

Thermal stability and microstructural analysis of inorganic polymer binders based on Italian and Australian fly ash

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ABSTRACT

A comparative study between Italian and Australian fly ash and their use as precursors for inorganic polymer binders is carried out with the aim to find an alternative to the current valorisation of Italian fly ash as supplementary cementitious material. As the coal origin and combustion temperature directly influence fly ash nature and composition, the final products of the two precursors obtained by alkali activation at room temperature behave differently both at the fresh and hardened state. Single mode pore size distributions and largely distributed pore dimensions have been determined for Australian and Italian fly ash based samples. Thermal properties are also influenced by the different phases formed during the activation process, thus confirming that the chemical composition of the precursor is a key element to understanding this new class of materials.

Keywords. Geopolymer; alkali activated materials; fly ash; thermal stability; microstructure.

INTRODUCTION

Alkali activated materials (AAM) are a new class of inorganic materials derived from the activation of solid aluminosilicate sources by alkaline solutions at room conditions and/or moderate temperatures (<100 °C). This consolidation process, made up by breaking of chemical Si-O-Si, Al-O-Si bonds in a highly alkaline environment followed by formation of a cross-linked inorganic polymer structure which is x-ray amorphous, allows to obtain materials with binding properties and engineering performances equivalent or superior to ordinary Portland Cement (OPC) products (Duxson et al., 2007a, 2007b). The earliest studies of alkali-activation were focused on the use of calcined kaolin as the source material. Due to its reactive chemistry and very suitable oxide composition, metakaolin has been the “model system” for studying the activation process (Davidovits, 1991; Duxson et al., 2007c; Liew et al., 2012). However, many other aluminosilicate precursors can be alkali activated (Pacheco-Torgal et al., 2008a, 2008b; Xu et al., 2002) and some of them are industrial by-products such as fly ash (Fernandez-Jiménez et al., 2005; Komjenovic et al., 2010; Mandal et al.,

2009), blast furnace slag (Puertas et al., 2000; Ravikumar et al., 2012, Zivica, 2007) and steel slag (Bignozzi et al., 2012; Natali Murri et al., 2013), etc.

In terms of chemical composition, when the alkali activation process is applied to aluminosilicate sources with $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ content $> 80\%$, the resultant products are known as geopolymers. Inorganic polymers (IP) and alkali activated materials (AAM) are terms that are commonly applied to materials obtained by precursors based on both aluminosilicate and Ca-containing amorphous or crystalline phases. Geopolymers and inorganic polymers are both AAMs, with the primary binding phase being almost exclusively aluminosilicate for geopolymers, followed by a disordered silicate network and minor calcium content for IP and, finally for higher Ca content the silicate network also including calcium phases with products resembling Portland cement hydration products (AAM).

Valorisation of industrial by-products is becoming one of the main goals of international research representing a promising option of reaching sustainable development as proposed by the Kyoto protocol. In trying to achieve these goals, this paper describes the alkali activation of fly ash. In Europe fly ash derived from coal fired power stations is an industry by-product which is currently utilised in cement and concrete production. Due to its siliceous amorphous microstructure, fly ash can be used as supplementary cementitious material (SCM) for the manufacturing of pozzolan cement (CEM IV) and/or a special reactive additive for traditional and self-compacting concrete. Due to the recent economic crisis, the Italian and European building sector is experiencing a downturn and less cement and concrete is being produced. As a consequence, a large amount of fly ash is currently available for alternative usage in order to avoid disposal to landfill.

In Australia, fly ash is extensively studied and used as a precursor for inorganic polymer binders/geopolymers, as it is being considered as one of the possible sustainable alternatives to OPC (Rickard et al., 2010, 2011, 2012). Fly ash based inorganic polymer binders have also shown potential for use in high temperature applications such as furnace linings and fire resistant panels. The use of new types of binders made entirely from industrial by-products can result in a large saving of non-renewable raw materials and CO_2 emissions, when compared with OPC production (Li et al. 2011).

This paper reports the results of a comparative study between an Italian and an Australian fly ash and their use as precursors for inorganic polymer binders. Fly ash characteristics are highly variable and are strongly dependent on the coal source and burning conditions so that, in order to produce a suitable product, it is imperative to understand each different source and find specific balanced activation mixes. The investigated mix design and details of the resulting microstructure of the products are presented along with extensive thermal analysis measurements that show inorganic polymer binders/geopolymers can be manufactured into high temperature resistant products.

EXPERIMENTAL PART

Materials. Two types of coal fly ash characterised by different origin and chemical composition were selected. The Australian fly ash (named A_FA) was sourced from Collie power station in Western Australia. The Italian fly ash (named I_FA, kindly supplied by General Admixtures Spa, Ponzano Veneto, Treviso, Italy) was sourced from Enel Produzione S.p.A. UB Torre Valdaliga Nord power station located in Italy (Civitavecchia, Rome). The Italian fly ash complies with UNI EN 450-1 standard and it can be safely used for cement and concrete industry.

Particle size distributions of the starting materials, determined by a laser particle-size analyzer (Mastersizer 2000, Malvern Instruments, UK) are as follows: for A_FA: d (10% passing)= 2.44 μm ; d (50% passing)= 14.98 μm ; d (90% passing)= 83.03 μm ; for I_FA: d (10% passing)= 3.23 μm ; d (50% passing)= 22.11 μm ; d (90% passing)= 86.70 μm .

The composition of the investigated fly ashes as determined by ICP plasma optical emission spectrometry (OPTIMA 3200 XL Perkin Elmer) is reported in Table 1. Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 1.99$, density at 20 $^\circ\text{C} = 1.51 \pm 0.20 \text{ g/cm}^3$, viscosity at 20 $^\circ\text{C} = 250 \pm 150 \text{ mPa}\cdot\text{s}$ - Ingessil, Verona, Italy) and 8 M NaOH were used as activating solutions.

Samples preparation. Samples were prepared with constant fly ash content (FA= 69 wt%) and a liquid/solids ratio (L/S) of 0.45. The sodium hydroxide and sodium silicate solutions amounts were modified in order to achieve molar ratios of $\text{Na}_2\text{O}/\text{SiO}_2 = 0.12, 0.16, 0.18$ and 0.20 in both the geopolymer series based on Italian and Australian fly ash. The mix design of the investigated samples is listed in Table 2. Geopolymers were named with I and A representing the origin of the fly ash used as a precursor, followed by a two digit number indicating the nominal $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio multiplied by 100 (e.g. I_FA_16 represents the geopolymer sample obtained from Italian fly ash with an activating solution molar ratio of 0.16). Geopolymer samples were prepared in a planetary mixer, combining the fly ash with a premixed solution of sodium silicate and 8 M NaOH solutions. After 5 minutes of mixing, the slurry was cast into cylindrical moulds (diameter: 4.5 cm, height: 6.5 cm). Geopolymer samples were cured in the moulds at room temperature (T: 25 $^\circ\text{C}$, R. H. 65 %) for 24 h, then, after de-moulding, they were cured for a further 6 days at the same temperature and humidity.

Table 1. Fly ash composition (oxide wt.%)

	A_FA	I_FA
SiO_2	48.21	49.37
Al_2O_3	25.01	29.23
TiO_2	1.30	1.59
Fe_2O_3	15.20	2.71
CaO	1.67	6.63
MgO	1.02	1.05
K_2O	0.60	0.60
Na_2O	0.06	< 0.05
BaO	0.12	0.07
Cr_2O_3	0.01	0.02
SO_3	0.43	0.33
LOI	0.51	3.28
Insoluble residue	3.86 (black)	4.75 (black)

Characterization. Water absorption ($\text{WA}_{24\text{h}}$) tests were carried out on cylindrical geopolymer samples after immersion for 24 hours and drying at 100 $^\circ\text{C}$ for a further 24

hours. To evaluate thermal resistance of the investigated samples and the influence of high-temperatures on microstructural and physical properties, hardened cylindrical samples were calcined to 800 °C in an electric furnace. Samples were heated up to 800 °C with a heating rate of 8 °C/min, maintained for 2 hours at 800 °C and then allowed to cool naturally back to room temperature. Pore size distribution measurements were carried out by mercury intrusion porosimetry (MIP, Carlo Erba 2000) equipped with a macropore unit (Model 120, Fison Instruments) on samples obtained from the cylindrical specimens. A mercury surface tension of 0.48 N/m and a contact angle of 141.3° were set prior to the MIP measurement. Porosimetry samples, about 1 cm³, were cut by a diamond saw, dried under vacuum and kept under P₂O₅ in a vacuum dry box until testing. Thermo-Gravimetric Analysis (TGA) was performed using a TGA Q50, TA Instruments. Approximately 40 mg of the sample, previously milled and dried at 80 °C for at least 1 hour, was placed in a platinum pan and heated up to 900 °C with a constant heating rate of 20 °C/min under a nitrogen atmosphere.

Table 2. Mix design of the investigated samples

Sample	Liquid/Solid ratio	FA wt. %	8 M NaOH wt. %	Sodium silicate solution, wt. %	Molar ratio	
					SiO ₂ /Al ₂ O ₃	Na ₂ O/SiO ₂
I_FA_12	0.45	69.0	5.2	25.8	3.48	0.12
I_FA_16	0.45	69.0	15.5	15.5	3.22	0.16
I_FA_18	0.45	69.0	20.7	10.3	3.10	0.18
I_FA_20	0.45	69.0	25.8	5.2	2.97	0.20
A_FA_12	0.45	69.0	5.2	25.8	4.00	0.12
A_FA_16	0.45	69.0	15.5	15.5	3.70	0.16
A_FA_18	0.45	69.0	20.7	10.3	3.55	0.18
A_FA_20	0.45	69.0	25.9	5.2	3.41	0.20

RESULTS AND DISCUSSION

Both of the investigated fly ashes are mainly amorphous materials with similar silicon and aluminium oxide composition, but different Fe₂O₃ and CaO content. The A_FA is richer in Fe₂O₃ (15.2 wt.%) compared to I_FA (2.71 wt.%), whereas the opposite occurs for CaO (A_FA: 1.67 wt.%; I_FA: 6.63 wt.%). The particle size distribution of the A_FA is smaller than the I_FA, in particular for the size range smaller than 60 µm (for brevity sake particle size distribution of I_FA and A_FA is not reported). Small fly ash particles (< 20 µm) are more likely to have a higher amorphous content (ideal for geopolymerization), as small particles quench faster than larger particles (Hemmings, 1987), in addition smaller particles also have a combined larger surface area which leads to higher reactivity. Visual estimations of workability have been determined during sample preparation. According to the very fine particle size distribution, samples prepared with A_FA exhibited very good workability for all the mixes (Table 3). For I_FA based specimens, workability increased with the Na₂O/SiO₂ molar ratio due to a higher content of water with an increasing amount of 8 M NaOH in the mix. Water absorption results range between 15.7-27.5 wt.% for both the geopolymer series (Table 3), showing that the observed values are also influenced directly by the content of 8 M NaOH solution. The comparison between the two types of fly ash

suggests that slightly higher values of WA_{24h} are shown by A_FA based samples for $Na_2O/SiO_2 \geq 0.18$. Efflorescence on sample surfaces was only visible after the water absorption test. As only limited efflorescence formed for both I_FA and A_FA, visual estimations did not allow a clear trend to be defined (Table 3).

Weight loss due to calcining of cylindrical samples is also listed in Table 3. For I_FA based geopolymers, weight loss ranges between 8.5-9.1 wt.%, whereas lower values, in the range of 4.8-5.9 wt.%, have been measured for A_FA based samples. The different behaviour for the two geopolymer series might be influenced by several factors; (i) the LOI value of the starting fly ash; (ii) the phases formed during the geopolymerization and their thermal stability; (iii) the free sodium content in the geopolymers, which can cause the low temperature dissolution/melting of the mullite (present as FA impurity) as alkali's are known to be excellent sintering agents (Rickard et al., 2012). It is worth highlighting that the highest values of weight loss in each geopolymer series have been determined for samples I_FA_16 and A_FA_16, which were prepared with 8 M NaOH and sodium silicate solutions in a weight ratio 1:1. A detailed XRD analysis is being conducted on the investigated geopolymers, before and after calcining treatment, in order to identify the crystalline phases though the results are not currently available.

Table 3. Workability and physical properties (uncertainty: 1%)

Sample	Workability ^(a)	Tendency to form efflorescence ^(a,b)	Water Absorption (wt.%)	Weight loss during calcining (wt.%)
I_FA_12	1	no	15.7	8.6
I_FA_16	2	4	20.2	9.1
I_FA_18	3	1	21.9	9.0
I_FA_20	4	3	25.6	8.5
A_FA_12	4	1	15.7	5.1
A_FA_16	4	1	16.6	5.9
A_FA_18	4	1	22.9	5.1
A_FA_20	4	2/3	27.5	4.8

(a) Visual evaluations: 1=poor, 2=medium, 3=good, 4=very good. (b) Efflorescence was evaluated after the water absorption test.

Pore size distributions of the investigated samples are collectively reported in Fig. 1. The total intruded volumes increase with the increasing molar ratio of Na_2O/SiO_2 for A_FA geopolymers. The two series behave differently in regards to pore size distributions. A_FA samples (Fig. 1c) mainly present single mode pore size distributions featured by an average pore dimension increasing with Na_2O/SiO_2 , whereas all I_FA geopolymers are characterized by quite largely distributed pore sizes (Fig. 1a). Based on the reported results it appears that, from a microstructural point of view, different phases or at least phases with different porosity are formed during the activation process of the Italian and Australian fly ashes. MIP measurements of calcined samples of both the series (Fig. 1b, d) generally show an increase in the total open porosity and a noteworthy increment in the average pore dimension, which tends $>1 \mu m$.

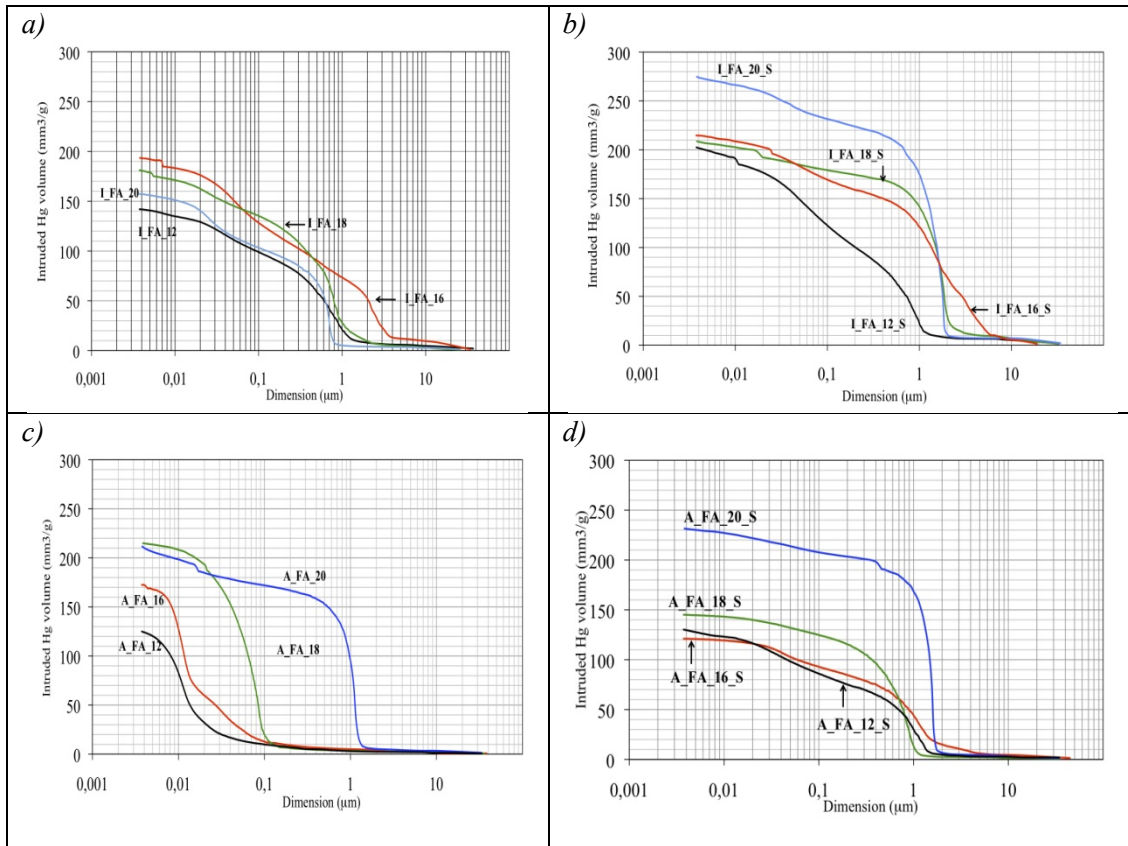


Figure 1. Pore size distribution for I_FA and A_FA based samples (*a* and *c*: after 1 week of curing at room temperature; *b* and *d*: after calcining process)

Figure 2 compares the thermograms of I_FA and A_FA based samples, collected together as a function of the investigated molar ratio of $\text{Na}_2\text{O}/\text{SiO}_2$. There is a continuous loss of mass up to 700 °C for all the A_FA geopolymers, then it remains constant up to 900 °C with a total mass loss of about 4.5-5.5 wt.%. A similar behaviour for Australian fly ash based geopolymers prepared with different amounts and concentrations of activating solutions is reported elsewhere (Bakharev, 2006; Rickard et al., 2010).

I_FA geopolymers exhibited a different trend that become more evident with the increasing of the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio. The I_FA_12 sample behaved similarly to the A_FA_12 sample with a total mass loss slightly lower (about 4.3 wt.%). However, for the other I_FA geopolymers the mass loss did not stop at 700 °C, but continued up to 900 °C with a mass loss rate higher than the comparable A_FA sample. Such behaviour is particularly evident for I_FA_18 and I_FA_20.

The continuous mass loss measured for I_FA based samples is likely to be influenced by the phases formed during the activating and hardening process, and in turn, such phases are influenced by the chemical composition of the fly ash. The content of CaO (≈ 6.7 wt.%) in I_FA is likely to promote the formation of calcium silicate hydrate and/or calcium silicate aluminate hydrate phases, which have been found to coexist with aluminosilicate phases in

alkaline activated systems (Garcia-Lodeiro 2010, 2011; Bignozzi, 2012; Natali Murri et al. 2013).

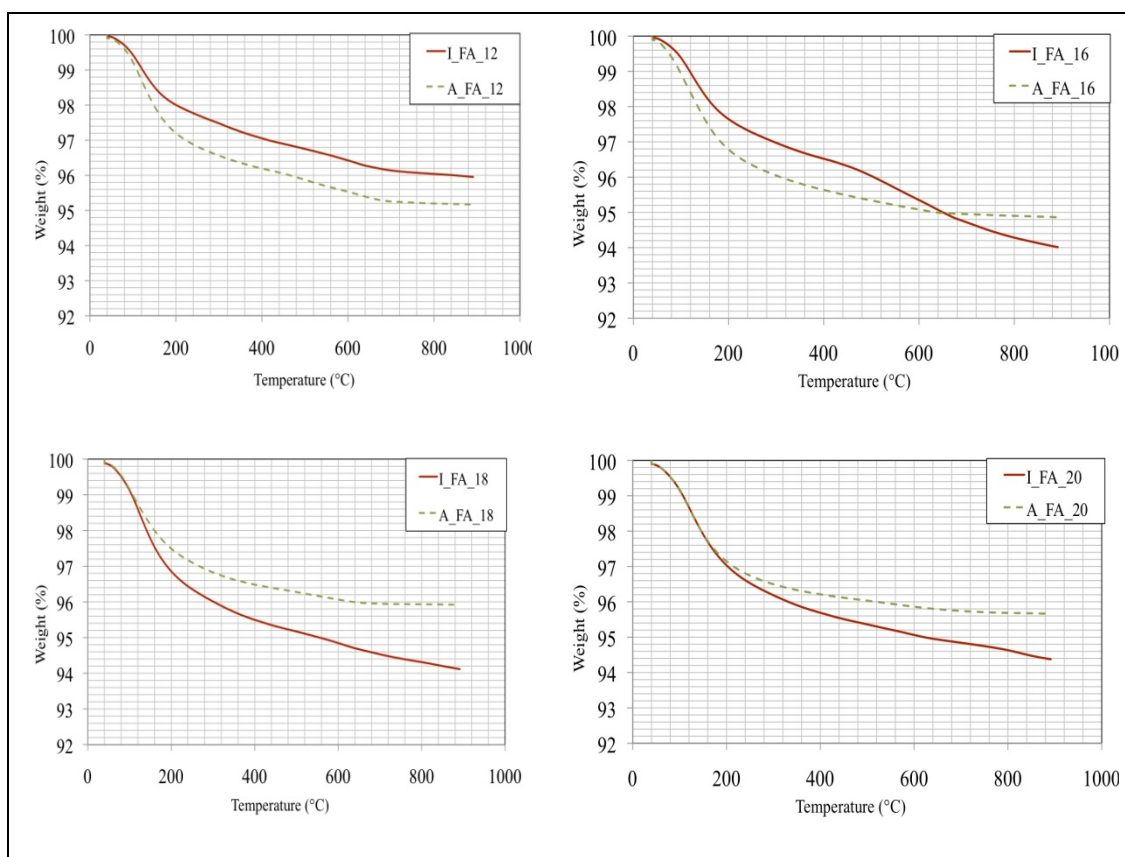


Figure 2. Mass loss with temperature for two sets of geopolymer samples.

CONCLUSIONS

The comparison of new inorganic polymer binders based on Italian and Australian fly ash allows the following conclusions to be drawn:

- the very fine particle size distribution of the A_FA promotes very good workability for all the investigated molar ratios of $\text{Na}_2\text{O}/\text{SiO}_2$, whereas I_FA performs more efficiently in the fresh state when a high content of 8 M NaOH is used. All the binders were completely hardened in the first 24 h at room temperature;
- high temperature treatment has shown limited weight loss in the samples, which is lower for A_FA based geopolymers. Weight loss is related to the phases formed during the activation process, which are likely strongly influenced by the CaO content in the starting fly ash;
- porosimetry analysis indicate that the I_FA and A_FA geopolymers are formed with different pore size distributions. A_FA based samples mainly exhibited single mode pore size distributions, whereas I_FA based geopolymers were characterized by pores with largely distributed dimensions.

It would appear that Italian fly ash shows promise as an alkali activated precursor and this potential should be exploited in Europe. Comparisons with an Australian fly ash suggest that the particle size of the fly ash precursor is important for workability of the fresh geopolymer slurry. Manufacturing binders and products fully based on fly ash and completely free of cement is a goal that must be pursued in order to promote sustainability in the civil and building engineering sector.

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