of fly ash include use as a structural fill material, stabilised bases or sub-bases for road and pavement substructure, flowable fill, mineral filler in asphalt paving mixtures, and for waste stabilisation and solidification.

Table 2.3 lists figures for the production and use of fly ash for the year 2000 in the U.S. (ACAA, 2000). The corresponding figures for South Africa were 25 million metric tons produced and 1.2 (0.9 for cement and concrete, 0.3 for bricks and blocks) million tons used.

Table 2.3. Production and use of coal fly ash in 2000 in the USA

Use	
Cement/Concrete/Grout	9 527 551
Raw feed for cement clinker	1 020 520
Flowable fill	627 008
Structural fills	2 349 949
Road base/Sub-base	1 086 975
Soil modification	100 706
Mineral filler	107 110
Snow and ice control	2 768
Mining applications	1 036 382
Waste stabilization	1 787 649
Agriculture	12 581
Miscellaneous	410 018
Total usage	18 069 217
Total production	56 649 358
Percentage usage	31.9 %

2.1.4. Disposal: environmental considerations

The burning of coal for electricity production around the world generates enormous quantities of solid wastes, in the form of fly ash, flue gas desulphurisation (FGD) material, bottom ash and boiler slag. In the year 2000, some 97.2 million metric tons of coal conversion solid wastes was generated in the United States alone; less than 30 % of this was put to practical use, the rest being land-filled or stockpiled near power stations (ACAA, 2000). South Africa (Eskom and Sasol) generated 34 million metric tons of solid waste from coal combustion

(Kruger, 2002). A common method of disposal is placement of the solid wastes in worked surface mines and back filling with overburden. The main environmental concern associated with the landfilling of fly ash is its leachability in the presence of groundwater flowing in the surrounding area, especially the leaching of potentially toxic trace metals.

Although the levels of toxic metals in the leachates studied by several workers reportedly falls within government regulated standards, research is ongoing. Groenewold et al. (1985) found that the levels of As, Se, Mo and Cd in a fly ash disposal site leachate under study did not pose long-term environmental problems. This was attributed to the self-cementing property of buried fly ash, which leads to decreased leachability over time. Similarly, Garcez and Tittlebaum (1985) reported a decrease in the concentration of Al, As and Mo in the leachate after fly ash was stabilised with soil for use as a road base.

2.2. Slag

2.2.1. Origin

Iron ore, scrap iron, and fluxes (limestone and dolomite) are charged into a blast furnace, along with coke for fuel in the manufacturing of iron. The coke undergoes combustion to produce carbon monoxide, which reduces the iron ore to a molten iron product. Slag is a non-metallic by-product of the process, formed by the

combination of the earthy (silica and alumina) constituents of the iron ore with lime and magnesia in the flux. About 14 million metric tons of blast furnace slag is produced annually in the United States (USDI, 1993).

The slag, which floats on the molten iron at the bottom, is tapped from the blast furnace as a molten stream (ca. 1450 °C). Widely different forms of slag are produced depending on the method used to cool the molten slag. These include air-cooled slag, expanded or foamed slag, pelletised slag, and granulated slag.

Granulated slag is produced when the molten slag is chilled, by spraying jets of water on the red-hot liquid. The slag is cooled so rapidly that crystallisation is prevented and it solidifies as a glass (Lea, 1970). The quenching also breaks up the material into small particles. Ground (to ca. 350 m²/kg) granulated blast furnace slag (GGBFS) is sold in South Africa under the trade name Slagment (Mantel, 1991). This is the form of slag used for this study.

2.2.2. Properties

GGBFS is a latent hydraulic binder, that is, it hardens slowly in water by itself to form cementitious hydration products, but on addition of an activator (e.g. lime) its rate of hardening is greatly enhanced. The latency is due to the slow release of

calcium ions out of the glass and the subsequent formation of a protective layer of hydrates.

The composition of slag can vary over a wide range depending on the nature of the iron ore, the composition of the flux, the coke consumption, and the kind of iron being manufactured (Lea, 1970). The four major constituents are lime, silica, alumina and magnesia, with sulphur in the form of sulphide, and ferrous and manganese oxides as minor components. Table 2.4 shows the oxide chemical analysis of a typical South African slag (Mantel, 1991).

Table 2.4 Composition of a typical South African slag

Constituent	Mass percentage
SiO ₂	36.6
Al ₂ O ₃	13.2
Fe ₂ O ₃	0.6
Mn ₂ O ₃	1.2
TiO ₂	1.9
CaO	33.0
MgO	10.7
SO ₃	2.5
Na ₂ O	0.2
K ₂ O	0.9
LOI	0.6

There can be considerable variability in the physical and mechanical properties of blast furnace slag, depending on the iron production process. Emery (1980) reported specific gravity and compacted unit weight values of 2.0-2.5 and 1120-

1360 kg/m³, respectively, for an air-cooled blast furnace slag (ACBFS); this is the slag type that is most commonly used as an aggregate material. This is due to favourable mechanical properties such as good abrasion resistance, good soundness characteristics, and high bearing strength (Noureldin, 1990).

2.2.3. Utilisation

GBFS is used as a mineral admixture for Portland cement concrete, as well as a hydraulic cement when ground to cement fineness (ACI, 1990). The ground slag (GGBFS) is also used to produce slag/Portland cement blends, either by being introduced into and milled with the cement feedstock, or blended in after the cement clinker is ground to its required fineness (AASHTO, 1986). ACBFS has been used as an aggregate in Portland cement concrete, asphalt concrete, and road bases. Almost all the blast furnace slag generated in the United States is reportedly utilised, with less than 10 percent disposed of in landfills (RMRC, 2002).

2.3. Ordinary Portland cement (OPC)

2.3.1. Manufacture

The processes involved in the manufacture of Portland Cement have been described in several publications (Mantel, 1991; PCA, 2002). The sequence of processes may be represented as follows:

Quarrying \Rightarrow Raw Milling \Rightarrow Blending \Rightarrow Burning \Rightarrow Cement Milling

Most plants depend on a nearby quarry for the required calcareous- and argillaceous raw materials; commonly limestone (for calcium oxide) coupled with smaller quantities of clay or shale and sand (for silica, alumina, and iron oxide). Lumps of rock blasted from the quarry face are crushed down to particles smaller than 19 mm and then transported to the raw mill, where the material is ground to a fine powder. Layers of the various raw materials are laid down alternately in a blending silo and blended in the proper proportion (Ca: Si: Al: Fe). The meal then goes into a 4-stage pre-heater kiln, where they are heated to 800-900 °C by hot gases produced by burning finely ground coal.

As the temperature increases in the kiln, Al_2O_3 and Fe_2O_3 start to react with CaO to form molten calcium aluminates (mainly C_3A) and calcium aluminoferrite (C_4AF , ferrite). Then silicate reactions start to take place as the temperature rises further (up to 1500 °C in the burning zone), solid CaO and SiO_2 reacting in the liquid melt to form di-calcium silicate (C_2S , belite) and tri-calcium silicate (C_3S , alite). The material from the kiln, now called clinker, is air-cooled, a small quantity of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) added (for set-retardation), then proceeds to the cement mill. Here, steel balls in a rotating steel tube grind the clinker to a fine powder with specific surface area in the range 300-350 m^2/kg , known as OPC

(S.A. CEM I 42,5; U.S.A. ASTM Type I).

2.3.2. Properties

Portland cements are hydraulic cements composed primarily of hydraulic calcium silicates. The main properties of interest of OPC may be divided into three groups, namely, composition- chemical analysis and compound composition, fineness-density and specific surface area, and quality- setting time, heat of hydration, compressive strength, workability, and soundness of the OPC-containing concrete mix.

The constitution of Portland cement has been studied by phase equilibria, optical microscopy and X-ray examination, and chemical analysis. Table 2.5 shows the chemical analysis of a typical OPC (Mantel, 1991), as well as the compound composition of the alite (C_3S), belite (C_2S), aluminate (C_3A) and ferrite (C_4AF) major phases.



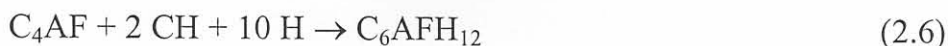
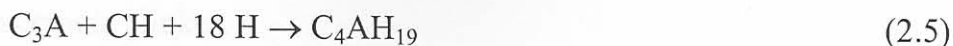
Table 2.5. Constitution of a typical OPC

Constituent	Mass %
SiO ₂	22.9
Al ₂ O ₃	4.2
Fe ₂ O ₃	3.8
Mn ₂ O ₃	0.4
TiO ₂	--
CaO	65.0
MgO	3.3
P ₂ O ₅	--
SO ₃	0.2
Na ₂ O	0.1
K ₂ O	0.6
LOI	--
C ₃ S	52.0
C ₂ S	26.0
C ₃ A	4.0
C ₄ AF	12.9

The most important property of OPC is the hydration reactions it undergoes when mixed with water, which leads to strength development in the concrete mix. The development of strength comes from the growth of a solid 3-D hydrated calcium silicate crystalline network, C-S-H, mainly from the hydration of C₃S. The reactions involved, which are very complex, may be approximated as (Mantel, 1991):



Hydrated calcium aluminate also contributes to early strength, but the contribution of hydrated calcium aluminoferrite (hydrogarnet) is very small (due to the much lower heat of hydration involved):



The reactions above are preceded by a period of slow reaction (the induction period) during which a protective film of micro-crystalline calcium sulphoaluminate (ettringite) forms around the individual C_3A crystals from the reaction of gypsum with the initial hydration products of C_3A :



2.3.3. Utilisation

The use of Portland cement concrete in the construction of buildings, bridges, dams, pavements, etc. is well known. OPC has also been put to some lesser-known innovative uses. For example, it has recently been used in the environmental clean-up of old industrial sites in the United States (PCA, 2002) by binding waste (contaminated soil or sediment) for solidification and stabilisation.

2.4. OPC/Fly ash and OPC/Slag blends

As already mentioned in Sections 2.1.3 and 2.2.3, an important use of the by-product materials fly ash and slag is to produce blended cements, usually by inter-grinding with cement clinker.

The chief reason for the use of slag and fly ash as partial Portland cement replacement is to take advantage of the energy already invested in the slag making process. The production of Portland cement is an energy intensive process. In South Africa (Mantel, 1991), for example, ca. 15 tonnes of coal has to be burnt in order to produce 100 tonnes of clinker. Grinding slag for cement replacement, on the other hand, requires only about 25 percent of the energy required to manufacture Portland cement (RMRC, 2002).

In addition to the energy savings, the use of these blended cements has been found to improve the workability and durability of concrete. Slag and fly ash refine the pore structure by reacting with the CH liberated in the hydration of the C_3S and C_2S in the Portland cement (See equations 2.3 and 2.4), thereby forming additional or secondary C-S-H within the framework of the hardened cement paste. The improved durability has been largely attributed to reduced permeability (and reduced ion diffusion) that results from this pore structure refinement (Hooton, 1986). In addition, Montemor et al., reported improvements in concrete

carbonation rates (1995), passivation (1998), as well as induction and corrosion rates (2000).

2.5. The aim of the study

This study was focused on using fundamental research techniques to investigate the feasibility of utilizing OPC and its blends with slag and fly ash for phosphate removal from aqueous solution. This would involve establishing whether these materials remove significant amounts of phosphate and investigating the factors that can be expected to influence the rate and efficiency of phosphate removal. Such factors would include the particle size of the solid material, concentration of dissolved phosphate, contact time, pH and temperature. Adsorption capacities would also be measured as a measure for quantifying the capabilities of these materials for immobilizing dissolved phosphate.

OPC was considered to be a good candidate for the sorption of phosphate due to its fineness and porosity, coupled with the large amount of Ca it contains (elements such as Al, Mg, Mn, Fe and Ti are also present and can be expected to contribute). It was logical to extend the study to OPC/slag and OPC/fly ash (and slag and fly ash) because these blends are utilized for certain applications in the construction industry to take advantage of some important desirable properties that the industrial by-products slag and fly ash impart to the concrete.

If these materials do remove phosphate from aqueous solution, it would definitely add value to the process if the spent phosphate medium could be utilized in some beneficial way. To explore this, it was also envisaged that bricks would be manufactured from the materials after exposure to phosphate-containing water. Their compressive strengths would then be measured in order to assess whether they meet the national standard for strength that is required for masonry units.

The study was also motivated by certain economic and environmental considerations.

Firstly, commercial activated carbon recommended for liquid phase adsorption systems is marketed in South Africa at a cost of 73 euros for a packet of 2 kg (Aldrich, 2003-2004), which translates to more than R 300/kg. On the other hand, a 50 kg bag of OPC costs about R 30; this makes OPC a potential low cost alternative for sorption studies. Blending it with slag or fly ash leads to a further reduction in cost, as both are by-products.

Secondly, there is an on-going search to find effective ways to utilise the huge amounts of fly ash and slag that is land filled or stockpiled every year. In the year 2000, only 18 out of the over 56 million metric tons of fly ash generated in the United States were utilised, i.e. 32 % usage (see Table 2.3); for South Africa the percent usage was even lower, at 1.2 out of 25 million metric tons production, i.e.

less than 5 % usage (Kruger, 2002). Slag presents somewhat less of a disposal problem; about 10 % of the 14 million metric tons of blast furnace slag produced annually in the United States is disposed of in landfills (RMRC, 2002).

3.1. Particle size analysis by FOPA

Thirdly, if OPC, OPC/slag and OPC/fly ash do remove phosphate from aqueous solution then these materials, traditionally used almost exclusively in the construction industry, may have a potential use in reducing the effects of the well-known environmental problem of eutrophication, caused by excessive amounts of phosphate (and nitrate) in bodies of water.