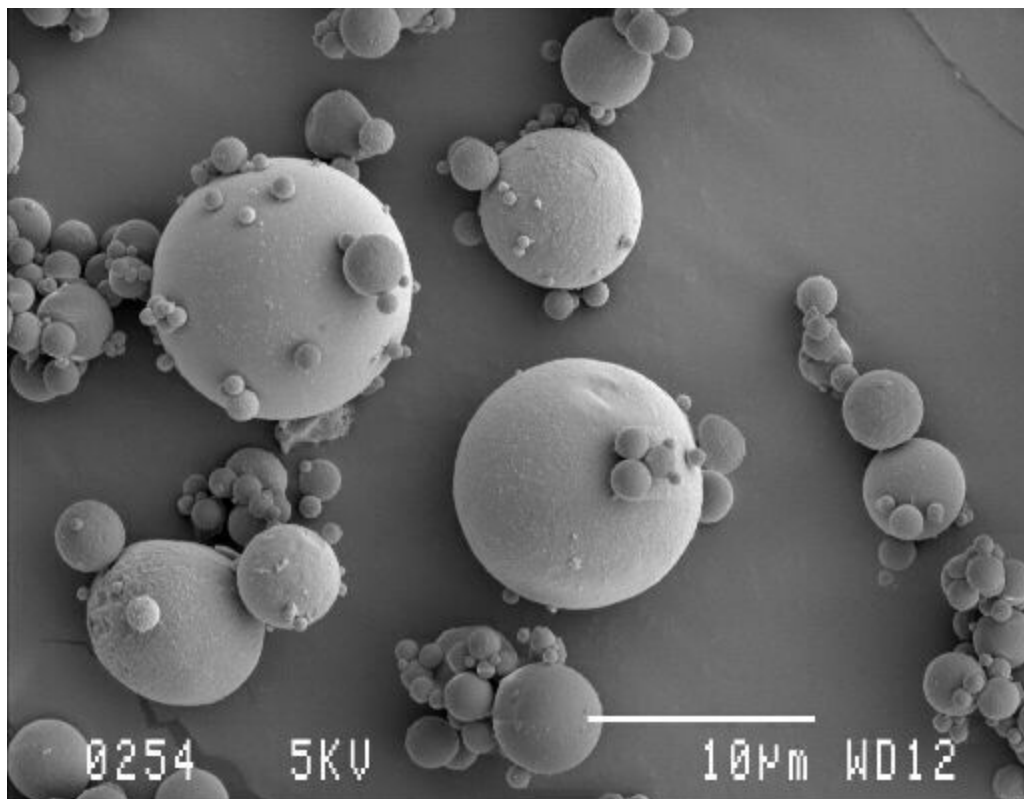


CHAPTER 1

LITERATURE REVIEW OF FLY ASH

IN

Aspects of solid-state chemistry of fly ash and ultramarine pigments



1. LITERATURE REVIEW OF FLY ASH

1.1. Introduction

Kruger reports that the US Congress has classified fly ash as the sixth most abundant resource in the United States of America.¹ Israel could sell good-quality fly ash, based on imported South African coal, at \$20 per tonne in 1999.² Yet, few chemists in South Africa see fly ash as a field worthy of study. What follows aims to highlight the opportunities within the field of fly ash research.

Fly ash is a predominantly inorganic residue obtained from the flue gases of furnaces at pulverised coal power plants. When coal is burnt in pulverized coal boilers, the minerals, entrained in the coal, are thermally transformed into chemical species that are reactive or could be chemically activated, for example by the addition of calcium hydroxide.³ The finely divided glass phase, the predominant phase in fly ash, reacts as a pozzolan, defined by Manz as "...a siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties."⁴

Eskom, a major power utility in the Republic of South Africa, is a major producer of fly ash. South African fly ash for use as a cement extender is processed and marketed by Ash Resources (Pty) Ltd.⁵

Worldwide, the cement industry has almost reached its maximum consumption level of fly ash, so too its use as landfill. Sphere-Fill (Pty) Ltd, which sources fly ash from the Lethabo (a Tswana word, which means "good living" or "happiness"⁶) Power Station in the Northern Free State of the Republic of South Africa, aims to extend the market for this by-product.

The coal in the Republic of South Africa is high in ash content; therefore, the use of fly ash is an environmentally important issue. Eskom produced approximately 27 megatonnes of fly ash in 2001 of which only 1.2 megatonnes were sold

(Table 1-1). Emission control legislation has led to an increasing amount of fly ash in a recovered form (Table 1-2).⁷

Table 1-1: Eskom statistics regarding coal consumption and ash production⁸

Item	2001	2000	1999	1998	1997
Total electricity sold, GWh	181511	178193	173412	171457	172550
Total electricity for Eskom system (Stations and purchased), GWh	198790	194601	188475	185583	187850
Total produced by Eskom stations, GWh (net)	189590	189307	181818	183093	187811
Total available for distribution, GWh	196613	191123	184968	182284	184339
Coal burnt, kt	94136	92289	88470	87225	90169
Average ash content, %	28.8	28.6	28.5	29.1	28.4
Particulate emissions, kt	59.64	66.08	67.08	65.21	83.43
Ash produced, Mt	26.5	24.6	24.3	24.7	23.7
Ash sold, Mt	1.2	1.1	1.1	1.2	1.1

Table 1-2: Environmental implications of using 1 kW of power⁸

Grams per 1 kW of power	2001	2000	1999	1998	1997	1992
Coal burnt	500	500	500	500	500	500
Ash produced	140	130	134	135	126	–
Ash emitted	0.3	0.4	0.4	0.4	0.4	1.0

Sphere-Fill (Pty) Ltd markets several size fractions of fly ash. Super-Pozz is a fine fraction of fly ash with a 90 % top cut passing of 11 μm and a 99 % top cut passing of 25 μm .⁹ The material safety data sheet reports the specific gravity as 2.25, the melting point as 1 350 °C and that Super-Pozz is not classified as a hazardous material.¹⁰ Pozzfill is a coarser grade fly ash, varying in size between 40 and 150 μm .¹¹ A finer fraction of fly ash is marketed as Plasfill, with a size less than 12 μm .

Much of the research into fly ash focuses on the measurement of trace concentrations, and the effects of leaching, by X-ray fluorescence, atomic absorption, inductively coupled plasma-optical emission spectroscopy, gas chromatography - mass spectroscopy and laser ionisation mass spectroscopy. Another field of study is the surface adsorbed dioxins and other pollutant chemicals. These were not treated in this review.

Fly ash can be classified as either cementitious or pozzolanic. The cementitious fly ash is labelled as Class C, with $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ making up at least 50 mass percent.^{11,12} In pozzolanic fly ash, Class F, $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ makes up more than 70 mass percent of the composition of the fly ash.^{11,12}

There are two primary sources of fly ash: fly ash from a pulverised coal power plant and fly ash from a municipal waste incineration plant.¹³ This review focuses on class F fly ash from a pulverised coal power plant.

1.2. Need for Research into Fly Ash

In 2000, the *Journal of Hazardous Materials* published a special issue on fly ash, its characterization and uses.¹⁴ The following comment is made in the preface to that special issue:

Of the hundreds of millions of metric tons of fly ash that are produced annually on a worldwide basis, only a small portion e.g., 20% to 40% of the fly ash is re-used for productive purposes, such as an additive or stabilizer in cement. The remaining amount of fly ash produced annually must either be disposed in controlled landfills or waste containment facilities, or stockpiled for future use or disposal. As a result of the cost associated with disposing these vast quantities of fly ash, a significant economical incentive exists for developing new and innovative, yet environmentally safe, applications for the utilization of coal fly ash.¹⁴

In an article discussing the beneficiation of fly ash, Kruger¹¹ urges researchers

... to a better understanding of the fundamental characteristics of ash; for example, to what degree do surface characteristics control the reactivity, and what beneficiation techniques are applicable to maximize a particular characteristic? Can fly ash be

beneficiated to enrich it as a pre-concentration step for the recovery of gallium? Is a particular fraction more suited to producing slow-release fertilizers? How can beneficiation play a role in selecting a portion of fly ash more appropriate to geopolymerization? Knowledge of the needs in the market-place and the symbiotic relation between research and product development is paramount in creating these new opportunities for fly ash.¹¹

Scheetz and Earle¹² comment on the use of fly ash in America. Only 27.4 % of the ash produced in 1996 was used in non-landfill applications (confirmed by Hower and others⁷). Scheetz and Earle¹² challenge researchers with the following remark:

...[Fly ash] was imparted with an excess energy, either chemical or stored surface energy, which can be utilized to participate in chemical reactions, if properly activated. The challenge for the scientific community is to exploit these resources, as low tech materials, to solve large-volume societal-environmental needs.¹²

Malhotra and others¹⁵ report on the use of fly ash in America in 2002. They estimate that only 30 % of the fly ash produced is used. Two thirds is used in the concrete industry, which has reached a maximum consumption figure. Malhotra and others¹⁵ challenge researchers to find low cost but high volume applications of fly ash, and to convert ashes into value- added products.¹⁵

Foner and others² emphasize the role of developing new applications of fly ash in 1999, by pointing out that Israel would produce 1.3 megatonnes of coal ash per annum by 2001 and that only 0.6 megatonnes could be used by the cement industry.² Nathan and others¹⁶ estimated the figures as 1.2 megatonnes and 0.8 megatonnes respectively by 2000.

In the United Kingdom approximately 50 % of the fly ash produced is used,¹⁷ and in India only 6 %.¹⁸

1.3. Characteristics of Fly Ash

Fly ash is a diverse substance. The characteristics of fly ash differ depending on the source of the coal used in the power plant and the method of combustion.^{3,12,19} Cenospheres, hollow spherical particles as part of fly ash, are believed to be formed

by the expansion of CO₂ and H₂O gas, evolved from minerals within the coal being burnt.²⁰ The predominant forces are, however, the pressure and surface tension on the melts,²⁰ as well as gravity. The predominantly spherical microscopic structure of fine fly ash is related to the equilibrium of the forces on the molten inorganic particle as it is forced up the furnace or smoke stack against gravity. The molten inorganic particles cool down rapidly, maintaining their equilibrium shape. A similar situation is found in spherical drops of water falling from a faucet.

Because cenospheres are hollow, they have a low bulk density. The percentage cenospheres increase with the ash content in the coal, and decrease with the concentration of Fe₂O₃.²¹ This indicates that Fe₂O₃ is concentrated in the higher density fraction of fly ash,²¹ which is to be expected from the high density of Fe₂O₃ (5.25 g/cm³)²² and Fe₃O₄ (5.17 g/cm³).²² The iron species should not contribute significantly to the infrared spectra.²¹

The inorganic material entrained over years in the coal melt during the combustion of coal in the furnace, and with some, but limited, fusing of the molten particles.¹⁹ Some of the vaporized low boiling elements, for example alkali metal salts, coalesce to form submicron particles.¹⁹ Some of the vaporised compounds, most notably the polynuclear aromatic hydrocarbons and polycyclic aromatic hydrocarbons, adsorb onto the surface of the fly ash particles.¹⁹ The surface of fly ash particles is, therefore, commonly enriched in carbon, potassium, sodium, calcium and magnesium.¹⁹

Fly ash has, as mentioned before, a characteristic spherical microscopic structure (Figure 1-1). This microscopic structure is, in fact, so beautiful that a scanning electron microscope photograph of fly ash was published on the cover of Science magazine, 7 May 1976, vol 192, no 4239; and again on 19 December 1980, vol 210, no 4476.

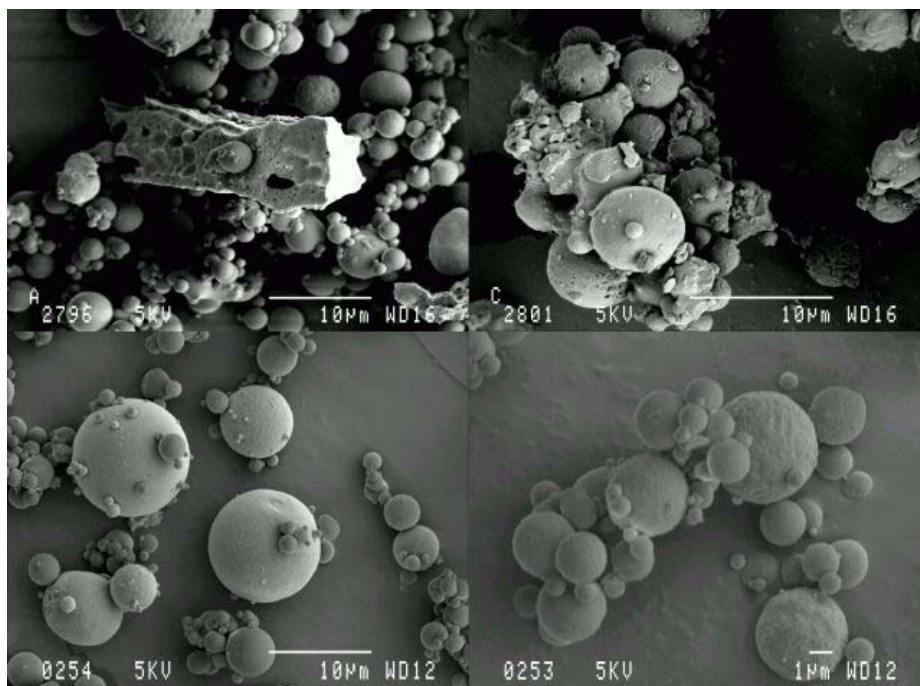


Figure 1-1: The predominantly spherical microscopic structure of fly ash

Fly ash can be approximated as an aluminosilicate and can be used like other minerals. The amorphous aluminosilicate nature of fly ash makes the chemical structure of fly ash difficult to characterise, but also very versatile, since the glassy phase reacts first before the crystalline phase, and also goes into solution first.

X-ray diffraction is mainly used to describe the mineralogy of fly ash. The mineralogy of fly ash is closely related to the minerals entrained in the coal and several different minerals have been identified as part of fly ash (Table 1-3). The main phases are glass, mullite, quartz, magnetite, haematite^{19,23} and anhydrite. Methods of quantifying these minerals, and therefore the glass content, have been developed.⁴⁷ The samples analysed, showed similar mineralogy (Figure 1-2). The mullite present in fly ash forms by the decomposition of kaolinite⁶² which is entrained in the coal.

Table 1-3: X-ray diffraction mineralogy of fly ash

Glass ^{2,3,7,24-52}	Quartz ^{2,3,7,16,24-34,36-72}
Mullite ^{2,3,16,24,27-55,60,61,64-74}	Sillimanite ^{38,67,68}
Haematite ^{3,16,24,26,28-32,34,37-39,44, 46,47,55,60-62, 66,70,71,73,75}	Magnetite ^{3, 16,24,27-30,32-34,38,39,44-47,55,62, 66,71,76}
Anhydrite ^{2,26,29-31,39,47,60,63,77}	Plagioclase ^{3,26,52,63}
Gehlenite ^{26,34,63}	Calcite ^{2,3,26,28,39,44,52,63,71}
Cristobalite ^{3,28,45,46,52}	Anorthite ^{66,70,72}
Lime ^{2,3,26,28,29,31,39,16,62,63}	Alkali Feldspars ^{3,16,26,28,30,37,39,52,55,63}
Bassanite ^{26,63}	Gypsum ^{3,26,39,62,63,75}
Mica ^{3,26,39,63}	Amorphous Al-Fe silicates ¹⁶
Amorphous Ca-Al-Fe silicates ¹⁶	Melilite ^{3,31}
Merwinite ³¹	Brown millerite ^{31,63}
Enstatite ^{70,72}	Sodalite ³¹
Illite ⁶⁵	Kianite ⁵⁵
Calcium Silicate ⁴⁴	Unburnt coal ^{26,27,39,63}

The magnetite referred to in Table 1-3 should be classified as ferrite, due to the different rates of substitution of Fe²⁺ and Fe³⁺ by other ions, for example vanadium, chromium, manganese, cobalt, nickel and zinc.^{42,71} Spinels containing mainly iron, and some chromium and nickel impart magnetic properties to approximately 39 % of the particles (more so in the finer fractions).⁷⁸ This leads to the concentration of these elements in these fractions, and makes fly ash a valuable "ore" for these elements.

Although fly ash contains many potentially toxic trace elements (Table 1-4), leaching tests have shown that these are stable within the aluminosilicate matrix.^{27,79,80} Accordingly fly ash is not classified as a hazardous waste in America.²⁷ The only element that might pose a problem is hexavalent chromium.² The Ministry of the

Environment of Israel, however, considers the use of fly ash as landfill potentially harmful, and forbids its use as landfill,² possibly in reaction to the greater leaching test results of Nathan and others¹⁶ for arsenic, selenium and chromium. The leaching behaviour is influenced by several factors;^{79,81} therefore results can be expected to vary for fly ash samples from different sources.

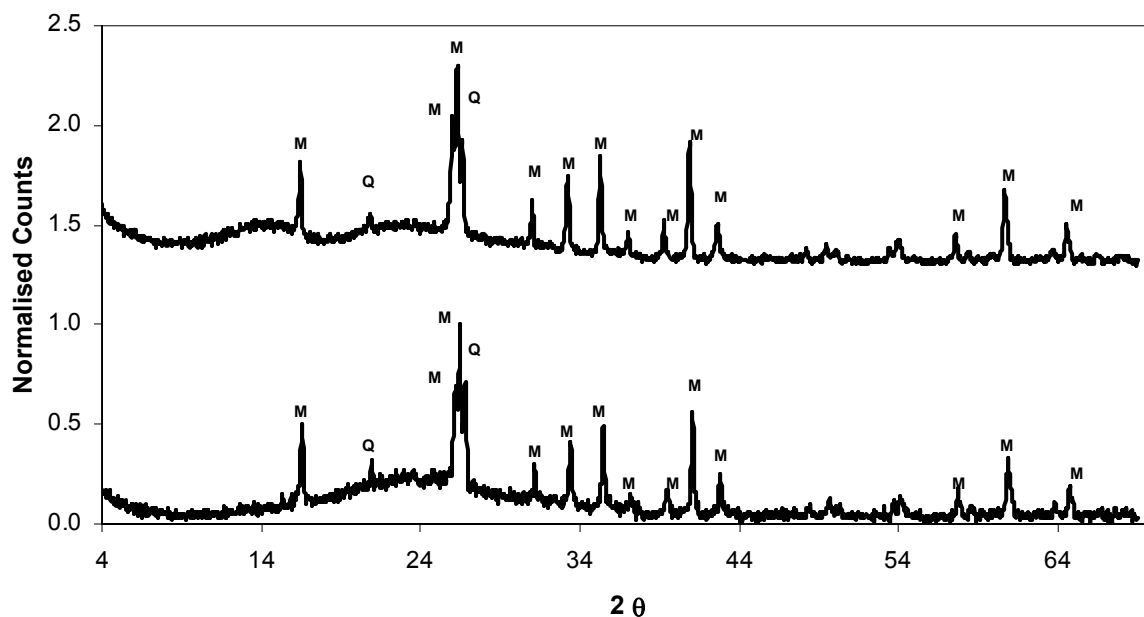


Figure 1-2: The mineralogy of fly ash; M: mullite, Q: quartz

Several atomic force microscopy studies on fly ash have been done.^{45,46,82,83} Fine fly ash has a spherical microscopic structure (Figure 1-1). Not all particles are spherical (Figure 1-1). The size distribution can also be assessed by investigation of the micrographs. The present micrographs are similar to those in literature.^{19,20,24,26,33,35,38,39,46,50,53,54,72,75-77, 83-108} Quantitative work by energy dispersive X-ray analyses indicates the heterogeneous nature of the fly ash particles.^{19,20,40,53,54,71, 83,96,100-105}

The infrared spectra of fly ash have also been reported^{41,45,46,53,54,104,109} but these results differ from the infrared spectra for fly ash used in our studies (Figure 1-3). Mollah and others⁴⁶ assign the bands in their spectra. The band at 1080 cm^{-1} is assigned to the antisymmetric stretching vibration of Si-O-Si and the band at

792 cm^{-1} to the corresponding symmetric vibration.⁴⁶ The band at 1135 cm^{-1} is tentatively assigned to the antisymmetric stretching vibration of Si-O-Al and the band at 700 cm^{-1} to the symmetric Si-O-Al stretching vibration.⁴⁶ The band at 481 cm^{-1} is assigned to the O-Si-O bending vibration.⁴⁶ The shoulder at 950 cm^{-1} is assigned to a non-bridging oxygen ion band, Si-O-Na.⁴⁶ The bands at 800 and 481 cm^{-1} are assigned to the presence of cristobalite, and the band at 700 cm^{-1} to the presence of mullite.⁴⁶

Table 1-4: XRF determined composition of fly ash and Kaolin

Compound	Mass (g/100g) ^a		Compound	Mass (g/100g) ^a	
	Fly ash	Kaolin ^b		Fly ash	Kaolin ^b
SiO ₂	50.9(7)	45.53(9)	MnO	0.038(8)	
Al ₂ O ₃	37.1(6)	37.3(2)	ZnO	0.024(4)	0.0035(3)
CaO	4.5(3)	0.0331(5)	La ₂ O ₃	0.018 ^d	
Fe ₂ O ₃	3.0(2)	0.647(3)	NiO	0.017(4)	0.0014(6)
TiO ₂	1.8(1)	0.852(3)	As ₂ O ₃	0.016 ^d	0.0009(7)
MgO	0.8(3)	0.286(3)	PbO	0.015(2)	0.0108(2)
K ₂ O	0.62(4)	0.949(4)	Y ₂ O ₃	0.014(5)	0.00573(8)
P ₂ O ₅	0.48(4)	0.1519(5)	CeO ₂	0.012(9)	
SO ₃	0.2(2) ^c	0.0198(5)	Ga ₂ O ₃	0.012(3)	0.0110(2)
SrO	0.15(2)	0.01944(6)	CuO	0.010(3)	0.0008(5)
BaO	0.11(5)		Rb ₂ O	0.01 ^d	0.0192(2)
Na ₂ O	0.058(9)	0.049(3)	Nb ₂ O ₅	0.007(2)	0.0095(6)
ZrO ₂	0.055(9)	0.00470(9)	Sc ₂ O ₃	0.006 ^d	0.0043(2)
Cr ₂ O ₃	0.052(5)	0.0074(6)	Ag ₂ O	0.005 ^d	
V ₂ O ₅	0.039(8)	0.0195(3)	MoO ₃	0.0005(2)	0.0002(2)

- The data represents the average of four XRF analyses on fly ash and fly ash treated at 1 000 °C with the standard deviation indicated in brackets, that is 50.9(7) implies 50.9 ± 0.7 g/100g sample.
- The data represents the average of four XRF analyses on Kaolin, content found in Kaolin but not in fly ash is omitted, for example uranium.
- The uncertainty in the value of SO₃ is related to the heat treatment of the samples and the analysis method.
- The compound occurred only once in the set of four repeat analyses.

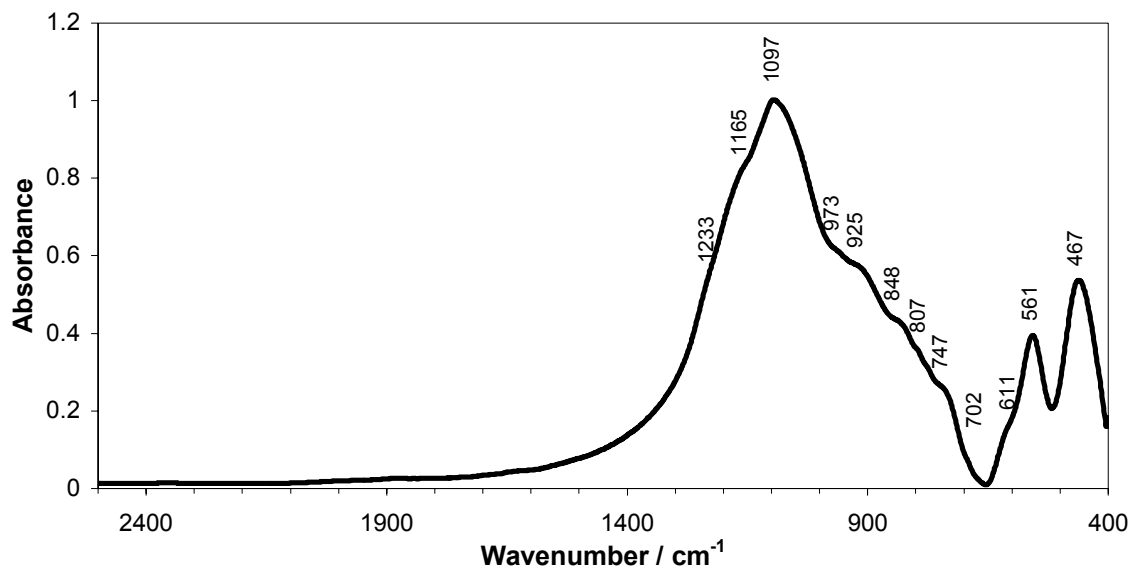


Figure 1-3: Infrared spectrum of fly ash

The pH of a suspension of 10 g of fly ash in 200 ml of water is 11.473 ± 0.009 after 10 minutes of agitation. After treating the fly ash at 1 000 °C, the pH under similar conditions only reaches 8.28 ± 0.03 , a statistically different pH, even at the 99.99 % confidence level. This possibly indicates that some of the alkali and alkaline-earth salts on the surface of the particles decomposed to their respective oxides, and were not free to go into solution. Ding and others⁷⁴ identify Ca^{2+} , K^+ and Na^+ as the soluble constituents of fly ash and find that a suspension of fly ash in water gives a pH of 12.2, in agreement with the present study as well as the work of Foner and others.² Bayat³¹ observes similar trends in pH development over time, to a maximum of approximately 12.5, although some fly ash samples gave peak values as low as 9.7 and 10.4. Bayat³¹ further determines, through leaching experiments, that sodium and potassium are almost entirely in their free ionic states, whereas calcium and magnesium are only predominantly in their free ionic states. Hydroxides and sulphates are also common in the fly ash suspensions.³¹

Further investigation needs to be done on the characterisation of fly ash, since the validity of any result regarding fly ash for one batch would need to be tested for other batches. Furthermore, fly ash can be studied in its different fractions. Fly ash can be

separated based on particle size, magnetic characteristics, and density. The order of these fractionation steps can be swapped around, possibly yielding different results.⁴⁵

1.4. Past Applications of Fly Ash

Many patents are claimed for the use and beneficiation of fly ash. The classification of fly ash is not discussed, and is reviewed by Kruger.¹¹ The most important use of fly ash is in the cement industry, where the presence of fly ash adds strength to concrete. The minerals in South African fly ash are not hydraulic, that is the minerals do not add strength to cement.¹¹⁰ The glass phase is believed to react with lime released from cement while the cement is curing.¹¹⁰ This pozzolanic reaction adds strength to the cement.¹¹⁰ In general fly ash reduces the water consumption of cement, increases the setting time, reduces the heat of hydration and adds long-term strength to cement products, for example concrete.³ The unreactivity of the mineral or crystalline phases in fly ash is also evident during zeolite formation.^{24,73,77} The unreactivity of the crystalline material in fly ash in terms of cement strength development does not mean that these parts of the fly ash particles are unreactive in all situations, nor does it imply that these minerals prevent the glassy phases from reacting.

Different applications of fly ash are tabulated below (Tables 1-5 to 1-8). The focus is on the period January 1980 to August 2003. In compiling the list of applications, applications regarding cement and concrete have largely been ignored, as well as non-coal based fly ash, for example municipal solid waste incineration ash. Helmuth¹⁹ and Wesche²³ review the use of fly ash in cement, giving background on the characteristics of fly ash. Solid stabilisation of waste products has not been included either.¹¹¹

Fly ash is used as cement extender, or filler in the manufacture of building material such as panels and boards (Table 1-5), and is also added to gypsum boards.

Fly ash retains water, which makes it a good soil amender. Boron and selenium enrichment seems to be the most detrimental aspect of fly ash amended soils. In these applications, fly ash is often mixed with sewage sludge (Table 1-5). The

possibility exists that the high levels of boron and selenium originate from the sewage sludge rather than from the fly ash. An extension of these soil amendment applications is the formation of artificial reefs.^{80,112,113}

Polymers are expensive chemical species. To make up volume without using unnecessary amounts of polymer other inexpensive materials are added, known as fillers. Functional fillers are fillers that add extra quality to the final plastic, for example colour, fire retardancy, or UV stability. Fly ash has the potential to be a good functional filler (Table 1-5), due to its spherical microscopic structure (Figure 1-1). Cu-coated cenosphere particles are used in conducting polymers for EMI-shielding applications.¹⁰⁵

The mullite and quartz in the non-magnetic fraction of fly ash could be a valuable resource in the ceramics industry (Table 1-5). The use of fly ash in frictional or brake material for the automotive industry is a high technology application of the hardness of fly ash.¹⁵ Some transition metals are concentrated in the magnetic fraction of fly ash and can, therefore, be extracted from this concentrated matrix (Table 1-6).¹⁰² Minerals essential to humans and animals can also be recovered from fly ash.¹¹⁴ Ferrospheres exist in fly ash⁸⁴ and have found direct use as part of copier toner.¹¹⁵⁻¹¹⁸

Fly ash is used as an adsorbent for organic wastes (Table 1-7). Whether this adsorbent nature of fly ash can be ascribed to the porous nature of the silicates or to the activated carbon particles embedded on the surface of the fly ash particle is still a matter for debate. To remove SO_x from gas streams, fly ash is usually mixed with Ca(OH)₂ (Table 1-7). Fly ash is also used for the removal of heavy metals from aqueous samples (Table 1-7). This property of fly ash is dramatically enhanced by the formation of zeolites from fly ash (Table 1-8). The zeolites formed from fly ash (Table 1-8) cover a substantial range of the known structures for zeolites, and have been reviewed by Querol and others.¹¹⁹ Smith,¹²⁰ Suib,¹²¹ and Cundy and Cox¹²² review the structure of these, and other, zeolites. Mullite is the least reactive component in fly ash during the formation of zeolites,^{24,73,77} while the glass phase reacts first. Hollman and others⁸⁶ emphasize that the formation of the zeolite takes place on the surface of the fly ash particles. This leads to an impure product. In a

two-step synthesis, designed to separate the silica-rich leached fraction from the fly ash, 85 g of pure zeolite can be produced from 1 kg of fly ash.⁸⁶

Table 1-5: Applications in which fly ash acts as an additive

Building Industry	
Cement and Concrete ^{1,2,4,11,12,17,19,23,31,123-126}	Grout ^{11,12,17,127}
Roof Tiles ^{12,128-131}	Roads ^{123,125,132}
Bricks ^{11,12,30,1,123-125,131,133-135}	Patches on Roads ^{12,133,136,137}
Panels and boards ^{2,12,131,133,138-144}	Binder ¹⁷
Soil Beneficiation ^{1,30,31,44,124,125,132,145-163}	
Sewage treatment ^{164,165}	Landfill ^{12,124,133,166-168}
Soil stabilization ¹⁶⁹⁻¹⁷¹	Sludge stabilization ¹⁷²⁻¹⁷⁴
Soil stabilization for roads ¹⁷⁵	Coagulation and sludge conditioning agents ^{97,172,176}
Fertiliser or composting ^{30,49,177-181}	
Filler Material ¹⁸²⁻¹⁸⁴	
Foams ¹¹	Polyisocyanurate or polyurethane foam ^{185,186}
Phenolic resole foam ¹⁸⁷	Polyester-polyurethane hybrid resin foams ¹⁸⁸
Polyurethane foam ¹⁸⁹	Polymers ^{11,133,190}
Polypropylene ^{191,192}	PVC ¹⁹³
Epoxy resin ^{105,194}	Polyester ¹⁹⁵
Resins ¹¹	Rigid shaped articles based on fly ash and resin ¹⁹⁶
Polyurethane ¹⁹⁷	Fibreglass ^{11,198}
Mineral foam ¹⁹⁹	Fibre reinforced fly ash ^{107,200}
Insulating Material ¹²⁵	
High temperature ¹¹	Low temperature applications. ^{2,201,202,203}
Ceramic Material ^{11,18,30,69,108,132,133,204-207}	
Mineral wool ^{124,133,208}	Coated cellular glass pellet ²⁰⁹
Glass-ceramics ^{70,72,124,133,210-212}	Glass ²¹³

Table 1-6: Applications in which fly ash acts as a metal and metal oxide source
1,31,133,214

Iron ^{34,53,97,215-226}	Gallium ^{215,227-230}
Germanium ^{228,229}	Lead and Zinc ²³¹
Antimony ²³²	Chromium ^{232,233}
Vanadium ^{227,232,234}	Molybdenum ^{232,234}
Aluminium ^{53,75,97,215,222-226,234-238}	Boron ^{234,239}
Uranium ^{31,222}	Silica ^{215,97,223-226}
Selenium ²³⁴	Titanium ^{234,222,226}
Thorium ²²²	Cobalt ²³⁴

Table 1-7: Applications in which fly ash acts as an adsorbent

Adsorbent for Organic wastes ¹⁷³	
Chlorophenols ²⁴⁰	Phenol ^{241,242}
o-xylene ²⁴³	Toluene ²⁴⁴
Oil and tar ²⁴²	
Adsorbent for Inorganic Wastes ^{12,31,170,173,245,246}	
SO _x ^{41,50,53,65,89-94,98,247-255}	NO _x ^{250,252,253}
Nitrates ²⁵⁶	Phosphate ^{67,68,256-258}
Cadmium ^{24,28,77,145,259-261}	Lead ^{28,43,77,256}
Selenium ^{262,263}	Mercury ²⁶⁴⁻²⁶⁶
Radium ²⁶⁷	Barium ^{24,28,77}
Strontium ⁶¹	Copper ^{24,28,77,88,246,256,259,261,268,269}
Zinc ^{24,28,77,86,269}	Cobalt ^{24,270}
Chromium ^{246,259,271}	Caesium ^{64,272}
Nickel ^{24,28,77,86,259,269,273}	Iron ^{28,274}
Fluoride ²⁷⁵	Ammonia ^{28,36,86,88}

Fly ash is used to aid in the oxidation of Na_2S ²⁷⁶ and organic material²⁷⁷ in wastewater, and of H_2S and ethanethiol in gas streams.²⁷⁸ This catalytic effect can also be used in other areas of chemistry, such as catalyst support, for example in the selective catalytic reduction of NO .²⁷⁹ Fly ash is used as carbon monoxide disproportionating catalyst, useful in the production of hydrogen and methane,²⁸⁰ and for hydrocracking.²⁸¹

Fly ash is composited with aluminium,^{103,282,283} tin,²⁸² zinc,²⁸² and sulphur,²⁸⁴ by melting the elements in the presence of the fly ash. A less high technology and a malodorous application is the manufacture of cat litter.²⁸⁵

Table 1-8: Applications in which fly ash acts as starting material for zeolite synthesis¹⁴⁵

Zeolite Na-P1 ^{2,24,28,43,77,86,95}	Zeolite P ^{24,36,37,48,61,64}
Zeolite P1 ⁸⁷	Phillipsite ^{2,28,77,37}
Zeolite K-G, ZK19 and Linde A ²⁴	MCM41 ²⁸⁶
Merlinoite and nosean ⁷⁷	K-Chabazite ^{28,287}
Hydroxy-cancrinite, perialite and Kalsilite ²⁸	Zeolite F Linde ^{28,37}
Na-Chabazite ^{60,287}	Herschelite and tobermorite ²⁸
Nepheline hydrate ^{29,37}	Zeolite A ^{24,28,36,60,64,86,95,270,288}
Faujasite ^{28,36,48,64}	Analcime ^{28,29,37,77}
Gmelinite ²⁹	Sodalite and cancrinite ⁵³
Hydroxy-sodalite ^{28,37,43,48,60,86,95}	Zeolite Y ^{48,88}
Zeolite X ^{48,60,73,86,270,288}	Zeolite J and M ²⁸⁷
Zeolite R ⁶⁰	Geopolymers ^{51,53,54,109,289-291}

1.5. Potential Uses of Fly Ash

The amorphous aluminosilicate nature of fly ash makes fly ash a possible starting point for many industrial reactions, such as the synthesis of ultramarine blue (Chapter 3).²⁹²

Repeated harvesting of foodstuff depletes the trace elements in soil. Although the use of fly ash as soil amendment has been studied, the full-scale application of this technology has not been implemented. In future, farmers might use fly ash, rather than lime, to enrich their soil. The trace elements in fly ash might be used to replace the trace elements in the soil, and to increase the mineral content of the foodstuff.

Fly ash can be considered a valuable resource and needs to be studied, in order to facilitate the application of fly ash to new and innovative areas of economic interest. This review aimed to act as a stepping-stone for the prospective researcher into the rewarding field of fly ash.

1.6. Conclusion

Several non-cement applications of fly ash were reported briefly, for example as filler in plastics. The characteristics of fly ash were also discussed, with the goal of challenging the scientific community to study and evaluate further potential uses of fly ash.

REFERENCES

- 1 R.A. Kruger, *South African Journal of Science*, 1986, **82**, 177.
- 2 H.A. Foner, T.L. Robl, J.C. Hower, U.M. Graham, *Fuel*, 1999, **78**, 215-223.
- 3 S.V. Vassilev, C.G. Vassileva, *Fuel Processing Technology*, 1996, **47**, 261-280.
- 4 O.E. Manz, *Fuel*, 1999, **78**, 133-136.
- 5 J.E. Kruger, *An Overview*, in: Guides on the use of South African fly ash as a cement extender Guide 1, J.E. Kruger (ed), The South African Coal Ash Association (SACAA), Cresta, p. 2, 01 July 1998.
- 6 *Eskom - Lethabo Visitor Centre*, Eskom, http://www.eskom.co.za/education/visit/lathabo/Lethabo_body.htm, 2002, downloaded 17 December 2002 - 15:30.
- 7 J.C. Hower, T.L. Robl, G.A. Thomas, *Fuel*, 1999, **78**, 701-712.
- 8 *Statistics*, Eskom, <http://www.eskom.co.za/Enviro%20data%202002/report01/stats.htm>, 2002, downloaded 9 September 2002 - 16:00.

-
- 9 *Product Specifications*, Sphere-Fill, <http://www.superpozz.com/product.shtml>, 2002, downloaded 10 September 2002 - 9h36.
 - 10 *Safety Data Sheet*, Sphere-Fill, <http://www.superpozz.com/contact1.html>, 2002, downloaded 10 September 2002 - 9h50.
 - 11 R.A. Kruger, *Fuel*, 1997, **76** (8), 777-779.
 - 12 B.E. Scheetz, R. Earle, *Current Opinion in Solid State & Material Science*, 1998, **3**, 510-520.
 - 13 S.V. Vassilev, C. Braekman-Danheux, P. Laurent, *Fuel Processing Technology*, 1999, **59**, 95-134.
 - 14 C.D. Shackelford, *Journal of Hazardous Materials*, 2000, **76**, vii-viii.
 - 15 V.M. Malhotra, P.S. Valimbe, M.A Wright, *Fuel*, 2002, **81**, 235-244.
 - 16 Y. Nathan, M. Dvorachek, I. Pelly, U. Mimran, *Fuel*, 1999, **78**, 205-213.
 - 17 M.J. McCarthy, R.K. Dhir, *Fuel*, 1999, **78**, 121-132.
 - 18 L.N. Satapathy, *Ceramics International*, 2000, **26**, 39-45.
 - 19 R. Helmuth, *Fly Ash in Cement and Concrete*, Portland Cement Association, Skokie, 1987, pp 36-61.
 - 20 G.L. Fisher, D.P.Y. Chang, M. Brummer, *Science*, 1976, **192** (4239), 553-555.
 - 21 S. Ghosal, S.A. Self, *Fuel*, 1995, **74** (4), 522-529.
 - 22 *CRC Handbook of Chemistry and Physics*, D.R. Lide (Ed), CRC Press LCC, Boca Raton, 1998-1999, 79th edition, p 4-141.
 - 23 J.L. Alonso, K. Wesche, *Characterization of Fly Ash*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First edition, E & FN Spon, London, 1991, p. 8.
 - 24 P. Catalfamo, F. Corigliano, P. Primerano, S. Di Pasquale, *J. Chem. Soc. Faraday Trans.*, 1993, **89** (1), 171-175.
 - 25 G. Steenbruggen, G.G. Hollman, *J. Geochem. Explor.*, 1998, **62**, 305-309.
 - 26 V. Sakorafa, K. Michailidis, F. Burragato, *Fuel*, 1996, **75** (4), 419-423.
 - 27 J.C. Hower, J.D. Robertson, G.A. Thomas, A.S. Wong, U.M. Graham, R.F. Rathbone, T.L. Robl, *Fuel*, 1996, **75** (4), 403-411.
 - 28 X. Querol, J.C. Umana, F. Plana, A. Alastuey, A. Lopez-Soler, A. Medinaceli, A. Valero, M.J. Domingo, E. Garcia-Rojo, *Fuel*, 2001, **80**, 857-865.
 - 29 X. Querol, A. Lopez-Soler, *Fuel*, 1997, **76** (8), 793-799.
 - 30 I. Queralt, X. Querol, A. Lopez-Soler, F. Plana, *Fuel*, 1997, **76** (8), 787-791.
 - 31 O. Bayat, *Fuel*, 1998, **77** (9/10), 1059-1066.
 - 32 S. Gomes, M. François, *Cem. Concr. Res.*, 2000, **30**, 175-181.
 - 33 E.V. Sokol, N.V. Maksimova, N.I. Volkova, E.N. Nigmatulina, A.E. Frenkel, *Fuel Processing Technology*, 2000, **67**, 35-52.
 - 34 S. Prakash, J.K. Mohanty, B. Das, R. Venugopal, *Minerals Engineering*, 2001, **14** (1), 123-126.
 - 35 Y. Fang, Y. Chen, M.R. Silsbee, D.M. Roy, *Mater. Lett.*, 1996, **27**, 155-159.
 - 36 W-H. Shih, H-L. Chang, *Mater. Lett.*, 1996, **28**, 263-268.
 - 37 H. Höller, U. Wirsching, *Fortschr. Miner.*, 1985, **63** (1), 21-43.
 - 38 K. Tazaki, W.S. Fyfe, K.C. Sahu, M. Powell, *Fuel*, 1989, **68**, 727-734.
 - 39 S.V. Vassilev, *Fuel*, 1992, **71**, 625-633.
 - 40 A.R. Ramsden, M. Shibaoka, *Atmospheric Environment*, 1982, **16** (9), 2191-2206.
 - 41 C-S. Ho, S-M. Shih, *Can. J. Chem. Eng.*, 1993, **71**, 934-939.
 - 42 L.D. Hulett, A.J. Weinberger, *Environ. Sci. Technol.*, 1980, **14** (8), 965-970.
 - 43 C.D. Woolard, K. Petrus, M. Van der Horst, *Water SA*, 2000, **26** (4), 531-536.
 - 44 B. Indraratna, P. Nutalaya, N. Kuganenthira, *Quarterly Journal of Engineering Geology*, 1991, **24**, 275-290.
 - 45 R.K. Vempati, A. Rao, T.R. Hess, D.L. Cocke, H.V. Lauer Jr, *Cem. Concr. Res.*, 1994, **24** (6), 1153-1164.
 - 46 M.Y.A. Mollah, S. Promreuk, R. Schennach, D.L. Cocke, R. Guler, *Fuel*, 1999, **78**, 1277-1282.
 - 47 M. van Roode, E. Douglas, R.T. Hemmings, *Cem. Concr. Res.*, 1987, **17**, 183-197.
 - 48 H. Tanaka, S. Matsumura, S. Furusawa, R. Hino, *J. Mater. Sci. Lett.*, 2003, **22**, 323-325.
 - 49 J.G. Yoo, Y.M. Jo, *J. Air & Waste Manage. Assoc.*, 2003, **53**, 77 - 83.
-

-
- 50 R-B. Lin, S-M. Shih, *Powder Technology*, 2003, **131**, 212-222.
- 51 H. Xu, J.S.J. Van Deventer, *Minerals Engineering*, 2002, **15**, 1131–1139.
- 52 S.V. Vassilev, R. Menendez, *Fuel*, 2004, **83**, 585-603.
- 53 W.K.W. Lee, J.S.J. van Deventer, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2002, **211**, 49-66.
- 54 W.K.W. Lee, J.S.J. van Deventer, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2002, **211**, 115-126.
- 55 J.F.C. Alcalá, R.M. Dávila, R.L. Quintero, *Trans. Iron Steel Inst. Jpn.*, 1987, **27**, 531-538.
- 56 D. Havlíček, R. Pribil, B. Kratochvíl, *Atmospheric Environment*, 1989, **23** (3), 701-706.
- 57 C.C. Hinckley, G.V. Smith, H. Twardowska, M. Saporoschenko, R.H. Shiley, R.A. Griffen, *Fuel*, 1980, **59**, 161-165.
- 58 J. Fernández, J. Renedo, A. Garea, J. Viguri, J.A. Irabien, *Powder Technology*, 1997, **94**, 133-139.
- 59 M. Park, C.L. Choi, W.T. Lim, M.C. Kim, J. Choi, N.H. Heo, *Microporous and Mesoporous Materials*, 2000, **37**, 81-89.
- 60 C. Poole, H. Prijatama, N.M. Rice, *Minerals Engineering*, 2000, **13** (8-9), 831-842.
- 61 W. Ma, P.W. Brown, S. Komarneni, *J. Mater. Res.*, 1998, **13** (1), 3-7.
- 62 S.C. White, E.D. Case, *J. Mater. Sci.*, 1990, **25**, 5215-5219.
- 63 A. Filippidis, A. Georgakopoulos, *Fuel*, 1992, **71**, 373-376.
- 64 H-L. Chang, W-H. Shih, *Ind. Eng. Chem. Res.*, 1998, **37** (1), 71-78.
- 65 R.A. Diefenbach, M.J. Hilterman, E.A. Frommell, H.B. Booher, S.W. Hedges, *Thermochim. Acta*, 1991, **189**, 1-24.
- 66 N.V. Russel, F. Wigley, J. Williamson, *Fuel*, 2002, **81**, 673-681.
- 67 N.M. Agyeia, C.A. Strydom, J.H. Potgieter, *Cem. Concr. Res.*, 2000, **30**, 823-826.
- 68 N.M. Agyeia, C.A. Strydom, J.H. Potgieter, *Cem. Concr. Res.*, 2002, **32**, 1889-1897.
- 69 N.N. Sampathkumar, A.M. Umarji, B.K. Chandrasekhar, *Mat. Res. Bull.*, 1995, **30** (9), 1107-1114.
- 70 M. Erol, A. Genç, M.L. Öveçoğlu, E. Yücelen, S. Küçükbayrak, Y. Taptik, *Journal of the European Ceramic Society*, 2000, **20**, 2209-2214.
- 71 U. Kukier, C.F. Ishak, *Environmental Pollution*, 2003, **123**, 255–266.
- 72 M. Erol, U. Demirler, S. Küçükbayrak, A. Ersoy-Meriçboyu, M.L. Öveçoğlu, *Journal of the European Ceramic Society*, 2003, **23**, 757-763.
- 73 N. Shigemoto, H. Hayashi, K. Miyaura, *J. Mater. Sci.*, 1993, **28**, 4781-4786.
- 74 M. Ding, M. Guesbroek, H.A. van der Sloot, *J. Geochem. Explor.*, 1998, **62**, 319-323.
- 75 K. Felker, F. Seeley, Z. Egan, D. Kelmers, *Chemtech*, 1982, **12** (2), 123-128.
- 76 S. Gomes, M. François, M. Abdelmoula, P.H. Refait, C. Pellissier, O. Evrard, *Cem. Concr. Res.*, 1999, **29**, 1705-1711.
- 77 X. Querol, A. Alastuey, J.L. Fernandez-Turiel, A. Lopez-Soler, *Fuel*, 1995, **74** (8), 1226-1231.
- 78 J.C. Hower, R.F. Rathbone, J.D. Robertson, G. Peterson, A.S. Trimble, *Fuel*, 1999, **78**, 197-203.
- 79 F. Ariese, K. Swart, R. Morabito, C. Brunori, S. Balzamo, J. Slobodnik, E. Korenková, P. Janox, M. Wildnerova, J. Hlavay, K. Polyák, P. Fodor, H. Muntau, *Intern. J. Environ. Anal. Chem.*, 2002, **82**(11-12), 751-770.
- 80 N. Kress, M. Tom, E. Spanier, *ICES Journal of Marine Science*, 2002, **59**, S231–S237.
- 81 J. Yan, I. Neretnieks, *The Science of the Total Environment*, 1995, **172**, 95-118.
- 82 C.M. Demanet, *Applied surface science*, 1995, **89**, 97-101.
- 83 S.R. Mishra, S. Kumar, A. Wagh, J.Y. Rho, T. Gheyi, *Mater. Lett.*, 2003, **57**, 2417-2424.
- 84 L. Cañadas, L. Salvador, C. Cortés, *Fuel*, 1990, **69**, 690-695.
- 85 E.V. Sokol, V.M. Kalugin, E.N. Nigmatulina, N.I. Volkova, A.E. Frenkel, N.V. Maksimova, *Fuel*, 2002, **81**, 867-876.
- 86 G.G. Hollman, G. Steenbruggen, M. Janssen-Jurkovicova, *Fuel*, 1999, **78**, 1225-1230.
- 87 M. Park, C.L. Choi, W.T. Lim, M.C. Kim, J. Choi, N.H. Heo, *Microporous and Mesoporous Materials*, 2000, **37**, 91-98.
- 88 S. Rayalu, S.U. Meshram, M.Z. Hasan, *Journal of Hazardous Materials*, 2000, **B77**, 123-131.
-

-
- 89 J.C. Martínez, J.F. Izquierdo, F. Cunill, J. Tejero, J. Querol, *Ind. Eng. Chem. Res.*, 1991, **30** (9), 2143-2147.
- 90 C-S. Ho, S-M. Shih, *Ind. Eng. Chem. Res.*, 1992, **31** (4), 1130-1135.
- 91 J.F. Sanders, T.C. Keener, J. Wang, *Ind. Eng. Chem. Res.*, 1995, **34** (1), 302-307.
- 92 H. Tsudhiai, T. Ishizuka, T. Ueno, H. Hattori, H. Kita, *Ind. Eng. Chem. Res.*, 1995, **34** (4), 1404-1411.
- 93 T. Ishizuka, H. Tsudhiai, T. Murayama, T. Tanaka, H. Hattori, *Ind. Eng. Chem. Res.*, 2000, **39** (5), 1390-1396.
- 94 A. Al-Shawabkeh, H. Matsuda, M. Hasatani, *Journal of Chemical Engineering of Japan*, 1995, **28** (1), 53-58.
- 95 M.W. Grutzeck, D.D. Siemer, *J. Am. Ceram. Soc.*, 1997, **80** (9), 2449-2453.
- 96 A. Hazrati, J.T. Schrodtt, *Surf. Interface Anal.*, 1988, **13**, 142-148.
- 97 J.W. Smith, J. Condra, *J. Envir. Enrg.*, ASCE, 1983, **109**, 1168-1180.
- 98 A. Al-Shawabkeh, H. Matsuda, M. Hasatani, *Can. J. Chem. Eng.*, 1995, **73**, 678-685.
- 99 S.J. Rothenberg, P. Denee, P. Holloway, *Appl. Spectrosc.*, 1980, **34** (5), 549-555.
- 100 H. Yokozawa, T. Kikuchi, K.F. Ando, K. Hoshino, *Anal. Chim. Acta*, 1987, **195**, 73-80.
- 101 K. Mukai, T. Kikuchi, K. Furuya, *Mikrochim. Acta*, 1988, **1988 III**, 41-56.
- 102 L.D. Hulett Jr, A.J. Weinberger, K.J. Northcutt, M. Ferguson, *Science*, 1980, **210** (4476), 1356-1358.
- 103 R.Q. Guo, P.K. Rohatgi, *Metall. Mater. Trans. B*, 1998, **29B**, 519-525.
- 104 M.Y.A. Mollah, T.R. Hess, D.L. Cocke, *Cem. Concr. Res.*, 1994, **24** (1), 109-118.
- 105 S. Shukla, S. Seal, Z. Rahaman, K. Scammon, *Mater. Lett.*, 2002, **57**, 151-156.
- 106 S.M. Kulkarni, Kishore, *J. Mater. Sci.*, 2002, **37**, 4321-4326.
- 107 S.R. Kaniraj, V. Gayathri, *Geotextiles and Geomembranes*, 2003, **21**, 123-149.
- 108 E. Benavidez, C. Grasselli, N. Quaranta, *Ceramics International*, 2003, **29**, 61-68.
- 109 J.G.S. van Jaarsveld, J.S.J. van Deventer, G.C. Lukey, *Mater. Lett.*, 2003, **57**, 1272-1280.
- 110 J.E. Kruger, *Pozzolanic and hydration reactions involving fly ash*, Guides on the use of South African fly ash as a cement extender Guide 3, J.E. Kruger (ed), The South African Coal Ash Association (SACAA), Cresta, p. 1, May 1999.
- 111 J.H. Potgieter, S.S. Potgieter, M. Loubser, E. Kearsley, C.A. Strydom, *Journal of Chemical Technology and Biotechnology*, 2002, **77** (3), 311-314.
- 112 W.H. Gehrmann III, C.E. Anderson, S.M. Ray, W.B. Baker Jr, *Artificial reefs manufactured from coal combustion by-products*, final patent no. 5,199,377, USA, 06 April 1993.
- 113 T.A. Wilding, M.D.J. Sayer, *ICES Journal of Marine Science*, 2002, **59**, S250-S257.
- 114 A.M. Vognsen, H. Boisen, *Element-rich composition*, final patent no. 4,442,215, USA, 10 April 1984.
- 115 R.G. Aldrich, G.H. Earl, D.W. Trunko, *Process for making ferrite spherical particulate toner core from raw fly ash*, final patent no. 4,6989,289, USA, 06 October 1987.
- 116 R.J. Hagenbach, *Carrier and developer compositions generated from fly ash particle*, final patent no. 4,894,305, USA, 16 January 1990.
- 117 R.G. Aldrich, G.H. Earl, D.W. Trunko, *Ferrite toner carrier core composition derived from fly ash*, final patent no. 4,592,988, USA, 03 June 1986.
- 118 R.J. Hagenbach, *Carrier and developer compositions generated from fly ash particle*, final patent no. 5,087,545, USA, 11 February 1992.
- 119 X. Querol, N. Moreno, J.C. Umaña, A. Alastuey, E. Hernández, *International Journal of Coal Geology*, 2002, **50**, 413-423.
- 120 J.V. Smith, *Chem. Rev.*, 1988, **88** (1), 149-182.
- 121 S.L. Suib, *Chem. Rev.*, 1993, **93** (2), 803-826.
- 122 C.S. Cundy, P.A. Cox, *Chem. Rev.*, 2003, **103**, 663-701.
- 123 K. Kautz, *Fortschr. Miner.*, 1984, **62** (1), 51-72.
- 124 E.J. DeGuire, S.H. Risbud, *J. Mater. Sci.*, 1984, **19**, 1760-1766.
- 125 G.S. Ghuman, M.P. Menon, K. Chandra, J. James, D.C. Adriano, K.S. Sajwan, *Water, Air, and Soil Pollution*, 1994, **72**, 285-295.
- 126 K.S. Rebeiz, A.P. Craft, *Journal of Energy Engineering- ASCE*, 2002, **128**(3), 62-73.
- 127 D.A. Smetana, R.J. Lenczewski, A.L. Wilson, *Pumpable backfill grout*, final patent no. 5,294,255, USA, 15 March 1994.
-

-
- 128 C.W. Pike, *Method of making asphaltic roofing material containing class F fly ash filler*, final patent no. 5,565,239, USA, 15 October 1996.
- 129 B.J. Morrison, *Roofing and similar materials*, final patent no. 4,745,032, USA, 17 May 1988.
- 130 P.J. Clearly, *Roofing composition and structure*, final patent no. 4,331,726, USA, 25 May 1982.
- 131 W.M. Strabala, *Structural products manufactured from fly ash*, final patent no. 5,534,058, USA, 09 July 1996.
- 132 E. Vazquez, *Fly Ash in Road Construction*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First edition, E & FN Spon, London, 1991, pp. 174-175.
- 133 L. Barbieri, I. Lancellotti, T. Manfredini, I. Queralto, J. Ma. Rincon, M. Romero, *Fuel*, 1999, **78**, 271-276.
- 134 J. Bijen, *Bricks and Blocks*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First edition, E & FN Spon, London, 1991, p. 169.
- 135 J.C. Howlett, *Process for forming solid aggregates including shaped articles*, final patent no. 5,718,857, USA, 17 February 1998.
- 136 T.W. Evans, *Method of repairing potholes in road surfaces by filling them with fly ash hardened in water*, final patent no. 4,431,335, USA, 14 February 1984.
- 137 E. Weill, G.A. Crenson, *Cement based patching composition for asphalt pavement*, final patent no. 5,244,304, USA, 14 September 1993.
- 138 J. Bijen, *Lightweight Aggregates*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First edition, E & FN Spon, London, 1991, pp. 172-174.
- 139 W.M. Strabala, *Fly ash composites and methods for making same*, final patent no. 6,200,379, USA, 13 March 2001.
- 140 R.B. Bruce, R.A. Kuntze, *Sag-resistant gypsum board containing coal fly ash and method for making same*, final patent no. 4,403,006, USA, 06 September 1983.
- 141 S. Matsuura, Y. Arai, S. Aoki, S. Ando, *Process for producing a fire-resistant, light-weight construction board*, final patent no. 4,586,958 and 4,812,169, USA.
- 142 H. Kawai, *Method of manufacturing a wood-cement board*, final patent no. 5,863,477, USA, 26 January 1999.
- 143 H. Kawai, *Wood-cement board product*, final patent no. 6,001,169, USA, 14 December 1999.
- 144 T.E. Clear, *Cementitious structural building panel*, final patent no. 6,079,175, USA, 27 June 2000.
- 145 C-F. Lin, S-S. Lo, H-Y. Lin, Y. Lee, *Journal of Hazardous Materials*, 1998, **60**, 217-226.
- 146 R. Sikka, B.D. Kansal, *Bioresource Technology*, 1995, **51**, 199-203.
- 147 R.J. Wright, E.E. Codling, S.F. Wright, *Chemosphere*, 1998, **36** (6), 1463-1474.
- 148 S.N. Singh, K. Kulshreshtha, K.J. Ahmad, *Ecological Engineering*, 1997, **9**, 203-208.
- 149 J.W.C. Wong, D.C. Su, *Bioresource Technology*, 1997, **59**, 97-102.
- 150 J.W.C. Wong, D.C. Su, *Bioresource Technology*, 1997, **59**, 57-62.
- 151 M. Fang, J.W.C. Wong, K.K. Ma, M.H. Wong, *Bioresource Technology*, 1999, **67**, 19-24.
- 152 N.W. Menzies, R.L. Aitken, *Scientia Horticulturae*, 1996, **67**, 87-99.
- 153 M.R. Khan, M.W. Khan, *Environmental Pollution*, 1996, **92** (2), 105-111.
- 154 S. Sharma, M.H. Fulekar, C.P. Jayalakshmi, *Critical reviews in environmental control*, 1989, **19** (3), 251-275.
- 155 P.J.A. Shaw, *Journal of Applied Ecology*, 1992, **29**, 728-736.
- 156 J.L. Fail Jr, *Plant and Soil*, 1987, **101**, 149-150.
- 157 J.S.C. Mbagwu, *Plant and Soil*, 1983, **74**, 75-81.
- 158 M.H. Wong, J.W.C. Wong, *Environ. Pollut. Ser. A.*, 1986, **40**, 127-144.
- 159 D.A. Toll, M.F. Arthur, *The Science of the Total Environment*, 1983, **31**, 243-261.
- 160 M. Ghodrati, J.T. Sims, B.L. Vasilas, *Water, Air, and Soil Pollution*, 1995, **81**, 349-361.
- 161 M.P. Menon, K.S. Sajwan, G.S. Ghuman, J. James, K. Chandra, B. Bacon, *Water, Air, and Soil Pollution*, 1993, **69**, 209-216.
- 162 G. Petruzzelli, L. Lubrano, S. Cervelli, *Water, Air, and Soil Pollution*, 1987, **32**, 389-395.
- 163 H. Veeresh, S. Tripathy, D. Chaudhuri, B. Ghosh, B. Hart, M. Powell, *Environmental Geology*, 2003, **43**(5), 513-520.
-

-
- 164 G.O. Schumacher, L. Weber, M. Nowicki, A. Dunbar, J.M. Douglas, *Method of treating municipal sewage sludge and product produced thereby*, final patent no. 5,143,481, USA, 01 September 1992.
 - 165 E.R. Markham, J.T. Markham, E.G. Markham, *Organic base fertilizer from municipal sewage sludge*, final patent no. 5,252,116, USA, 12 October 1993.
 - 166 W. Chesner, *Process for waste injection into landfills for waste management, landfill reclamation, enhanced biodegradation and enhanced methane gas generation and recovery*, final patent no. 5,139,365, USA, 18 August 1992.
 - 167 D.L. Hansen, *Pozzolanic mixture for stabilizing landfill leachate*, final patent no. 4,917,733, USA, 17 April 1990.
 - 168 C.L. Smith, J.J. Juzwiak, *Synthetic aggregate and landfill method*, final patent no. 5,211,750, USA, 18 May 1993.
 - 169 G. Cain, J.D. Teague, P.J. Wright, *Stabilization of earth subsurface layers*, final patent no. 4,084,381, USA, 18 April 1978.
 - 170 L.B. Spangle, S.E. Coleman, *Method for underground support and removal of hazardous ions in ground waters*, final patent no. 4,741,834, USA, 03 May 1988.
 - 171 T. Punshon, D.C. Adriano, J.T. Weber, *The Science of the Total Environment*, 2002, **296**, 209-225.
 - 172 C.L. Smith, W.C. Webster, *Process for treating aqueous chemical waste sludges and compositions produced thereby*, final patent no. RE 29,783, USA, 26 September 1978.
 - 173 R.M. Gleizes, *Coal ashes used for treating various media and facilities for using same*, final patent no. 6,015,498, USA, 18 January 2000.
 - 174 S. Lim, W. Jeon, J. Lee, K. Lee, N. Kim, *Wat. Res.*, 2002, **36**, 4177-4184.
 - 175 B.C. Young, A.L. Harris, *Soil stabilizing method and apparatus*, final patent no. 4,990,025, USA, 05 February 1991.
 - 176 H.H. Wardell, *Waste water clarification*, final patent no. 4,882,070, USA, 21 November 1989.
 - 177 H. Segawa, K. Akizuki, *Apparatus for producing potassium silicate fertilizer*, final patent no. 4,293,523, USA, 06 October 1981.
 - 178 S. Kamo, T. Watanabe, K. Nakayama, *Process for producing granular basic phosphate fertilizer*, final patent no. 4,248,617, USA, 03 February 1981.
 - 179 R.F. Stockel, *Coal ash fertilizer compositions*, final patent no. 4,469,503, USA, 04 September 1984.
 - 180 Y.B. Lee, H.S. Ha, K.D. Lee, K. Do Park, Y.S. Cho, P.J. Kim, *Soil Sci. Plant Nutr.*, 2003, **49**(1), 69-76.
 - 181 S. Gaiind, A.C. Gaur, *Bioresource Technology*, 2003, **87**, 125-127.
 - 182 R.W. Styron, K.S. Abiodun, *Method of making a mineral filler from fly ash*, final patent no. 6,139,960, USA, 31 October 2000.
 - 183 D.J. Najvar, B.G. Pope, N.R. Loeffler, *Fly ash reactive filler for dehydrating and bonding aqueous polymeric compositions*, final patent no. 4,714,722, USA, 22 December 1987.
 - 184 R.W. Styron, K.S. Abiodun, *Method of making mineral filler and pozzolan product from fly ash*, final patent no. 6,242,098, USA, 05 June 2001.
 - 185 S.J. Glorioso, J.H. Burgess, *Extruded polymer foam with filler particles and method*, final patent no. 5,723,506 and RE37,095, USA.
 - 186 W.G. Stobby, *Rigid polyurethane modified polyisocyanurate containing fly ash as an inorganic filler*, final patent no. 4,661,533, USA, 28 April 1987.
 - 187 A. Albertelli, L.M. Hohmann, A.N. Curtis, *Foamed plastic materials*, final patent no. 4,843,103 and 4,595,710, USA.
 - 188 J.N. Mushovic, *Cured unsaturated polyester-polyurethane hybrid highly filled resin foam*, final patent no. 5,302,634, USA, 12 April 1994.
 - 189 E.L. Clay, J.L. Baker, *Natural sandwich of filled polyurethane foam*, final patent no. 4,164,526, USA, 14 August 1979.
 - 190 V.K. Srivastava, *Engng. Fracture Mech.*, 1992, **43** (6), 1093-1096.
 - 191 B.M. Sole, A. Ball, *Tribology International*, 1996, **29** (6), 457-465.
 - 192 P.A. Järvelä, P.K. Järvelä, *J. Mater. Sci.*, 1996, **31**, 3853-3860.
 - 193 F. Yang, V. Hlavacek, *Powder Technology*, 1999, **103**, 182-188.
-

-
- 194 V.K. Srivastava, P.S. Shembekar, *J. Mater. Sci.*, 1990, **25**, 3513-3516.
- 195 N. Chand, *J. Mater. Sci. Lett.*, 1988, **7**, 36-38.
- 196 J.G. Smillie, *Shaped rigid articles containing fly ash and resin*, final patent no. 4,352,856, USA, 05 October 1982.
- 197 R.C. Jenkins, *Carpet backing precoat, laminate coats, and foam coats prepared from polyurethane formulations including fly ash*, final patent no. 6,096,401, USA, 01 August 2000.
- 198 Y. Ahluwalia, *Coated structural articles*, final patent no. 5,965,257, USA, 12 October 1999.
- 199 C.N. Ferguson, *Foam composition and process*, final patent no. 4,328,034, USA, 04 May 1982.
- 200 A. Boominathan, S. Hari, *Soil Dynamics and Earthquake Engineering*, 2002, **22**, 1027–1033.
- 201 R. Bloembergen, J.A. Verhave, *Flame retardant thermally insulating material*, final patent no. 4,425,440, USA, 10 January 1984.
- 202 H. Sperber, *Method for insulating a cavity*, final patent no. 5,389,167, USA, 14 February 1995.
- 203 H. Sperber, *Method for insulating a cavity*, final patent no. 5,393,794, USA, 28 February 1995.
- 204 Y.M. Jo, R.B. Hutchison, J.A. Raper, *Powder Technology*, 1997, **91**, 55-62.
- 205 S. Kumar, K.K. Singh, P. Ramachandrarao, *J. Mater. Sci. Lett.*, 2000, **19**, 1263-1265.
- 206 I.G. Talmy, D.A. Haught, C.A. Martin, *Ash-based ceramic materials*, final patent no. 5,521,132, USA, 28 May 1996.
- 207 J.T. Golitz, J.F. Mainieri, B.H. Bennett, R.D. Moore, A.M. Paxton, *Ceramic products, of glass, fly ash and clay and methods of making the same*, final patent no. 5,583,079, USA, 10 December 1996.
- 208 G.J. Monaghan, *High quality mineral wool*, final patent no. 4,504,544, USA, 12 March 1985.
- 209 E. Tseng, M. Bassin, *Ash coated cellular glass pellet*, final patent no. 4,143,202, USA, 06 March 1979.
- 210 L. Barbieri, A.M. Ferrari, I. Lancellotti, C. Leonelli, J.M. Rincòn, M. Romero, *J. Am. Ceram. Soc.*, 2000, **83** (10), 2515-2520.
- 211 R.E. Byrne, *Production of amber glass*, final patent no. 4,065,281, USA, 27 December 1977.
- 212 H. Hojaji, P.B. de Macedo, T.A. Litovitz, *Method for making foam glass from diatomaceous earth and fly ash*, final patent no. 4,430,108, USA, 07 February 1984.
- 213 J. Sheng, B.X. Huang, J. Zhang, H. Zhang, J. Sheng, S. Yu, M. Zhang, *Fuel*, 2003, **82**, 181-185.
- 214 J. Shabtai, G. Fleminger, J. Fleming, *Extraction of metal oxides from coal fly ash by microorganisms and a new microorganism useful therefor*, final patent no. 5,231,018, USA, 27 July 1993.
- 215 Z. Fang, H.D. Gesser, *Hydrometallurgy*, 1996, **41**, 187-200.
- 216 T.M. Gilliam, R.M. Canon, B.Z. Egan, A.D. Kelmers, F.G. Seely, J.S. Watson, *Resources and Conservation*, 1982, **9**, 155-168.
- 217 M.S. Dobbins, G. Burnet, *Resources and Conservation*, 1982, **9**, 231-242.
- 218 R.G. Aldrich, *Separation of high grade magnetite from fly ash*, final patent no. RE31,540, USA, 20 March 1984.
- 219 R.G. Aldrich, *Separation of high grade magnetite from fly ash*, final patent no. 4,319,988, USA, 16 March 1982.
- 220 J.W. Brown, *Process for recovering magnetite from fly ash*, final patent no. 4,191,336, USA, 04 March 1980.
- 221 M.S. Dobbins, M.J. Murtha, *Recovery of iron oxide from coal fly ash*, final patent no. 4,386,057, USA, 31 May 1983.
- 222 W.J. McDowell, F.G. Seeley, *Recovery of aluminum and other metal values from fly ash*, final patent no. 4,254,777, USA, 24 February 1981.
- 223 J.J. Russ, J.S. Russ, R.T. Heagy, *Process for recovering mineral values from fly ash*, final patent no. 4,130,627, USA, 19 December 1978.
-

-
- 224 J.J. Russ, J.W. Smith, *Method for separating and recovering silica, aluminum and iron from fly ash, mineral ores and mine tailings*, final patent no. 4,539,187, USA, 03 September 1985.
- 225 J.E. Reynolds, A.R. Williams, *Process for recovering aluminum and other metal values from fly ash*, final patent no. 4,159,310, USA, 26 June 1979.
- 226 W.E. Dunn Jr, *Two stage chlorination process for aluminum value containing source*, final patent no. 4,355,007, USA, 19 October 1982.
- 227 I. Tsuboi, S. Kasai, E. Kunugita, I. Komasaawa, *Journal of Chemical Engineering of Japan*, 1991, **24** (1), 15-20.
- 228 B. Lisowyj, D. Hitchcock, H. Epstein, *Direct fuel-fired furnace arrangement for the recovery of gallium and germanium from coal fly ash*, final patent no. 4,643,110, USA, 17 February 1987.
- 229 B. Lisowyj, D. Hitchcock, H. Epstein, *Process for the recovery of gallium and germanium from coal fly ash*, final patent no. 4,678,647, USA, 07 July 1987.
- 230 B. Lisowyj, D.C. Hitchcock, *Beneficiation of gallium in fly ash*, final patent no. 4,686,031, USA, 11 August 1987.
- 231 S. Santen, B. Johansson, *Treatment of fly ash*, final patent no. 6,155,965, USA.
- 232 C. Kersch, M.J.E. Van Roosmalen, M.J.E. Roosmalen, G.F. Woerlee, G.J. Witkamp, *Ind. Eng. Chem. Res.*, 2000, **39** (12), 4670-4672.
- 233 G.P. Dasmahapatra, T.K. Pal, B Bhattacharya, *Sep. Sci. Technol.*, 1996, **31** (20), 2843-2853.
- 234 R. Fass, J. Geva, Z.P. Shalita, M.D. White, J.C. Fleming, *Bioleaching method for the extraction of metals from coal fly ash using thiobacillus*, final patent no. 5,278,069, USA, 11 January 1994.
- 235 M.J. Murtha, *Process for the recovery of alumina from fly ash*, final patent no. 4,397,822, USA, 09 August 1983.
- 236 W.J. McDowell, F.G. Seeley, *Salt-soda sinter process for recovering aluminum from fly ash*, final patent no. 4,254,088, USA, 03 March 1981.
- 237 M. Boybay, T. Demirel, *Process for preparing cryolite from fly ash*, final patent no. 4,362,703, USA, 07 December 1982.
- 238 A.E. Torma, *Process for the recovery of alumina from fly ash and production of cement constituents*, final patent no. 4,242,313, USA, 30 December 1980.
- 239 I. Tsuboi, E. Kunugita, I. Komasaawa, *Journal of Chemical Engineering of Japan*, 1990, **23** (4), 480-485.
- 240 P-C. Kao, J-H. Tzeng, T-L. Huang, *Journal of Hazardous Materials*, 2000, **76**, 237-249.
- 241 T. Viraraghavan, F.D. Alfaro, *Journal of Hazardous Materials*, 1998, **57**, 59-70.
- 242 B. Zinke, *Method for absorbing organic pollutants*, final patent no. 5,769,777, USA, 23 June 1998.
- 243 K. Banerjee, P.N. Cheremisinoff, S.L. Cheng, *Wat. Res.*, 1997, **31** (2), 249-261.
- 244 A. Peloso, M. Rovatti, G. Ferraiolo, *Resources and Conservation*, 1983, **10**, 211-220.
- 245 J. Bijen, *Waste Neutralization and Stabilization*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First, E & FN Spon, London, 1991, pp. 177-178.
- 246 S. Babel, T. A. Kurniawan, *Journal of Hazardous Materials*, 2003, **B97**, 219-243.
- 247 A. Garea, M.I. Ortiz, J.R. Viguri, M.J. Renedo, J. Fernandez, J.A. Irabien, *Thermochemica Acta*, 1996, **286**, 173-185.
- 248 A. Garea, I. Fernández, J.R. Viguri, M.I. Ortiz, J. Fernandez, M.J. Renedo, J.A. Irabien, *Chemical Engineering Journal*, 1997, **66**, 171-179.
- 249 A. Garea, J.R. Viguri, A. Irabien, *Chemical Engineering Science*, 1997, **52** (5), 715-732.
- 250 H. Tsudhiai, T. Ishizuka, H. Nakamura, T. Ueno, H. Hattori, *Ind. Eng. Chem. Res.*, 1996, **35** (3), 851-855.
- 251 A.P. Simko, *Process for removing sulfur dioxide in a wet scrubber*, final patent no. 4,164,547, USA, 14 August 1979.
- 252 N.C. Samish, *Removal of SO_x and NO_x gases from flue gas by absorption using an absorbent*, final patent no. 4,980,138, USA, 25 December 1990.
- 253 R.G. Hooper, *Method for SO_x/NO_x pollution control*, final patent no. 5,002,741, USA, 26 March 1991.
-

-
- 254 L. Zhang, A. Sato, Y. Ninomiya, E. Sasaoka, *Fuel*, 2003, **82**, 255-266.
- 255 M.J. Renedo, J. Fernández, *Fuel*, 2004, **83**, 525-532.
- 256 G. Gupta, N. Torres, *Journal of Hazardous Materials*, 1998, **57**, 243-248.
- 257 A. Demirbaş, *Cem. Concr. Res.*, 2003, **33**, 935.
- 258 N.M. Agyeia, C.A. Strydom, J.H. Potgieter, *Cem. Concr. Res.*, 2003, **33**, 937.
- 259 B. Bayat, *Journal of Hazardous Materials*, 2002, **B95**, 275-290.
- 260 S. Chatterjee, R.K. Asthana, A.K. Tripathi, S.P. Singh, *Process Biochemistry*, 1996, **31** (5), 457-462.
- 261 J. Ayala, F. Blanco, P. García, P. Rodríguez, J. Sancho, *Fuel*, 1998, **77** (11), 1147-1154.
- 262 D.J. Hassett, K.E. Eylands, *Fuel*, 1997, **76** (8), 807-809.
- 263 R. Renk, *Selenium adsorption process*, final patent no. 4,971,702, USA, 20 November 1990.
- 264 A.K. Sen, A.K. De, *Wat. Res.*, 1987, **21** (8), 885-888.
- 265 H.C. Hsi, M.J. Rood, M. Rostam-Abadi, S.G. Chen, R. Chang, *J. Envir. Enrg.*, ASCE, 2002, **128**(11), 1080-1089.
- 266 G.E. Dunham, R.A. DeWall, C.L. Senior, *Fuel Processing Technology*, 2003, **82**, 197-213.
- 267 F.M. Scheitlin, *Removal of radium from acidic solutions containing same by adsorption on coal fly ash*, final patent no. 4,431,609, USA, 14 February 1984.
- 268 K.K. Panday, G. Prasad, V.N. Singh, *Wat. Res.*, 1985, **19** (7), 869-873.
- 269 B. Bayat, *Journal of Hazardous Materials*, 2002, **B95**, 251-273.
- 270 H-L. Chang, W-H. Shih, *Ind. Eng. Chem. Res.*, 2000, **39** (11), 4185-4191.
- 271 G.S. Gupta, G. Prasad, K.K. Panday, V.N. Singh, *Water, Air, and Soil Pollution*, 1988, **37**, 13-24.
- 272 G.S Gupta, G Prasad, V.N Singh, *Wat. Res.*, 1990, **24** (1), 45-50.
- 273 P. Ricou-Hoeffler, V. Héquet, I. Lécuyer, P. Le Cloirec, *Wat. Sci. Tech.*, 2000, **42** (5-6), 79-84.
- 274 M. Ding, M. Guesebroek, H.A. van der Sloot, *J. Geochem. Explor.*, 1998, **62**, 319-323.
- 275 A.K. Chaturvedi, K.P. Pathak, V.N. Singh, *Water, Air, and Soil Pollution*, 1990, **49**, 51-61.
- 276 D. Mallik, S.K. Chaudhuri, *Wat. Res.*, 1999, **33** (2), 585-590.
- 277 S.K. Chaudhuri, B. Sur, *J. Envir. Enrg.*, ASCE, 2000, **126** (7), 583-594.
- 278 J.R. Kastner, K.C. Das, N.D. Melear, *Journal of Hazardous Materials*, 2002, **B95**, 81-90.
- 279 X. Xuan, C. Yue, *Fuel*, 2003, **82**, 575-579.
- 280 D.R. Corbin, L.J. Velenyi, M.A. Pepera, S.R. Dolhyj, *Activation of fly ash*, final patent no. 4,607,021, USA, 19 August 1986.
- 281 C.P. Khulbe, R. Ranganathan, B.B. Pruden, *Hydrocracking of heavy oils/fly ash slurries*, final patent no. 4,299,685, USA, 10 November 1981.
- 282 R.B. Pond Sr, *Metal composites with fly ash incorporated therein and a process for producing the same*, final patent no. 4,888,054, USA, 19 December 1989.
- 283 N. Sobczak, J. Sobczak, J. Morgiel, L. Stobierski, *Materials Chemistry and Physics*, 2003, **81**, 296-300.
- 284 E.J. Schwoegler, *Compositions of sulfur and fly ash and shaped articles produced therefrom*, final patent no. 4,134,775, USA, 16 January 1979.
- 285 R.F. Stockel, *Animal litter composition*, final patent no. 4,129,094, USA, 12 December 1978.
- 286 H-L. Chang, W-H Shih *Ind. Eng. Chem. Res.*, 1999, **38** (3), 973-977.
- 287 H. Höller, U. Wirsching, *Fortschr. Miner.*, 1985, **63** (1), 21-43.
- 288 N. Shigemoto, S. Sugiyama, H. Hayashi, K. Miyaura, *J. Mater. Sci.*, 1995, **30**, 5777-5783.
- 289 J.C. Swanepoel, C.A. Strydom, *Applied Geochemistry*, 2002, **17** (8), 1143-1148.
- 290 J.G.S. Van Jaarsveld, J.S.J. Van Deventer, *Ind. Eng. Chem. Res.*, 1996, **38** (10), 3932-3941.
- 291 J.G.S. van Jaarsveld, J.S.J. van Deventer, G.C. Lukey, *Chemical Engineering Journal*, 2002, **89**, 63-73.
- 292 A.A. Landman, D. De Waal, *Materials Research Bulletin*, 2004, **39**, 655-667.
-