

Potential of a low-calcium fly ash (FA) for the production of alkali-activated materials.

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ABSTRACT: Coal-FA from power stations is an industrial waste abundantly produced in the world. FA can be used as a silicate precursor, and activated with an alkali-metal source to produce alkali-activated materials (AAMs). AAMs are more sustainable than other traditional products, as the use of waste for their production, reduces carbon emissions, and raw materials and energy consumption. This paper studies the properties, composition and reactivity of an Irish FA to establish its potential for the production of AAMs. The results clearly evidenced that the FA is reactive. It is ultrafine, it has a high specific surface area and is partially glassy. Furthermore, a substantial part of the total silica and alumina comprising the FA is amorphous, hence reactive and likely to form cements upon alkali activation. The main phases in the amorphous ash, determined during devitrification, are mullite ($2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and hematite (Fe_2O_3). They progressively crystallize between 600 and 1000°C, as evidenced with the exothermic curve obtained by differential scanning calorimetry. The FA is pozzolanic, and can be classified as class F in the ASTM C 618 standard. Its reactivity with lime - $\text{Ca}(\text{OH})_2$ - was experimentally proven by electrical conductivity. The FA also complies with the chemical requirements in the European standards (EN450-1) for the use of FA in concretes, mortars and grouts. The physical property results, as well as the chemistry, mineralogy and amorphousness of the FA evidence that the FA is suitable for alkali activation. Furthermore, the FA meets the specific requirements for the production of AAM in the literature.

KEY WORDS: fly ash; devitrification; alkali activation; amorphousness; pozzolanic activity.

1 INTRODUCTION

Fly ash is a by-product of power generation at coal-fired power plants. It is collected by filters and/or electrostatic precipitators which remove the solid particles from the smoke, making the smoke less harmful to the environment [1]. Currently, FA is regarded as one of the most abundantly produced industrial wastes in the world, particularly in India, China and the USA, and more than 300 million tons of FA are currently produced worldwide [2-4]. In Ireland, FA waste is produced and, although it is partially recycled into several applications, a significant amount ends in landfills.

The composition of FA depends on the coal used and on the various substances injected into the coal or gas stream to reduce gaseous pollutants or to improve the efficiency of the particulate collectors. [1, 5-7]. When limestone or dolomite are used for desulphurization of the exit gases, CaO and MgO contents increase in the FA. Conditioning agents such as sulphur trioxide, sodium carbonate and bicarbonate, sodium sulphate, phosphorus, magnesium oxide, water, ammonia and tri-ethylamine are often used to improve the collection efficiency and can alter the composition of the FA [1].

FA usually consists of small, spherical particles of high surface area, but it can also contain irregular or angular mineral particles and unburned coal remnants. FA is often highly amorphous, and consists predominantly of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) [8-10]. Due to their physical properties and composition, FAs are valuable raw materials for binder production, and they have been used as supplementary cementitious materials in Portland cement (PC) materials for several decades. FAs have been used

as partial clinker replacement in PC production since the 1930s [11-14]. The use of FA results in binders of lower carbon emissions and lower energy and raw material consumption. Currently, in the European standard, there are three types of Portland-fly-ash cements in the CEM II group, with clinker substitution by FA up to 35% (EN197-1) [14].

FAs have also been successfully allowed used for the production of alkali-activated materials (AAMs), being the most commonly used aluminosilicate precursors in alkali activation due to their low cost and wide availability [2,15]. AAMs can be produced with waste, leading to low carbon emissions and low raw material and fossil fuel consumption. Therefore, they have been proposed as a more sustainable alternative to PC. An alkali-activated-FA material was even commercialised in 1997 as Siloxo, and used to produce ready-mix concrete and a range of pre-cast products [11].

Depending on their composition, FAs can be either pozzolanic or cementitious. Low-CaO, fly ashes have very little or no cementitious properties. They are pozzolanic and display no significant hydraulic behaviour, hence they need either lime or an alkali solution to activate and produce cementing minerals. In contrast, in high-calcium ashes, the calcium forms hydraulic silicates that produce hydraulic cements upon contact with water. As well as calcium, other elements can also affect the performance of the FA including alkalis (Na_2O and K_2O), carbon (usually measured as loss on ignition-LOI) and sulfates (SO_3) [13].

The factors affecting the pozzolanic reactivity of FAs are the same as those that generally determine the activity of any pozzolan, primarily specific surface area, grading, chemical

and mineral composition and amorphousness [16]. The reactivity of FA or any other material with cementitious or pozzolanic properties is largely determined by the amount of reactive silica and alumina in the material, as these form cementing gels on reaction, hence defining the final properties of the resultant product. The quantities of silica and alumina are relatively easy to measure with a range of analytical techniques. However, how much of the total silica and alumina content is reactive is more difficult to quantify. It is generally accepted that the silica and alumina need to be amorphous to be reactive, as crystalline phases are essentially considered inert.

This paper studies the physical properties, chemical and mineral composition and reactivity of an Irish FA to establish its potential for the production of alkali activated binders. The paper studies the particle size, specific surface area, chemical and mineral composition and amorphousness of the FA. The reactivity is investigated measuring the amount of glass (amorphous material) in the FA, and the ability of the ash to combine lime in solution. X-Ray diffraction analyses are used in combination with thermal techniques to establish the composition of the amorphous phases and hence the reactivity of the ash. One of the thermal techniques applied is devitrification. Hemmings and Berry [17] first used devitrification to analyse the glassy phases in FA. Devitrification transforms amorphous phases into crystals so that they can be identified with XRD [11,17-18]. Based on the results, suitable alkali activators are proposed that would enhance the dissolution process of the ash and the production of cements.

2 MATERIALS AND METHODS

2.1 FA

FA was gathered from the coal-burning power station at Money point (Stáisiúin Chumhachta Ghob na Muine), on the River Shannon, near Kilrush in County Clare, Ireland's largest electricity generation station and only coal-fired power station. In Stáisiúin Chumhachta Ghob na Muine, a sub-bituminous coal of low sulphur content is burned at a temperature ranging from 1000 – 1150°C. Hydrated lime is used for flue-gas desulfurization and it is located after electrostatic precipitators in the gas flow. The lime (Ca(OH)₂) combines with the sulfur dioxide (SO₂) removing it from the exhaust flue gases and avoiding emissions. The process uses no conditioning agents.

2.2 Particle Size Distribution

The particle size distribution was measured by laser diffraction using a Mastersizer apparatus, composed of a Mastersizer 2000 unit; a hydro 2000MU pump for wet dispersion and an autosampler unit. This method measures the angular distribution and intensity of the light diffraction by the particles in suspension, and applies the Mie theory of diffraction for the prediction of the sizes of the particles.

2.3 Specific surface area

Surface chemistry is essential in the alkali activation process as the specific surface area of the particles determines their reactivity. The specific surface area of the ash particles was measured with a Quantachrome Nova 4200e and the BET method which records the surface area based on the physical

adsorption of gas molecules. The Brunauer–Emmett–Teller (BET) theory correlates the adsorption of gas molecules on the surface with the specific surface area of the particles.

2.4 Chemical composition and loss on ignition (LOI)

The chemical composition was determined by X-ray fluorescence (XRF) with a ThermoFisher Scientific and Edwards Analytical apparatus using a Quant'X EDX spectrometer and a UniQuant analysis package. The LOI was measured by calcination at 450 and 1000 °C to calculate the organic carbon and carbonate content of the FA according to EN196-2 [19].

2.5 Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The TGA recorded weight loss with increasing temperature, at temperatures ranging from 0 to 1000°C, and scanning rates from 0.1°C to 200°C/min in air atmospheres. The DSC recorded exothermic and endothermic events some of which are representative of glass transition and the onset of crystallization. Crystallization peak and melting point were also determined with this technique.

2.6 Devitrification

Phase transformation in the FA was studied by calcination in a kiln at 500°C, 800°C and 1000°C. The ashes were then cooled in a desiccator and their mineralogical composition and glass content studied with XRD as explained below.

2.7 Mineralogical composition

The mineral composition and amorphous character of the FA was analysed with X-Ray Diffraction (XRD) using the powder method, by means of a Phillips PW1720 XRD apparatus equipped with a PW1050/80 goniometer and a PW3313/20 Cu k-alpha anode tube, at 40kV and 20mA.

2.8 Assessment of reactivity with the chemical method

The reactivity of the FA was determined by measuring the conductivity loss of a FA / lime (Ca (OH)₂) solution over time. The capacity of the ash to combine Ca (OH)₂ and hence its pozzolanic activity was assessed according to de Luxan et al. [20,21]. The solutions were stored in sealed flasks to avoid evaporation and carbonation. They were constantly stirred and maintained at 20°C in a thermostatic bath. The conductivity was measured with a WTW meter and the conductivity loss (%) calculated according to the following equation:

$$C(\%) = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

Where, C_i is the electrical conductivity of the lime suspension; and C_t is the electrical conductivity at the time intervals.

3 RESULTS AND DISCUSSION

3.1 Physical characterization and chemical composition

As it can be seen from table 1, the FA is ultrafine, significantly finer than limestone cement (CEM II=1.88 m²/g). The mean particle size is 15 microns, and 90% of the particles are smaller than 100 microns. The high specific surface area of the particles, at 6500m²/kg, lies above the typical values reported

in the literature, agreeing with the grading range and suggesting that some of the particles might be porous.

The density of the FA particles is high, at the high end of the common FA densities reported by previous authors which vary between 1900 to 2800 kg/m³ [1]. The FA composition, especially the iron and carbon contents, cause differences in density (Minnick et al.1971 in [1]). Therefore, the significant iron content (Table 2) evidenced by XRF, coupled to the low carbon content recorded by calcination (LOI=1.67%) are partially responsible for the high density of the FA particles. The nature of the cooling process may have also enhanced density, as internal voids in the ash particles are mainly produced during cooling.

As expected, the silica and alumina contents are high (Table 2). In contrast, the calcium content is low (c.3%) and $\sum SiO_2 + Al_2O_3 + Fe_2O_3 > 70\%$ by mass (Table 3). According to this chemical composition, the FA belongs throughout Class F in the ASTM C618 standard [22]. Therefore, the FA is pozzolanic, it has very little or no cementitious properties, and its pozzolanic reactivity is mainly determined by the characteristics of the aluminosilicate glass and the fineness of the particles.

The FA investigated meets the European standard chemical requirements for the use of FA in concrete, mortar and grout (table 3). According to the LOI results, the residue of unburnt carbon is 1.67% (table 2) which classifies the FA in the category A ash of the European standard EN196-2 [19] with unburnt carbon not greater than 5% by mass of ash (table 3).

Table 1. Specific surface area and particle size of the FA.

	Specific surface area m ² /g	Particle density mg/m ³	size range & dominance			
			Mean µm	D90 µm	D50 µm	D10 µm
FA	6.50	2.28	15	100.63	14.96	1.95

Table 2. Chemical composition as percentage by weight and LOI. * same FA analysed by [16]

	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	Na ₂ O	K ₂ O	MgO
FA	53.40	21.18	4.14	9.99	0.70	3.24	1.86
FA*	65.32	24.72	0.94	4.84	-	1.37	0.68
LOI %							
	P ₂ O ₅	SO ₃	Cl-	TiO ₂	MnO	450°C	1000°C
FA	0.84	2.67	0.04	1.35	0.07	1.67	4.92
FA*	0.37	0.37	-	0.91	-	-	-

Table 3: FA compliance with the chemical requirements for the use of FA in European standards EN 450-1 [23]. All results as % by mass of ash.

	$\sum SiO_2$	Al ₂ O ₃	SO ₃	MgO	Cl-	LOI	Total alkali	Total P ₂ O ₅
EN 450	≥ 70	≤ 3	≤ 4	≤ 0.10	< 5	< 5.5	< 5.5	< 5.5
FA	89	1.4	1.0	0.04	4.92	2.4	0.5	0.5

3.2 Mineral composition and amorphousness

As aforementioned, the reactivity of FA or any other material with cementitious or pozzolanic properties is largely determined by the amount of reactive silica and alumina in the material. The chemical analysis demonstrated that total silica and alumina in the FA are high (59% and 23% respectively-table 2). However, it is necessary to measure how much of this material is amorphous (or reactive), as crystalline phases are essentially considered inert. To this aim, the mineral composition and glass content of the FA were investigated with XRD. Previous studies have reported 316 individual minerals and 188 mineral groups as present in FA [24]. Previous authors report that the most abundant phase in FAs is usually glass, while crystalline compounds account for 5-50% and include quartz, mullite, hematite, spinel, magnetite, melilite, gehlenite, kalsilite, calcium sulphate, alkali sulphate (Hemmings and Berry, 1988 in [1]).

The XRD analysis evidenced that there is significant glass in the FA (figure 1). A broad diffraction halo, which is attributed to the glassy phase, appears on the XRD traces. The glass content of the FA was roughly calculated as 40-60% based on the background area determined by the lifting of the diffractogram's baseline between 15 and 35 degrees (2θ) (figure 1), which indicates the presence of amorphous materials. Small amounts of quartz (SiO₂) and mullite (2Al₂O₃. 2SiO₂) were also determined with XRD, agreeing with Walker and Pavia [16] which, in a previous study, note the same FA as featuring intermediate amorphousness and quartz and mullite peaks. The lack of sulphates and calcium silicates in the Moneypoint FA is due to the composition of the sub-bituminous coal used in the power station (low in sulphur) and the low calcium content in the coal and the processing method.

The results (figure 1) also concur with former literature reporting quartz and mullite (3–24 wt%) as the two major crystalline phases in low-Ca (CaO< 8%) FA, and a content of crystalline minerals is in the 11–48 wt% range [Velandia et al. 2016; Li 2011, in 24].

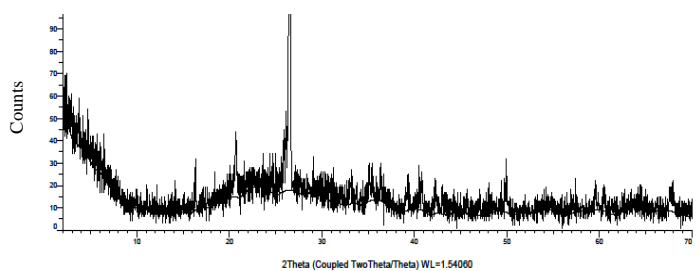


Figure 1. XRD trace of the FA with significant amorphous material and some crystalline phases including quartz (SiO₂) and a small amount of mullite (2Al₂O₃. 2SiO₂).

3.3 Devitrification

To produce power at the Moneypoint station, the sub-bituminous coal is burned at 1000–1150°C. At this temperature range, mullite is formed from the clay minerals in the coal: the dehydroxylation of the clay minerals is followed by reconstitution with nucleation and growth of mullite. Clay minerals usually decompose at temperatures from 550-800°C (although in non-carbonate materials they can stand higher

temperature) and mullite begins to form at 1100°C [25]. The coal firing temperature agrees with the presence of mullite.

In order to determine the mineral composition of the glass comprising the FA, several specimens were devitrified at 500, 800 and 1000°C. The results appear in figures 2-4 and Table 4.

Table 4: Mineral composition and amorphousness of the FA.

Material	% Glass	% Crystalline	Mineral composition
FA 0°C	40-60	60-40	glass quartz (SiO ₂) mullite (2Al ₂ O ₃ . 2 SiO ₂)
FA500°C	10-30	70-90	quartz (SiO ₂) mullite (2Al ₂ O ₃ . 2 SiO ₂) glass
FA 800°C	10-30	70-90	quartz (SiO ₂) mullite (2Al ₂ O ₃ . 2 SiO ₂) glass
FA 1000°C	10-30	70-90	quartz (SiO ₂) mullite (2Al ₂ O ₃ . 2 SiO ₂) hematite (Fe ₂ O ₃) possible Ca ₃ Al ₂ O ₆ and alkali sulphate glass

According to these results, at 500°C, most of the glass has become crystalline however, some glass still remains even at 1000°C.

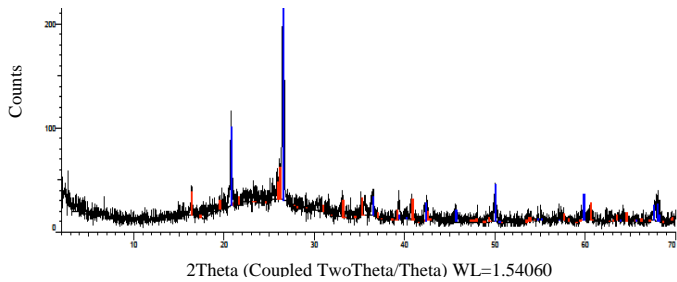


Figure 2. XRD trace of the FA at 500°C, there is still a background halo that indicates the presence of some amorphous material. The reflexions for the crystalline quartz and mullite are clearer and the amount of mullite has increased.

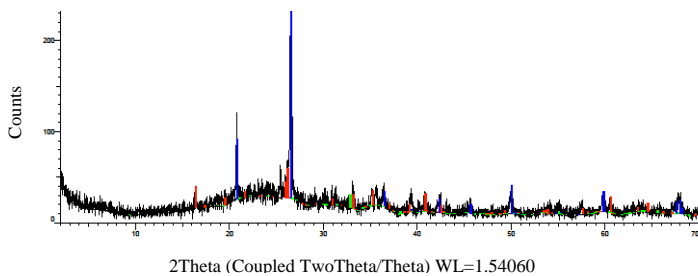


Figure 3. XRD trace of the FA at 800°C, no apparent difference exists between the traces of the FA at 500 and 800 degrees.

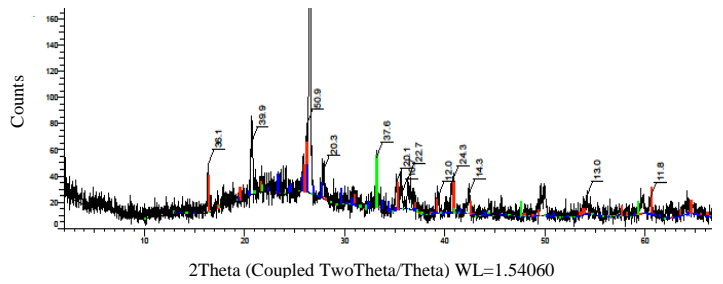


Figure 4. XRD trace of the FA at 1000°C, is still slightly amorphous, the amounts of mullite (2Al₂O₃. 2 SiO₂) and hematite (Fe₂O₃) are significant. It is likely that a small quantity of tricalcium aluminate (Ca₃Al₂O₆) and some alkali sulphate (at d-spacing=3.20) have appeared.

The results were compared to a reference slag sample that was also devitrified. According to the results, approximately half of the mass of the FA is amorphous therefore, a significant fraction of the total silica as well as most of the alumina are reactive.

3.4 Thermal analyses

The FA was studied with differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) (figures 5-6). The TGA analysis evidenced the weight loss over a temperature ranging from 0 - 1000°C, while the DSC displayed thermal events such as crystallization, dehydroxilation or combustion either as exothermic or as endothermic peaks. As it can be seen from figure 5, the FA progressively loses mass with increasing temperature: the mass of the FA drops suddenly and significantly between 1 and 90°C, and then remains more or less stable until the temperature reaches approximately 500°C, at which point there is a slight and gradual drop in mass (between 500 and 750°C). The first sudden mass loss is likely due to dehydration, while the second gradual loss at c.500°C is due to the evolution of organic carbon, agreeing with the LOI at 450°C which amounts to 1.67%. The slight steady mass loss at high temperature might be partly caused by the evolution of carbonates as CO₂, agreeing with the 4.92% LOI result at 1000°C.

In the differential scanning calorimetry (DSC) curve (Figure 5), the mass loss coincides with a marked endothermic peak just before 100°C, likely due to the ash absorbing heat in order to fully dehydrate.

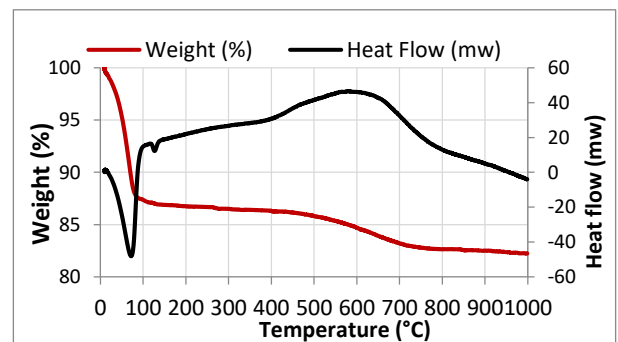


Figure 5. Results of the TGA and DSC of the FA.

There is also a broad exothermic area between roughly 100 and 600°C, after which the ash begins to absorb heat again and the DSC curve becomes markedly endothermic indicating the crystallization of the amorphous phase. According to the devitrification experiment above, the steady heat released between 600 and 1000°C is due to the progressive crystallization of mullite ($2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and some hematite (Fe_2O_3).

3.5 Reactivity by electrical conductivity

The conductivity tests demonstrated that the FA reacts with lime, leading to a gradual decrease in electrical conductivity over time, hence showing reactivity (figure 6). The initial conductivity was 3.07 ms/cm and the conductivity loss 20.19% over the time of the experiment. The steep slope at stage I (3 to 6 hours), where the conductivity increased, is likely due to a lack of seal in the suspension flask, allowing evaporation and carbonation to take place. Phase II shows a slight drop in conductivity suggesting that, initially (up to approximately 20 hours), the FA combines lime at a slow rate, and hence there is marginal reactivity. However, at stages III and IV, there is an increase on the reaction rate, and the FA combines a greater amount of lime producing steep curves. The results are in agreement with previous authors who evidenced the typical low speed of the pozzolanic reaction [26].

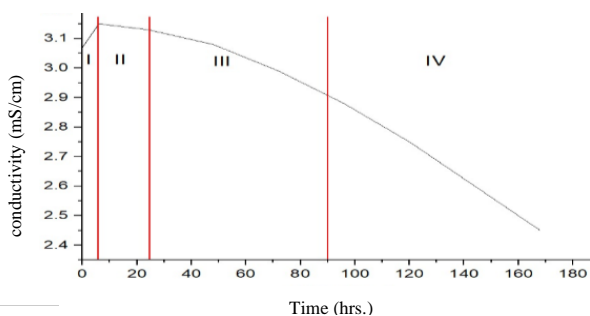


Figure 6. Electrical conductivity of the lime/FA suspension over time.

4 CONCLUSION

The results of the physical, chemical and mineralogical analyses concur on that the FA is reactive. It is ultrafine, it has a high specific surface area and is partially glassy. Furthermore, a substantial part of the total silica and alumina comprising the FA is amorphous, hence reactive and likely to form cements upon alkali activation. In addition, the reactivity with lime - $\text{Ca}(\text{OH})_2$, a low alkalinity activator, is evident. Therefore, the reactivity of the FA with any of the stronger alkalis generally used for alkali activation it is likely to be faster and greater. Also, the FA is clearly pozzolanic, as the silica and alumina contents (> 70% by mass) complying with ASTM C 618 standard class F [22]. The FA also complies with the chemical requirements in the European standards for the use of FA in concretes, mortars and grouts. The physical properties and low unburnt carbon content of the FA are likely to enhance workability, even with the most viscous alkali activators. Combining all the results in this research (physical properties, chemistry and mineralogy/amorphousness), it can be concluded that the FA is suitable for alkali activation. Furthermore, the FA meets the requirements set by Garcia-

Lodeiro et al. [27] for a FA to be suitable for the production of AA cements (Table 5).

Table 5. Evaluation of the FA investigated against the requirements for a FA to be deemed suitable for the production of AA cements in Garcia-Lodeiro et al. [27].

Properties	FA	Requirements in Garcia-Lodeiro et al. [27]
Unburned C	1.7%	<5%
Fe_2O_3	4.8%	$\leq 10\%$
CaO	1-4%	$\leq 10\%$
Vitreous phase	40-60%	>50%
SiO_2 reactive	65% total SiO_2 includes glass-	>40%
Reactive $\text{SiO}_2/\text{Al}_2\text{O}_3$	2.56	>1.5
Particle size	50% <15 μm ; 90% <100 μm	80-90% <45 μm

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