Fly ash characteristics of Spanish coal-fired power plants

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Propiedades de las cenizas volantes de las centrales térmicas de carbón españolas

Propietats de les cendres volants de les centrals tèrmiques de carbó espanyoles

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RESUMEN

Las cenizas volantes del carbón son unas partículas finas que pueden contener algunos metales pesados. Su gestión es uno de los mayores problemas en el mundo. En este artículo se presenta un estudio sobre las diferencias en composición química de las cenizas volantes españolas que permitirá, inicialmente, su clasificación y, posteriormente, su utilización industrial potencial en diferentes aplicaciones. Por tanto, se han caracterizado las cenizas volantes españolas con relación a su composición química, se han clasificado y se recomiendan algunas aplicaciones. El alcance del trabajo se limita a las cenizas volantes procedentes de las centrales térmicas de carbón. Las cenizas de fondo y escorias así como las cenizas obtenidas en otros procesos industriales se encuentran fuera del alcance del presente trabajo.
La conclusión principal es la posible utilización preferente de las cenizas volantes en la construcción y como adsorbente para la eliminación de algunos compuestos. Las cenizas volantes con una reducida pérdida por calcinación son aptas para el primer caso mientras que las que tienen una elevada pérdida por calcinación para el segundo.

Palabras clave: Cenizas volantes; Central térmica de carbón; Composición química; Reutilización de cenizas; Reciclado.

SUMMARY

Coal-fly ash consists of fine particles that could contain some heavy metals. The management of coal fly ash remains a major problem all over the world. An attempt has been made in the present paper to highlight the differences on chemical composition of Spanish fly ashes which allows first their classification and second their potential utilization in several industrial applications. Therefore, Spanish fly ash characterization in terms of chemical analysis, their classification and recommendation of utilization is assessed. The scope of this paper is limited to fly ash from coal fired in thermal power plants. Bottom ash and slag as well as fly ash generated from other industrial sources are beyond the scope of this paper.
The major conclusions are related to the utilization of fly ash in construction and as adsorbent for the removal of some compounds. Fly ash with a lower loss on ignition can be used in the first field, whereas fly ash with a higher loss on ignition can be used in the second one.

Key words: Fly ash; coal fired power plants; chemical composition; fly ash re-use; recycling

RESUM

Les cendres volants del carbó són unes partícules fines que poden contenir alguns metalls pesants. La seva gestió és un dels problemes principals en el món. En aquest article es presenta un estudi sobre les diferències en composició química de les cendres volants espanyoles. Inicialment permetrà la seva classificació i posteriorment la seva utilització industrial potencial en diferents aplicacions. Per tant, les cendres volants espanyoles s'han caracteritzat amb relació a la seva composició química, s'han classificat i es recomanen algunes aplicacions. L'àmbit del treball es limita a les cendres volants procedents de les centrals tèrmiques de carbó. Les cendres de fons i escòries així com les cendres obtingudes en altres processos industrials es troben fora de l'àmbit del present treball.La conclusió principal és la possible utilització preferent de les cendres volants en la construcció i com adsorbent per a l'eliminació d'alguns compostos. Les cendres volants amb una reduïda pèrdua per calcinació són aptes per la construcció, mentre que les que tenen una elevada pèrdua per calcinació ho són com adsorbent.

Paraules clau: Cendres volants; Central tèrmica de carbó; Composició química; Reutilització de cendres; Reciclatge.

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INTRODUCTION

Coal-fired power plants generate significantly large quantities of a solid residue called fly ash. Coal-fly ash consists of fine particles that contain leachable heavy metals and, therefore, is classified as a toxic waste [1-3]. The management of fly ash produced by coal fired power plants remains a major problem in the world. Although, significant amounts of fly ash could be used in a range of applications. At present, it is extensively used for a variety of construction materials. However, there is a need to address the problems encountered during the re-use fly ash in construction materials.

Industrialization is a worldwide necessity of society, and then, in many cases inevitable. However, one has to look into its negative impacts on the global environment and social life and try to minimize them. The major negative effect of this global process is the production of large amounts of industrial wastes such as coal fly ash, and the problems related with its safe management, recycling or disposal.

The population increase and industrial growth are two typical characteristics of present day society, which require more electricity generated from the coal based thermal power plants. Coal based thermal power plant installations in Spain contributed about 12% of the total installed capacity for power generation accounting 10635 MW/year in April, 2011. Currently, the energy sector in Spain generates over two million tons of fly ash (FA) annually and this amount will decrease as annual coal consumption decreases as result of alternative energies use increase in Spain. Nowadays, fly ash price at a power plant in Spain is about 6€/ton.

Currently, the annual production of coal ash worldwide is estimated around 700 million tones, with fly ash about 80% of the total ash produced [2]. In the United States, the coal ash produced annually by coal-burning power plants amounts to more than 100 million tons [4] and 49 million tons in Europe [5]. In Spain, the production capacity is about 5 million tons, but the current production is much lower. An estimated 21 million tons of fly ash in Europe is used for cement production, construction of roads and brick manufacture [5]. The fly ash utilization for these purposes is expected to increase by 2015–2020 [6]. However, a significant amount of ash is still expected to be disposed of in landfills. A large fraction of the coal ash in the world, about 70% of the total production, is typically disposed of as a waste in utility disposal sites. Disposal of fly ash will soon be too costly, if not forbidden. Considerable research is being conducted worldwide on the use of waste materials in order to avoid undesirable environmental effects.

The use of coal ash to make construction materials is beneficial to society, but other uses are being developed, for instance, as adsorbents. From the perspective of power generation, fly ash is a waste material, while from a coal utilization perspective, fly ash is a potential resource.

Research on the potential applications of these wastes has environmental relevance, because fly ash particles are considered to be highly contaminating, due to their enrichment in trace elements which condense from the flue gas. Fly ash is a fine, powdery collection of particles predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The carbonaceous material in the fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ash is generally similar to that of silt (less than a 0.075 mm). However, although sub-bituminous coal fly ash is also silt-sized, it is generally coarser than bituminous coal fly ash. The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area may vary from 170 to 1000 m^2/kg [7]. The colour of fly ash can vary from gray to black, depending on the amount of unburned carbon in the ash.

The mineralogical composition of fly ash, which depends on the geological factors related to the formation and deposition of coal, its combustion conditions, can be established by X-ray diffraction (XRD) analysis. The dominant mineral phases are quartz, kaolinite, ilite, and siderate. The less predominant minerals in the unreacted coals include calcite, pyrite and hematite. Quartz and mullite are the major crystalline constituents of low-calcium ash, whereas high-calcium fly ash consists of quartz, C_3A, CS and C_4AS. The wastes generated from different Spanish coal fired power plants are of complex characteristics and different chemical compositions and hence, their safe management and re-use could be also intricate and complex.

EXPERIMENTAL

Characterization of 18 Spanish fly ashes was made. Elemental analyses of these samples were carried out by X-ray fluorescence (XRF) spectrometry technique with a Bruker S8 Tigger 4kW model. Therefore, chemical analyses of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, SO_3 were determined.

At present in Spain, about 22 coal-fired power plants are producing about 3.5 million tons of fly ash in 2012 (almost 5 million tons of fly ash in 2010). Most of them are classified as simple cycle power plants with traditional boiler, and two of them have fluidized-bed (La Pereda, Mieres, HUNOSA and Escucha, Teruel, EON). Only one of them has an Integrated Coal Gasification Combined-cycle Technology (GICC) in Puertollano (ELCOGAS). Fly ash generated in the GICC process amounts from 10.000 to 11.000 tons per year and has a high fineness. In the coal gasification process, the organic part is converted into gas and the inorganic one into ashes which are removed as a vitrified slag from the bottom of the gasifier. Part of the ashes comes out with the gas as a fine powder called also fly ash. Most of fly ashes have fineness similar to that of the cement; therefore, grinding is not necessary in such cases.

RESULTS AND DISCUSION

Chemical Characteristics of Spanish Fly ash

Fly ash, generated during the combustion of coal for energy production, is an industrial by-product which is recognized as an environmental pollutant. Because of the environmental problems presented by the fly ash, considerable research has been undertaken on the subject worldwide. In this paper, the utilization of most of the Spanish fly ash in construction and as adsorbent of contaminants among other applications is addressed.

Figure 1 shows the 22 coal-fired Spanish power plants [8]. The fly ash were characterized by conducting tests in laboratory. The chemical analyses of 18 of them considered in the present paper are shown in table 1. Elemental analyses of Spanish fly ashes were carried out by X-ray fluorescence (XRF) spectrometry technique.

Table 1. *Chemical composition of the Spanish fly ashes from 18 different Spanish coal-fired power plants tested in the present study.*

Coal-fired power plants	Chemical composition of the Spanish fly ashes (%)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI	SiO_2/ Al_2O_3	SiO_2+Al_2O_3 +Fe_2O_3
Meirama	49.0	24.8	7.8	5.5	1.8	0.7	0.9	0.4	4.11	2.0	81.6
Soto de Ribera	48.8	25.6	7.7	6.6	1.4	0.5	3.1	0.4	6.40	1.9	82.1
Narcea	48.9	23.1	7.8	3.9	2.3	0.7	3.2	0.1	2.18	2.1	79.8
Aboño	48.6	29.2	10.1	5.2	1.8	1.1	2.7	0.3	2.20	1.7	87.9
Lada	46.8	30.6	3.7	5.5	1.6	0.3	1.2	0.2	4.17	1.5	81.1
Compostilla	48.9	23.7	11.6	2.8	1.6	0.8	3.9	0.5	4.00	2.1	84.2
Anllares	49.9	25.8	7.8	3.1	2.1	0.8	4.1	0.4	4.80	1.9	83.5
La Robla	46.8	25.1	10.6	6.0	1.8	0.6	3.2	0.5	3.87	1.9	82.5
Pasajes	51.2	23.2	8.1	7.3	2.2	1.4	2.1	0.2	3.40	2.2	82.5
Puertollano	54.8	25.2	9.8	3.7	1.3	1.1	2.4	0.2	1.84	2.2	89.8
Teruel-Andorra	41.0	25.6	19.0	7.8	1.4	0.1	1.3	1.1	2.10	1.6	85.6
Puente Nuevo	56.0	27.2	5.9	1.9	1.4	0.6	4.0	0.2	2.45	2.1	89.1
Carboneras (C.T. Litoral)	49.2	27.1	4.0	4.5	1.8	0.3	1.0	0.3	2.18	1.8	80.3
Los Barrios	49.8	24.8	6.1	8.4	1.3	0.4	1.1	0.5	4.35	2.0	80.7
Velilla	51.1	16.7	17.2	4.7	1.5	0.4	2.1	0.4	4.97	3.1	85.0
ELCOGAS. Puertollano (GICC)	53.8	27.2	5.3	6.4	0.9	0.3	2.2	2.5	1.25	2.0	86.3
Viesgo-Escucha (Fluidized bed)	39.7	24.1	7.2	6.8	1.6	0.1	2.8	1.7	2.61	1.6	71.0
La Pereda (Fluidized bed)	37.8	22.1	6.4	17.1	1.3	0.2	3.5	5.4	3.9	1.7	66.3
Average value	48.5	25.1	8.7	6.0	1.6	0.6	2.5	0.9	3.5	2.0	82.2
Maximum value	56.0	30.6	19.0	17.1	2.3	1.4	4.1	5.4	6.4	3.1	89.8
Minimum value	37.8	16.7	3.7	1.9	0.9	0.1	0.9	0.1	1.8	1.5	66.3

LOI = Loss on ignition

Figure 1. *Location of the 22 electrical coal-fired power plants in Spain.*

The major parameters of chemical characteristics were as follows: SiO_2, Al_2O_3, Fe_2O_3 and CaO as main compounds. Also, minor constituents were considered such as MgO, Na_2O, K_2O, SO_3.

An important parameter is the LOI (loss on ignition) which is related to the carbon content among other (less than 1%). These values usually range between 0.60% and 6.40% depending on the type of carbon and coal-firing process among other parameters. The highest value of loss on ignition (6.40%) was found in a fly ash from a power plant using a low-grade Spanish coal and the lowest result (1.25%) was found in Gasification Combined-cycle Technology (GICC). Therefore, it can be said that the unburned carbon in the ash was determined by the loss on ignition (LOI) determination which is a good estimation of remaining carbon.

As expected, the chemical properties of fly ash are influenced to a great extent by the properties of the coal being burned and the combustion techniques used. There are four main types of coal (anthracite, bituminous, sub-bituminous and lignite), each vary in higher calorific value (HCV), chemical composition, ash content, and geological origin.

Utilization of fly ash in accordance with its physical property and chemical composition is restricted by different standards. According to the American Society for Testing Materials (ASTM C618-08a) [9], the ash containing more than 70 wt% SiO_2+Al_2O_3+Fe_2O_3 and being low in lime are defined as class F, while those with a SiO_2+Al_2O_3+Fe_2O_3 content between 50 and 70 wt% and high in lime are defined as class C.

The low-calcium Class F fly ash is commonly produced from the burning of bituminous coals or anthracites coals, that are pozzolanic in nature, i.e. hardening when reacted with $Ca(OH)_2$ and water. Most of the coal fired in Spain in power plants is bituminous. Then, the principal components of such bituminous coal fly ash are silica, alumina, iron oxide, and calcium oxide (Table 1), with varying amounts of carbon, as measured by the loss on ignition (LOI).

On the contrary, lignite and sub-bituminous coal fly ash is characterized by higher concentrations of calcium oxide and reduced percentages of silica and iron oxide, as well as lower carbon content, compared with bituminous coal fly ash. In Spain, this can only be observed in Escatron and Serchs power plants (Table 2). Also, lignite and sub-bitumi-

Table 2. *Chemical Composition of the Spanish fly ashes obtained in 1995 (10, 11), 2007 (8) and in the present experimental work.*

Coal-fired power plants	Year	Chemical composition of the Spanish fly ashes (%)										
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI	SiO_2/Al_2O_3	SiO_2+ Al_2O_3 +Fe_2O_3
Puentes de García Rodríguez	1995	46.0	32.0	9.5	4.9	1.5	0.4	2.0	2.0	-	1.4	87.5
Meirama	1995	66.1	16.5	10.3	1.3	0.3	0.3	0.7	1.5	-	4.0	92.9
	2007	53.4	17.3	8.5	9.0	1.8	0.8	0.7	-	-	3.1	79.2
	2010	49.0	24.8	7.8	5.5	1.8	0.7	0.9	0.4	4.11	2.0	81.6
Soto de Ribera	1995	47.2	29.2	7.4	4.9	1.8	0.7	2.8	0.4	-	1.6	83.8
	2007	48.4	25.1	7.8	5.3	1.3	-	2.5	-	-	1.9	81.3
	2010	48.8	25.6	7.7	6.6	1.4	0.5	3.1	0.4	6.40	1.9	82.1
Narcea	1995	57.0	23.0	6.2	3.5	2.5	2.7	2.8	0.2	-	2.5	86.2
	2007	49.2	26.1	7.7	4.2	1.9	1.0	3.1	0.2	-	1.9	83.0
	2010	48.9	23.1	7.8	3.9	2.3	0.7	3.2	0.1	2.18	2.1	79.8
Aboño	1995	47.0	31.0	11.0	4.4	0.5	4.3	4.3	0.5	-	1.5	89.0
	2010	48.6	29.2	10.1	5.2	1.8	1.1	2.7	0.3	2.20	1.7	87.9
Lada	1995	49.9	28.6	7.6	3.4	1.9	0.7	2.8	0.3	-	1.7	86.1
	2007	45.7	31.2	3.6	8.2	2.0	0.4	0.9	0.8	-	1.5	80.5
	2010	46.8	30.6	3.7	5.5	1.6	0.3	1.2	0.2	4.17	1.5	81.1
Compostilla	1995	51.1	27.5	6.8	2.6	2.2	1.1	2.9	2.3	-	1.9	85.4
	2007	48.9	22.9	7.9	3.8	1.8	0.7	3.7	0.4	-	2.1	79.7
	2010	48.9	23.7	11.6	2.8	1.6	0.8	3.9	0.5	4.00	2.1	84.2
Anllares	1995	50.0	30.0	6.5	4.4	2.6	2.0	3.6	0.3	-	1.7	86.5
	2007	47.5	26.6	9.4	3.0	2.0	1.0	4.5	0.5	-	1.8	83.5
	2010	49.9	25.8	7.8	3.1	2.1	0.8	4.1	0.4	4.80	1.9	83.5
La Robla	1995	48.0	23.5	10.0	7.5	1.4	0.4	2.9	5.7	-	2.0	81.5
	2007	43.7	25.3	11.7	8.2	1.5	0.3	2.3	0.8	-	1.7	80.7
	2010	46.8	25.1	10.6	6.0	1.8	0.6	3.2	0.5	3.87	1.9	82.5
Guardo	1995	46.7	22.8	9.9	6.1	2.0	-	-	2.6	-	2.0	79.4
	2007	48.9	26.0	8.6	4.1	2.0	0.9	3.9	0.4	-	1.9	83.5
Pasajes	1995	44.5	23.1	10.2	10.0	2.5	0.3	1.3	0.4	-	1.9	77.8
	2007	52.5	23.6	7.3	7.0	2.6	1.6	2.8	0.4	-	2.2	83.4
	2010	51.2	23.2	8.1	7.3	2.2	1.4	2.1	0.2	3.40	2.2	82.5
Puertollano	1995	62.0	26.0	6.9	0.9	0.9	0.2	2.2	0.3	-	2.4	94.9
	2010	54.8	25.2	9.8	3.7	1.3	1.1	2.4	0.2	1.84	2.2	89.8
Teruel-Andorra	1995	47.5	24.6	18.6	3.5	1.0	0.4	2.5	0.4	-	1.9	90.7
	2007	43.2	29.2	16.2	6.3	1.4	0.4	1.6	0.7	-	1.5	88.6
	2010	41.0	25.6	19.0	7.8	1.4	0.1	1.3	1.1	2.10	1.6	85.6
Puente Nuevo	1995	53.6	30.7	7.1	1.4	1.7	0.5	4.7	0.8	-	1.7	91.4
	2007	55.2	29.2	5.8	1.8	0.7	-	-	0.1	-	1.9	90.2
	2010	56.0	27.2	5.9	1.9	1.4	0.6	4.0	0.2	2.45	2.1	89.1
Carboneras (C.T. del Litoral)	1995	42.5	31.1	3.7	7.0	1.9	0.2	0.7	0.1	-	1.4	77.3
	2007	48.7	29.4	3.8	6.8	1.9	0.2	0.6	0.1	-	1.7	81.9
	2010	49.2	27.1	4.0	4.5	1.8	0.3	1.0	0.3	2.18	1.8	80.3
Los Barrios	1995	50.5	30.1	5.0	5.3	1.2	0.7	1.1	0.7	-	1.7	85.6
	2007	47.5	26.0	4.4	8.5	1.9	0.3	0.8	0.4	-	1.8	77.9
	2010	49.8	24.8	6.1	8.4	1.3	0.4	1.1	0.5	4.35	2.0	80.7
Velilla	1995	46.9	17.3	18.1	5.8	1.6	0.5	2.3	0.1	-	2.7	82.3
	2010	51.1	16.7	17.2	4.7	1.5	0.4	2.1	0.4	4.97	3.1	85.0
Escatrón	1995	36.6	9.0	5.1	33.7	1.6	0.7	1.7	9.3	-	4.1	50.7
Serchs (Cenizas calcáreas)	1995	40.1	17.1	8.9	26.3	0.9	0.3	1.2	4.5	-	2.3	66.1
ELCOGAS. Puertollano (GICC)	2010	53.8	27.2	5.3	6.4	0.9	0.3	2.2	2.5	1.25	2.0	86.3
Viesgo-Escucha (Lecho fluidizado)	1995	62.2	23.2	9.8	1.3	1.0	-	-	3.3	-	2.7	95.2
	2010	39.7	24.1	7.2	6.8	1.6	0.1	2.8	1.7	2.61	1.6	71.0
La Pereda (Lecho fluidizado)	2010	37.8	22.1	6.4	17.1	1.3	0.2	3.5	5.4	3.9	1.7	66.3
Average value		49.0	25.2	8.6	6.3	1.6	0.7	2.4	1.1	3.4	2.0	82.8
Maximum value		66.1	32.0	19.0	33.7	2.6	4.3	4.7	9.3	6.4	4.1	95.2
Minimum value		36.6	9.0	3.6	0.9	0.3	0.1	0.6	0.1	1.3	1.4	50.7

LOI = Loss on ignition

nous coal fly ash may have a higher concentration of sulphate compounds than bituminous coal fly ash (Escatron: 9.3% SO_3 and Serchs: 4.5% SO_3). These high-calcium Class C fly ash has conclus properties, i.e. self-hardening when reacted with water without the need of $Ca(OH)_2$.
With regard to anthracite coal, it is not currently burned in Spain, so there is not anthracite coal fly ash.
Table 2 shows the average, maximum and minimum values of the chemical constituents of bituminous coal fly ash with those of lignite coal fly ash and sub-bituminous coal fly ash. From the table, it is evident that lignite and sub-bituminous coal fly ash has a higher calcium oxide content and lower loss on ignition (LOI) than fly ash from bituminous coals.
Figures 2 and 3 show the ternary SiO_2-Al_2O_3-CaO composition grid of the tested fly ashes provided by Spanish coal-fired power plants. It can be observed that the main difference between Class F and Class C fly ash is in the amount of calcium and the silica, alumina, and iron content in the ash. In Class F fly ash, calcium content ranges from 1.9 to 8.4% with an exception of 17.1% in La Pereda (Fluidized bed) (Table 1), mostly in the form of calcium hydroxide, calcium sulphate, and glassy components, in combination with silica and alumina. In contrast, Class C fly ash may have reported calcium oxide contents of 26.3 and 33.7% (Table 2). Another difference between Class F and Class C is that the amount of alkalis (combined sodium and potassium), and sulphates ($SO_4^{=}$), are generally higher in the Class C fly ash (4.5-9.3%) than in the Class F fly ash (0.1-5.4%). Fly ash produced in the Gasification

Combined-cycle Technology (GICC) showed a low Fe_2O_3 content of 5.3% and the lowest LOI (1.25%). On the contrary, the sum of SiO_2+Al_2O_3+Fe_2O_3 is quite high (86.3%). Taking into account all these data, the average chemical composition of the Spanish fly ashes from coal-fired power plants is established and showed in tables 1 and 2.

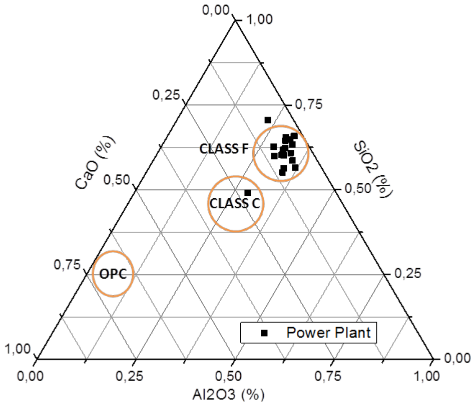

Figure 2. *Ternary SiO_2-Al_2O_3-CaO composition grid of the tested fly ashes provided by 18 Spanish coal-fired power plants*

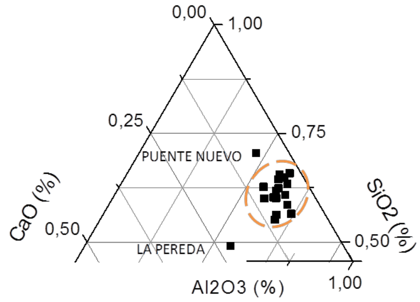

Figure 3. *Part of the Ternary diagram SiO_2-Al_2O_3-CaO of the tested fly ashes provided by 18 Spanish coal-fired power plants*

Hydraulic ratio of fly ash, SiO_2/Al_2O_3

The hydraulic ratio, SiO_2/Al_2O_3 gives an idea about the potential reactivity of fly ash. Figure 4 collects the hydraulic ratio SiO_2/Al_2O_3 of 18 Spanish coal fly ash. It can be evidenced a quite narrow range in class F coal fly ash between 1.5% and 3.1%, with an average value of 2.0%. The maximum value (3.1%) was obtained for fly ash Velilla (Table 1). However, Class C high-lime fly ash presented higher values of SiO_2/Al_2O_3 (2.3% and 4.1%), but within the range of Class F fly ash mentioned above.

Sum of fly ash main oxides, SiO_2+Al_2O_3+Fe_2O_3

The sum of SiO_2+Al_2O_3+Fe_2O_3 of fly ashes is a condition included in several international standards in order to classify fly ashes. Figure 4 shows such parameter corresponding to the 18 Spanish coal fly ash considered in the present study. It is clear that most of them belong to Class F type according to the American standard ASTM C 618-08a (Type F fly ash implies SiO_2+Al_2O_3+Fe_2O_3>70.0%) and are valid according to the requirements of the European standard EN 450-1:2012 [12]. Only fly ashes from Viesgo-Escucha (71.1%) and La Pereda (66.3%), are below 72%. According to the American Society for Testing Materials (ASTM C618-08a) [9], the ash containing less than 70 wt% SiO_2+Al_2O_3+Fe_2O_3 and which content between 50 and 70 wt% and high in lime are defined as class C. Therefore, the last one could be classified as high in lime fly ash.

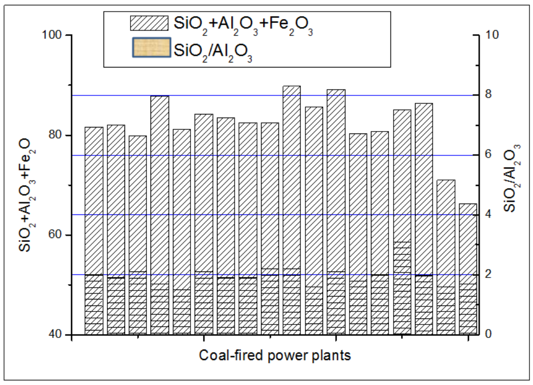

Figure 4. *Hydraulic ratio of Fly ash SiO_2/Al_2O_3 and sum SiO_2+Al_2O_3+Fe_2O_3 of the fly ashes provided by 18 Spanish coal-fired power plants*

Fly ash utilization

The application of Spanish fly ash will be discussed in this section. There are many reasons to increase the amount of fly ash being utilized. Firstly, disposal costs are minimized and it can replace some scarce natural resources. Fly ash is available at a low cost at the power plant of about 6 €/ton in Spain and, hence, only transportation cost and operation cost should be added.

In general, utilization of coal fly ash can be in the form of an alternative to another industrial resource or application. These applications include addition to cement and concrete products, structural fill and cover material, roadway and pavement utilization, addition to construction materials as a lightweight aggregate, infiltration barrier, underground void filling, and soil, water and environmental improvement. Loss on ignition (LOI) is a key parameter from the point of view of fly ash use in each potential application. Thus, EN 450-1:2012 classify the fly ashes with regard to the LOI value as: A (LOI<5.0%), B (LOI<7.0%) and C (LOI<9.0%). The following is a brief analysis of each of the previously mentioned alternative uses of Spanish fly ash.

Fly ash pozzolanic cements

Utilization of fly ash is technically feasible in the cement industry. There are essentially two main applications for fly ash in cement production, first as a raw material to produce Portland clinker and second as a pozzolanic addition. Thus, fly ash can be mixed with the Portland cement clinker as a pozzolanic constituent in the production of CEM II, Portland-composite cement, CEM IV, Pozzolanic cement or CEM V, Composite cement. All of them are common cements covered by the European standard EN 197-1:2011 [13, 14].

The typical use of fly ash as cement addition in Europe (CEM II/A-V, CEM II/B-V, CEM IV/A, CEM IV/B, CEM V/A and CEM V/B) is in the range of 6–55% (6–20%, 21-35%, 11-35%, 36-55%, 18-30% and 31-49%, respectively) according to the European standard EN 197-1:2011 [13]. Higher usage of fly ash is restricted, due to a decrease in the strength of cement, especially the early strength. This is attributed to the early low reactivity of fly ash, but such reactivity could be increased through mechanical activation by grinding [15, 16].

As said above, fly ash is normally classified into two main categories based on the percentage of CaO and on the type of coal used for burning as class F and class C fly ash. The sum of SiO_2+Al_2O_3+Fe_2O_3 of the 18 tested fly ashes was higher than 70 wt%, and then, they belong to ASTM C 618-08a Type F fly ash (SiO_2+Al_2O_3+Fe_2O_3≥70.0%) [9]. On the other hand, the calcium content is low.

Also, all the tested ashes complies the requirements of the European standard EN 450-1:2012 [12]. Also, in a previous paper was established that partial or complete replacement of fly ash by bottom ash in Portland-fly ash and pozzolanic cements has neither a significant effect on neither mechanical nor durability properties. The coal bottom ash mixed with fly ash is suitable for using in cement production. Therefore, it is recommended to standardize the bottom ash as a new main cement constituent [15].

Chemical compositions of the fly ash samples are presented in Table 1. They are mainly composed of CaO, SiO_2, Fe_2O_3 and Al_2O_3, accounting for 80–90% of the material on a dry weight basis. The ternary composition plot for the coal fly ashes based on the content of the SiO_2, CaO and Al_2O_3 is depicted in Figure 2. It shows the typical composition range for ordinary portland cement (OPC) and coal fly ash based on their typical Si, Al and Ca oxides content. It is apparent that the Class C coal fly ash sample positions in the ternary diagram have pozzolanic and also binder properties (La Pereda, 17.1% CaO). Whereas Class F coal fly ash only have pozzolanic properties.

Its use is environmentally positive because of fly ash cements helps to reduce the energy involved in the cement production process. Taking into account that cement is the most energy intensive component of concrete the result will be important from the point of view of the whole life cycle.

Technically, fly ash used as an addition to Portland cement has a number of positive effects on the resulting concrete, such as, lower water demand than ordinary Portland cement (opc or CEM I –EN 197-1:2011-) for similar workability. A decrease in water demand means a decrease in the water-cement ratio and capillary porosity. Also, fly ash blended cements enhances concrete workability and reduces bleeding. In mass concrete, cement with high-percentage of fly ash (e.g. CEM IV according to EN 197-1:2011), provides a lower heat of hydration compared to concrete made of ordinary Portland cement (opc or CEM I –EN 197-1:2011-), particularly when Class F fly ash is used. By contrary, class C fly ash from Escatrón, Serchs and La Pereda, may not lower the heat of hydration. Such a lower heat evolution is recommendable in mass concrete applications and large volume structures in order to minimize expansion promoted by heat of hydration to reduce cracking at early ages. Fly ash cements can produce less concrete permeability and porosity because of the spherical particles and, therefore, improved packing, leading to a more dense paste. Also, the ball bearing effect due to the spherical fly ash particles may result in a better pumping capability. Thus, fly ash blended cements could provide a good quality concrete cover to the reinforcement against natural weathering effects.

With regard to concrete resistance to sulphate ions attack, fly ash increases durability by reacting with calcium hydroxide in cement into a stable calcium silicate hydrate. Calcium hydroxide is soluble, whereas the calcium silicate hydrate in fly ash concrete is less soluble. In addition, such calcium silicate hydrate tends to fill capillary pores in the cement paste, thereby reducing permeability of the concrete [17-20]. A sulphate resistance upper limit ratio of CaO/Fe_2O_3 was proposed. When CaO/Fe_2O_3 ratio is less than 1.5, fly ash addition improves concrete sulphate resistance [21]. The ratio CaO/Fe_2O_3 is lesser than 1.5 for all the tested fly ashes (0.7-1.5) except for La Pereda (Fluidized bed system) where CaO/Fe_2O_3 ratio is equal to 2.67.

A method to reduce freezing and thawing damage of concrete, is the addition of 5–6 vol% air entraining admixtures (AEAs) in the concrete in order to include air bubbles of less than 250 mm. This improves concrete workability and cohesion [22-23], but, on the other hand, it reduces the strength of the concrete [24]. Air entraining admixtures (AEAs) are aqueous mixtures of ionic or non-ionic surfactants derived from either natural sources (Vinsol resin extracted from pinewood and other wood resins) or based on synthetic chemicals [25]. The surfactants adsorb to the air–water/cement interface, having their non-polar end toward the interior of the air bubble and their polar end in the aqueous phase or on the cement particle [24]. Fly ash in concrete affects the required dosage of AEAs [26]. The AEAs are strongly adsorbed by some fractions of the fly ash, leading to a reduced amount of AEAs stabilizing the entrained air [27, 28]. Particularly, the unburned carbon appears to be responsible for the adsorption of AEAs [29]. Then, Fly ashes with high amounts of carbon are not recommendable to this application.

Precast elements

The fly ash composition dictates the way the material is used in concrete. With regard to precast elements, Class F fly ash can be suitably used in cements for use in precast elements (CEM II/A-V), and reinforced cement concrete construction (CEM II/A-V and CEM IV/A). The use of high volumes of Class F fly ash cement in concrete could decrease its 28-day compressive, splitting tensile and flexural strength, modulus of elasticity, and abrasion resistance of the concrete [30]. Also, mechanical activation (grinding) may be made. It depends on the type of activation device. In structural concrete at levels of around 20-35% of fly ash, it has been observed that similar or enhanced performance compared to that of Portland cement concrete of equivalent 28-days strength is possible. Higher levels may be used in special situations where control of heat is important.

Roller compacted concrete (RCC)

Roller compacted concrete (RCC) application is a wide spread practice, such as, roads, dams, and large floor construction [31-32]. The utilization of fly ash in the construction of concrete dams [33] may decrease the deformation of dam concrete and reduce the shrinkage and expansive strain.

Road sub-base

Fly ash cements have been used in embankment soil stabilization, sub-grade base materials, as aggregate filler, as bituminous pavement additive and as a mineral filler for bituminous concrete. For instance, shear strength is an important characteristic for soil stabilization using fly ash, which is partially due to fly ash pozzolanicity. When fly ash cements are used as a soil stabilizer for road bases, the importance is given to the self-hardening properties of fly ash [34]. The majority of fly ash stabilization projects have devoted more to the measurement of strength and durability of the material rather than its environmental hazards [34].

Lightweight aggregate

Lightweight aggregates are commercialized under different trademarks, such as Perlita, Arlita, Terlite, Lytag, Waylite Corsonalite, Sinterlite, and so on. The main advantage of construction products made of fly ash used as lightweight aggregate in construction is the economic saving associated with the reduced freight costs of shipping. For instance, fly ash bricks are as durable as clay bricks and in certain aggressive environments perform better than clay bricks [35-39]. Also, fly ash has been utilized in the manufacture of lightweight roofing products providing good fire-resistance.

Adsorbents for cleaning of flue gas

Another interesting possibility might be use as a low-cost adsorbent for gas and water treatment. The retention of hazardous elements by fly ash produced in combustion plants has been extensively studied in recent years [40-41]. Fly ash may be used as adsorbent for cleaning of flue gas from sulphur compounds, NO_x, mercury and organic gases among other contaminants. This is, in low NO_x burners, the carbon content of fly ash increases significantly, up to 20% in some cases, due to the low oxygen and/or low temperature combustion conditions required by those low NO_x combustion. Since the unburned carbon separated from fly ash is a by-product, any practical application of such material would be economically and environmentally advantageous. In view of the significant variations in the properties of fly ash obtained from different coals [42], apparently, fly ashes from Soto de Ribera (LOI=6.4%), Anllares (LOI=4.8%) and Velilla (LOI=5.0%), particularly, could be used to this application. Also, fly ash from Meirama, Lada, Compostilla and Barrios (LOI from 4.0 to 4.4%) could be used but with less efficiency.

- Sulphur compounds

With regard to the sulphur compounds absorption, coal fly ash might be a cheap absorbent for dry-type FGD replacing activated carbon which is used to oxidize reduced sulphur compounds. Dry-type FGD does not require wastewater treatment; but, it requires a large amount of absorbent compared to wet-type FGD. Therefore, it could be too costly for large-scale environmental remediation applications. Currently, the FGD process using coal ash has been implemented in some power stations. Summing up, fly ash treated with calcium hydroxide may be a good reactive adsorbent for SO_2 removal [43, 44].

- Adsorption of NO_x

As for sulphur compounds absorption, coal fly ash could be proposed as adsorbent for NO_x removal from flue gases [45]. The unburned carbon remaining in the fly ash can be activated to improve the fly ash adsorption performance due to the high surface area of the coal fly ash [46].

- Removal of mercury

Unburned carbon from fly ash may also adsorb elemental mercury. In the activated carbon injection process, activated carbon powder is injected into the flue gas stream and collected after adsorption [47]. The adsorption of mercury on carbon can be explained by the physical and chemical interactions which occur between the carbon surface and mercury [48]. The concentration of unburned carbons and their respective ability to capture Hg have also been related to their textural properties [49]. Usually the unburned carbon content in fly ash is in the range of 2–12%, but in the eighteen tested Spanish fly ashes this range is much lower (LOI= 0.1-5.4%).

- Adsorption of gaseous organics

Apart from the adsorption of NO_x, SO_x and mercury in flue gas, fly ash has also been used for adsorption of organic gas. Fly ash aggregation and thermal activation showed satisfactory adsorption performance for toluene [50, 51], aromatic hydrocarbon and m-xylene [52].

Removal of metals from waste water

Spanish fly ashes could be used in waste water treatment of heavy metals which are a human health problem. Currently, they are removed from aqueous solutions by several processes such as, chemical precipitation, solvent extraction, ion exchange, reverse osmosis, adsorption, and so on. Among them, the adsorption process may be effective for the heavy metals removal from wastewater using coal fly ash. Heavy metals which can be removed using coal fly ash as adsorbent are Zn^{2+} [53, 54], Cd^{2+} [55], Pb^{2+} [56, 57], Cu^{2+} [58], Cr^{6+} [59], Hg^{2+} [60], As^{3+} and As^{5+} [61], among others. In general, it is necessary to adjust the pH of wastewater using lime and sodium hydroxide in order to maximize metal adsorption by hydrous oxides [62, 63]. Once the coal fly ash has been used as immobilization agent for heavy metal ions in aqueous solution, and thus, loaded to saturation with heavy metals, it can be solidified to form concrete blocks to avoid any risk to the environment.

Summing up, it can be said that the utilization of industrial wastes as fly ash for effluent treatment and then ultimate disposal of adsorbents laden with pollutants in cementitious materials by fixation is a reliable wastewater treatment. This treatment followed by a solid waste management allows preparing mortars that have strength comparable to mortars made of only Portland cement [64-65]. Therefore, this metal-laden fly ash cement could be considered for use in secondary construction materials.

CONCLUSIONS

In this paper, the main characteristics of 18 Spanish coal based thermal power plants are presented. An attempt has been made in the present paper to highlight on the differences on chemical composition of Spanish fly ashes which allows first their classification and second their potential utilization in several industrial applications. The utilization of fly ash in construction, as cement addition, in precast elements, in roller compacted concrete (RCC), road sub-base and as lightweight aggregate and, finally, as adsorbent for the removal of some compounds has been reported.

The overall summary of this paper is as follows:

•The current worldwide production of the coal ash is more than 700 million tons, and about 80% are fly ash.

•In Spain, 22 coal based thermal power plants are producing more than 3 million tons of coal fly ash per annum.

•Spanish thermal power plants generate both class F and class C fly ash according to ASTM C618-08a and are mostly re-use and, in few cases, are disposed in landfills.

•Fly ash is now recognized as valuable substance which confers certain desirable characteristics in its many applications.

•Utilization of fly ash is already well established in various construction and waste solidification and stabilization process.

•The fly ash utilization rate in the construction field in Europe is 48%. Thus, it is assumed that the remaining portions of the fly ash are stored in landfills, stockpiled or destined to other minor applications.

•Finally, it can be said that it is possible to prepare mortars with metal-laden fly ash. These mortars present a compressive strength similar to that of Portland cement mortars. Therefore, metal-laden fly ash binders could be considered for using as secondary construction materials.

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REFERENCES

1. Ural, S.: "Comparison of fly ash properties from Afsin–Elbistan coal basin, Turkey". J. Hazard. Mater., vol. B119 (2005) pp. 85–92.
2. Ferreira, C.; Ribeiro, A.; Ottosen, L.: "Possible applications for municipal solid waste fly ash". J. Hazard. Mater., Vol. B96 (2003) pp. 201–216.
3. Carlson, C.L.; Andriano, D.C.: "Environmental impacts of coal combustion residues". J. Environ. Qual., vol. 22 (1993) pp. 227–247.
4. ACAA, 2007. Coal Combustion Product (CCP) Production & Use Survey Results. ACAA 15200 E. Girard Ave., Ste. 3050. Aurora, CO 80014. 9/15/2008. 1pp.
5. ECOBA, 2005. European Coal Combustion Products Association e.V. Annual Report 2005. 14pp.
6. EPA, Study on Increasing the Usage of Recovered Mineral Components in Federally Funded Projects Involving Procurement of Cement or Concrete to Address the Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users. United States Environmental Protection Agency in conjunction with the U.S. Department of Transportation and the U.S. Department of Energy. Report to Congress. June 3, 2008. United States Environmental Protection Agency Washington, D.C. 20460. EPA530-R-08-007. 227pp.
7. Mattigod, S.V.; Dhanpat, R.; Eary, L.E.; Ainsworth. C.C.: "Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements". J. Environ. Quality., vol. 19 (1990) pp. 188–201.
8. Sanjuán, M.A.: "Spanish Blended cements from 2000 to 2005". Cemento-Hormigón, vol. 909 (2007) pp. 4-55 (In Spanish).
9. ASTM C618-05, Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, Annual book of ASTM standards, 2005, concrete and aggregates, vol. 04.02, pp. 1-4.
10. Vadillo, L.; López, C.; González, J.; González, A.; Navarro, E.; Vázquez, A.: "Waste re-use Manual from the mine, metallurgical and electrical industry", Spanish Geological Institute, Madrid, 1995, 308pp. (In Spanish).
11. Galarón, A.: "Materials: components", in: Third Roller Compacted Concrete Dams Course, Madrid, 17 -18 September, 1996 (In Spanish).
12. European standard EN 450-1:2012, Fly ash for concrete. Definition, specifications and conformity criteria. August 2012.
13. European standard EN 197-1:2011, Cement. Part 1: Composition, specifications and conformity criteria for common cement.
14. Sanjuán, M.A.; Argiz, C.: "The new European standard on common cements specifications EN 197-1:2011". Materiales de Construcción, vol. 62 (2012) pp. 425-430 (Bilingual English&Spanish).
15. Argiz, C.; Menéndez, E.; Sanjuán, M.A.: "Effect of mixes made of coal bottom ash and fly ash on the mechanical strength and porosity of Portland cement". Materiales de Construcción, vol. 63, nº 309 (2013) pp. 49-64 (Bilingual English&Spanish).
16. Sanjuán, M.A.; Menéndez, E.: "Experimental analysis of pozzolanic properties of pulverized coal combustion bottom ash compared to fly ash in portland cements with additions", in: XIII International Congress on Cement Chemistry (iccc2011), Cementing a sustainable future, Madrid, Spain, 3-8 July, 2011, 7pp.
17. Antiohos, S.K.; Papageorgiou, D.; Chaniotakis, E.; Tsimas, S.: "Mechanical and durability characteristics of gypsum-free blended cements incorporating sulphate-rich reject fly ash". Cem. Concr. Compos., vol. 29 (2007) pp. 550–558.
18. Mehta, P.K.: "Effect of fly ash composition on sulfate resistance of cement". J. Am. Concr. Ins., vol. 83 (1986) p. 994.
19. Mehta, P.K.: "Mechanism of sulfate attack on portland cement concrete –another look". Cem. Concr. Res., vol. 13 (1983) pp. 401–406.
20. Mehta, P.K.; Monterio, P.J.M.: "Effect of aggregate, cement and mineral admixtures on the transitional zone", Mater. Res. Soc. Symp., vol. 114 (1988) pp. 65-75.
21. Dunstan, E.R.: "A Possible Method for Identifying Fly Ashes that Will Improve the Sulfate Resistance of Concretes". ASTM Cement, Concrete and Aggregates, vol. 2 (1980) pp. 20-30.
22. Paillère, A.M.: "Application of admixtures in concrete". 1st ed. London, E & FN Spoon, 1995. pp. 17–22.
23. Rixom, R.: "The economic aspects of admixture use". Cem. Concr. Compos., vol. 20 (1998) pp. 141–147.
24. Bruere, G.M.: "Air-entraining actions of anionic surfactants in Portland cement pastes", J. Appl. Chem. Biotechnol, vol. 21 (1971) pp. 61–64.
25. Neville, A.M.; Brooks, J.J.: "Concrete Technology", 2nd ed.Longman Group UK Limited, London, 2010.
26. Dhir, R.K.; McCarthy, M.J.; Limbachiya, M.C.; El Sayad, H.I.; Zhang, D.S. "Pulverized fuel ash concrete: air entrainment and freeze/thaw durability". Mag. Concr. Res., vol. 51 (1999) pp. 53–64.
27. Freeman, E.; Gao, Y-M.; Hurt, R.; Suuberg, E.: "Interactions of carbon containing fly ash with commercial air-entraining admixtures for concrete". Fuel, vol. 76 (1997) pp. 761–765.
28. Hill, R.L.; Sarkar, S.L.; Rathbone, R.F.; Hower, J.C.: "An examination of fly ash carbon and its interactions with air entraining agent". Cem. Concr. Res., vol. 27 (1997) pp. 193–204.
29. Helmuth, R. A.: "Fly Ash in Cement and Concrete", SP040T, 1st ed. Portland Cement Association, Illinois, 1987, 203 pages.
30. Siddique, R.: "Performance characteristics of high-volume Class F fly ash concrete". Cem. Concr. Res., vol. 34 (2004) pp. 487–493.
31. Hansen, K.D.; Reinhardt, W.G.: "Roller-compacted concrete dams". McGraw-Hill, New York, 1991, 298 pages.
32. Nanni, A.; Ludwig, D.; Shoenberger, J.: "Roller compacted concrete for highway pavements". Concr. Int., vol. 18 (1996) pp. 33–38.

33. Gao, P.; Lu, X. H.; Lin, H.; Li, X.; Hou, J.: "Effects of fly ash on the properties of environmentally friendly dam concrete". Fuel, vol. 861 (2007) pp. 208–211.
34. Mohapatra, R; Rao, R.J.: "Review: Some Aspects of Characterization, Utilization and Environmental Effects of Flyash". Journal of Chemical Technology and Biotechnology, vol.76 (2001) pp. 9-26.
35. Lin, K.L.: "Feasibility study of using brick made from municipal solid waste incinerator fly ash slag". J. Hazard. Mater., vol. B137 (2006) pp. 1810–1816.
36. Lingling, X.; Wei, G;. Tao, W.; Nanru, Y.: "Study on fired bricks with replacing clay by fly ash in high volume ratio". Constr. Build. Mater., vol. 19 (2005) pp. 243–247.
37. Cicek, T. Tanriverdi, M.: "Lime based steam autoclaved fly ash bricks". Constr. Build. Mater., vol. 21 (2007) pp. 1295–1300.
38. Cultrone, G.; Sebastián, E.; Elert, K.; de la Torre, M.J.; Cazalla, O.; Rodriguez Navarro, C.: "Influence of mineralogy and firing temperature on porosity of bricks". J. Eur. Ceram. Soc., vol. 24 (2004) pp. 547–564.
39. Reidelbach, J.A.: "An industrial evaluation of fly ash bricks", in: The US Department of the Interior, Bureau of Mines, Information Circular Number 8488, Washington, DC, US Department of the Interior, 1970.
40. Hower, J.C.; Robl, T.L.; Anderson, C.; Thomas, G.A.; Sakulpitakpton, T.; Mardon, S.: "Characteristics of coal combustion products (CCP's) from Kentucky power plants, with emphasis on mercury content". Fuel, vol. 84 (2005) pp. 1338–50.
41. Pavlish, J.H.; Sondreal, E.A;. Mann, M.D.; Olson, E.S.; Galbreath, K.I.; Laudal, D.L.: "Status review of mercury control options for coal-fired power plants". Fuel Process. Technol., vol. 82 (2003) pp. 89–165.
42. Maroto-Valer, M.M.; Taulbee, D.N.; Hower, J.C.: "Characterization of differing forms of unburned carbon present in fly ash separated by density gradient centrifugation". Fuel, vol. 80 (2001) pp. 795–800.
43. Davini, P.: "Investigation of the SO_2 adsorption properties of $Ca(OH)_2$-fly ash systems". Fuel, vol. 75 (1996) pp. 713–716.
44. Davini, P.: "Investigation of flue gas desulphurization by fly ash and calcium hydroxide mixtures". Resou. Conserv. Recycl., vol. 15 (1995) pp. 193–201.
45. Lu, G.Q; Do, D.D.: "Adsorption properties of fly ash particles for NOx removal from flue gases". Fuel Process. Technol., vol. 27 (1991) pp. 95–107.
46. Rubel, A.; Andrews, R;. Gonzalez, R.; Groppo, J.; Robl, T.: "Adsorption of Hg and NOx on coal by-products". Fuel, vol. 84 (2005) pp. 911–916.
47. EPA, "Mercury Study Report to Congress", 1997, EPA-452/R-97–10.
48. Hall, B.; Schager, P.; Weesmaa, J.: "The homogeneous gas phase reaction of mercury with oxygen, and the corresponding heterogeneous reactions in the presence of activated carbon and fly ash". Chemosphere, vol. 30 (1995) pp. 611–627.
49. Maroto-Valer, M.M.; Taulbee, D.N.; Hower, J.C.: "Characterization of differing forms of unburned carbon present in fly ash separated by density gradient centrifugation". Fuel, vol. 80 (2001) pp. 795–800.
50. Peloso, A.; Rovatti, M.; Ferraiolo, G.: "Fly ash as adsorbent material for toluene vapours". Resour. Conserv. Recycl., vol. 10 (1983) pp. 211–220.
51. Rovatti, M.; Peloso, A.; Ferraiolo, G.: "Susceptibility to regeneration of fly ash as an adsorbent material". Resour. Conserv. Recycl., vol. 1 (1988) pp. 137–143.
52. Rotenberg, S.J.; Mettzler, G.; Poliner, J.; Bechtold, W.E.; Eidson, A.F;. Newton, G.J.: "Adsorption kinetics of vapor-phase m-xylene on coal fly ash". Environ. Sci. Technol., vol. 25 (1991) pp. 930–935.
53. Banerjee, S.S.; Jayaram, R.V.; Joshi, M.V.: "Removal of nickel(II) and zinc(II) from wastewater using fly ash and impregnated fly ash". Sep. Sci. Technol., vol. 38 (2003) pp. 1015–1032.
54. Bayat, B.: "Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel(II), copper(II) and zinc(II)". J. Hazard. Mater., vol. 95 (2002) pp. 251–273.
55. Papandreou, A.; Stournaras, C.J.; Panias, D.: "Copper and cadmium adsorption on pellets made from fired coal fly ash". J. Hazard. Mater., vol. 148 (2007) pp. 538–547.
56. Wang, S.; Terdkiatburana, T.; Tade, M.O.: "Single and co-adsorption of heavy metals and humic acid on fly ash". Sep. Purif. Technol., vol. 58 (2008) pp. 353–358.
57. Ricou, P.; Lecuyer, I.; Le Cloirec, P.: "Removal of Cu^{2+}, Zn^{2+} and Pb^{2+} by adsorption onto fly ash and fly ash/lime mixing". Water. Sci. Technol., vol. 39 (1999) pp. 239–247.
58. Papandreou, A.; Stournaras, C.J.; Panias, D.: "Copper and cadmium adsorption on pellets made from fired coal fly ash". J. Hazard. Mater., vol. 148 (2007) pp. 538–547.
59. Banerjee, S.S.; Joshi, M.V.; Jayaram, R.V.: "Removal of Cr (VI) and Hg (II) from aqueous solutions using fly ash and impregnated fly ash". Sep. Sci. Technol., vol. 39 (2004) pp. 1611–1629.
60. Sen, A.K.; De, A.K.: "Adsorption of mercury (II) by coal fly ash". Water. Res., vol. 21 (1987) pp. 885–888.
61. Pattanayak, J.; Mondal, K.; Mathew, S.; Lalvani, S.B.: "A parametric evaluation of the removal of As (V) and As (III) by carbon-based adsorbents". Carbon, vol. 38 (2000) pp. 589–596.
62. Bayat, B.: "Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel (II), copper (II) and zinc (II)". J. Hazard. Mater., vol. 3897 (2002) pp. 1–23.
63. Bayat, B.: "Comparative study of adsorption properties of Turkish fly ashes. II. The case of chromium (VI) and cadmium (II)". J. Hazard. Mater., vol. 3898 (2002) pp. 1–16.
64. Rao, M.; Parwate, A.V.; Bhole, A.G.: "Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash". Waste Manage., vol. 22 (2002) pp. 821–830.
65. Weng, C.H.; Huang, C.P.: "Treatment of metal industrial wastewater by fly ash and cement fixation". J. Environ. Eng., vol. 120 (1994) pp. 1470–1487.