Production of geopolymers using glass produced from DC plasma treatment of air pollution control (APC) residues

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ABSTRACT

Air pollution control (APC) residues are the hazardous waste produced from cleaning gaseous emissions at energy-from-waste (EfW) facilities processing municipal solid waste (MSW). APC residues have been blended with glass-forming additives and treated using DC plasma technology to produce a high calcium alumino-silicate glass. This research has investigated the optimisation and properties of geopolymers prepared from this glass. Work has shown that high strength geopolymers can be formed and that the NaOH concentration of the activating solution significantly affects the properties. The broad particle size distribution of the APC residue glass used in these experiments results in a microstructure that contains unreacted glass particles included within a geopolymer binder phase. The high calcium content of APC residues may cause the formation of some amorphous calcium silicate hydrate (C-S-H) gel. A mix prepared with S/L = 3.4, Si/Al = 2.6 and [NaOH] = 6 M in the activating solution, produced high strength geopolymers with compressive strengths of ∼130 MPa. This material had high density (2070 kg/m^3) and low porosity. The research demonstrates for the first time that glass derived from DC plasma treatment of APC residues can be used to form high strength geopolymer–glass composites that have potential for use in a range of applications.

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1. Introduction

Air pollution control (APC) residues are the fine granular waste generated from the emission control systems at EfW plants processing MSW. They are produced by both dry and semi-dry scrubber systems, and are a mixture of fly ash, lime and carbon. APC residues contain relatively high concentrations of volatile heavy metals and soluble salts, particularly leachable chlorides and trace levels of organic compounds, including dioxins and furans. The MSW composition, the combustion temperature and the configuration of the APC system determine the APC residue composition. They have high alkalinity (pH > 12) and are classified in the European Waste Catalogue (EWC) with an absolute hazardous waste code (19 01 07*). The incineration of 1 tonne of MSW produces approximately 40 kg of APC residues. Current management options for APC residues have recently been reviewed [1,2]. The amount of APC residues is expected to increase in the UK as the number of

EfW facilities increases, and so the development of more sustainable methods for managing APC residues is crucial for the UK EfW industry.

DC plasma technology provides an integrated solution for the management of APC residues. Plasma treatment of APC residues combined with glass-forming additives reduces the waste volume and produces an inert glass that has been qualified for product use as a resource [3]. Beneficial re-use of this glass would have significant economic and environmental benefits and there is increasing demand for low-carbon, sustainable construction materials and products containing recycled materials. The re-use of plasma derived glass from the treatment of APC residues in glass ceramics [4] and in pressed and sintered ceramic tiles [5] have been investigated.

DC plasma treatment of APC residues has been proven to be economically attractive, as the cost of the alternative management options are expected to increase as their overall availability reduces. The cost of pre-treatment and landfill disposal is expected to increase to about £150 per tonne by 2011, due to escalating landfill tax and gate fees and a shortage of void space. The cost of DC plasma treatment is expected to be in the range of £100–140 per tonne of APC residues, and this is therefore likely to be below the cost of landfill disposal, and is also immune to further escalations in landfill tax. In addition, DC plasma technology provides a more

sustainable waste management option that is a recovery solution rather than disposal.

Geopolymers are alumino-silicates consisting of silica (SiO_4) and alumina (AlO_4) based tetrahedra linked by sharing oxygen atoms [6]. The term *geopolymer* was first used by Davidovits [7] and describes the phases formed through re-precipitation of dissolved species generated by alkali attack of solid alumino-silicate materials [8]. The mechanism of geopolymer formation is based on the chemistry of alkali-activated inorganic binders and involves the chemical reaction of alumino-silicate oxides with alkali polysilicates to form polymeric Si–O–Al bonds [9]. The negative charge of Al^{3+} in IV-fold coordination is balanced by the presence of positive ions such as Na^+, K^+ and Ca^{2+} in framework cavities [10]. The empirical formula of geopolymers is therefore:

$$M_n(-(SiO_2)_z-AlO_2)_n, wH_2O$$
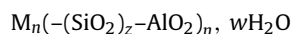
where M is a cation such as Na^+, K^+ or Ca^{2+}, z is 1, 2 or 3, and n is the degree of poly-condensation [10].

An advantage of geopolymers is that they are associated with low emissions of CO_2 compared to Portland cement. The microstructure and properties depend on the initial raw materials and they can have very high compressive strengths, low shrinkage, fast or slow setting, good acid and fire resistance and low thermal conductivity [7,11].

The geopolymer precursor is a source of silica and alumina that will dissolve in an alkaline solution [9]. Natural minerals and waste materials have been investigated as sources of geopolymers in recent years [12–18]. Pulverised fuel ash (PFA) from coal fired power stations, ground, granulated blast furnace slag (GGBS) from the steel industry and silt wastes from aggregate washing plants have all been used to form geopolymers [19].

The glass derived from the DC plasma treatment of APC residues is an alumino-silicate material and is therefore a potential candidate for geopolymer production. As-received APC residues contain lower levels of alumino-silicates and the use of untreated APC residues to form geopolymers is likely to be problematic particularly because of the high levels of leachable chloride salts present. In addition, this research was particularly focused on the development of beneficial re-use applications for the glass derived from DC plasma treatment of APC residues.

APC residues plasma derived glass contains relatively high levels of calcium, and previous research has shown that this can result in the formation of calcium silicate hydrate (C-S-H) gel in geopolymers [20–27]. Calcium can have a positive effect on geopolymerisation and on the compressive strength of the materials formed [21,28]. This is because it provides additional nucleation sites for precipitation of dissolved species [15], resulting in a decrease in porosity and the formation of amorphous Ca–Al–Si gel, which strengthens the final product [29,30]. The products that can be developed from alkali activation of alumino-silicate wastes in the presence of calcium are M-geopolymer, where M is a non-calcium alkali element, typically sodium or potassium, Ca-geopolymer, C-S-H gel, calcium aluminate, calcium alumino-silicate or other precipitates [21].

The glass derived from treating APC residues with DC plasma technology has not previously been used to produce geopolymers or alkali-activated materials. This research aimed to optimise the production of geopolymers from this industrial waste and characterise the properties and microstructures of the materials formed.

2. Materials and methods

2.1. Materials

The glass produced by the DC plasma treatment of APC residues was supplied by Tetronics Ltd. (Swindon, UK) as large, irregular pieces, which were crushed to a particle size of <2 mm. This material was then milled to form a fine powder using a Tema mill (TEMA Machinery Ltd.).

Sodium silicate solution (VWR, Lutterworth, UK) containing 26.5 wt% SiO_2, 8.5 wt% Na_2O and 65 wt% H_2O with a density of 1310 kg/m³, sodium hydroxide (Fisher Scientific, Loughborough, UK) and distilled water, formed the activating solution used in all experiments.

2.2. Characterisation

The bulk chemical composition of APC residue derived glass (APCDG) using DC plasma technology was determined by X-ray fluorescence spectroscopy (XRF, SPECTRO 2000). The mineralogical composition was determined by X-ray diffraction (XRD, Philips PW1700 diffractometer) using Cu Kα radiation in the range of 5–70° (2θ) with a 0.04° step size. Scanning electron microscopy (SEM) was used to examine gold-coated APCDG powder (JEOL JSM 5610LV) the particle size distribution of which was analysed by laser diffraction (Beckman Coulter LS-100) over the range 0.4–900 μm.

2.3. Preparation of geopolymer samples

Geopolymer preparation involved mixing milled APCDG with the activating solution. This was prepared by dissolving sodium hydroxide pellets in water and allowing the solution to cool to room temperature before adding the required amount of sodium silicate solution. The activating solution was then thoroughly mixed with APCDG powder for 10 min. The resulting paste was poured into rectangular moulds (80 mm × 25 mm × 25 mm) on a vibrating table to reduce the formation of air voids in the samples. The samples were de-moulded after 24 h and wrapped in cling film to inhibit evaporation of water. All samples were cured at room temperature.

Geopolymers were prepared using concentrations of sodium hydroxide in the activating solution that ranged from 2 to 12 M. The Si/Al ratio was 2.6 and the optimum solid/liquid ratio, determined in preliminary trials, was kept constant at 3.4. The solid content used in the starting mixtures was 77 wt% and this gave the highest compressive strengths in the preliminary trials which also showed that solid content higher than ~79 wt% could not be used as it resulted in a semi-dry powder and not a castable paste.

The geopolymers formed were characterised for a range of mechanical properties including compressive strength, density, water absorption and porosity. Unconfined compressive strength (UCS) was determined at a loading rate of 300 kPa/s, on four samples from each composition. The bulk density of geopolymer samples was determined by Archimedes' method. Water absorption was obtained from the weight gain of dry samples after 24 h saturation in water; porosity was calculated from the data obtained. Crystalline phases were analysed on powder samples using XRD (Philips PW1700 series) with Cu Kα radiation and a secondary graphite crystal as mono-chromator. After compressive strength testing, samples of the optimum mix were polished to a 1 μm surface finish and examined using SEM–EDS to give chemical composition and microstructural data.

3. Results and discussion

3.1. Characterisation of APCDG powder

The chemical composition of APCDG is presented in Table 1. This shows that the composition (wt%) in terms of major oxides was SiO_2 (41.1%), CaO (32.6%) and Al_2O_3 (14.8%). XRD data are given in Fig. 1. This shows a high background centred at about 30° 2θ, indicating that the APCDG is amorphous and that crystalline phases do not form during cooling.

Table 1
Chemical composition of APCDG.

Oxide	Composition weight%
Na_2O	2.88
MgO	2.31
Al_2O_3	14.78
SiO_2	41.10
P_2O_5	0.77
K_2O	0.03
CaO	32.59
TiO_2	1.19
Mn_3O_4	0.23
Cr_2O_3	0.06
Fe_2O_3	4.07
Cl	2.5

The angular particles produced by milling are shown in Fig. 2 and the corresponding particle size distribution data in Fig. 3. This shows a broad distribution of particle size with a mean size of approximately 36 μm and all particles were below 200 μm.

3.2. Properties of APCDG geopolymers

3.2.1. Mechanical properties

Compressive strength, density and water absorption data for APCDG geopolymers prepared with different sodium hydroxide concentrations in the activating solution are shown in Fig. 4a and b. The range bars indicate the maximum and minimum values obtained from the four samples tested for each composition.
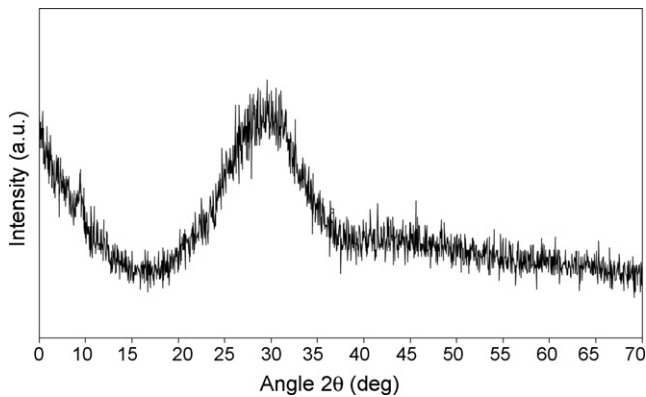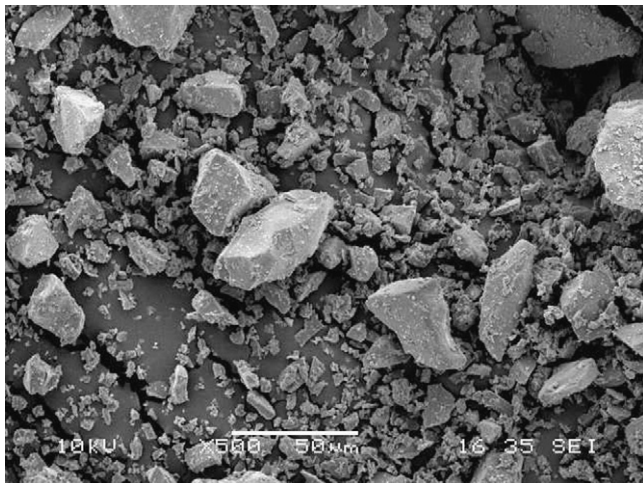

Fig. 1. XRD pattern of APCDG.

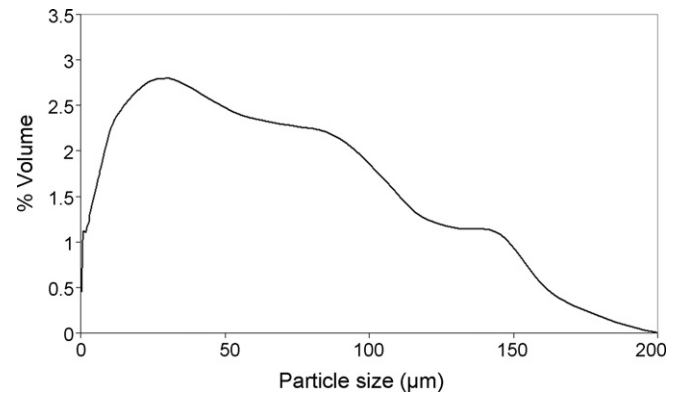**Fig. 2.** APCDG particles after 2 min of TEMA milling.

Fig. 3. Particle size distribution of APCDG after TEMA milling.

Strength increased with increasing concentration of NaOH, particularly between 2 and 4 M. Samples prepared with 6 M NaOH or above had high compressive strengths, ranging between 80 and 110 MPa after 28 days and 100–140 MPa after 92 days. The increase in compressive strength with curing time occurs because the later stages of geopolymerisation involving gelation and transformation continue after the point at which the geopolymer sets [15].

Density and water absorption also depend on the sodium hydroxide concentration; higher concentrations increase density and result in a decrease in water absorption. The lowest density (1893 kg/m³) was for samples prepared with 2 M NaOH, whereas samples made with higher concentrations exhibited densities between 2000 and 2100 kg/m³. The water absorption of the samples is relatively low, with values ranging between 8 and 10% for samples prepared with sodium hydroxide concentrations higher than 2 M, while the sample prepared with 2 M NaOH had higher water absorption (∼16%).
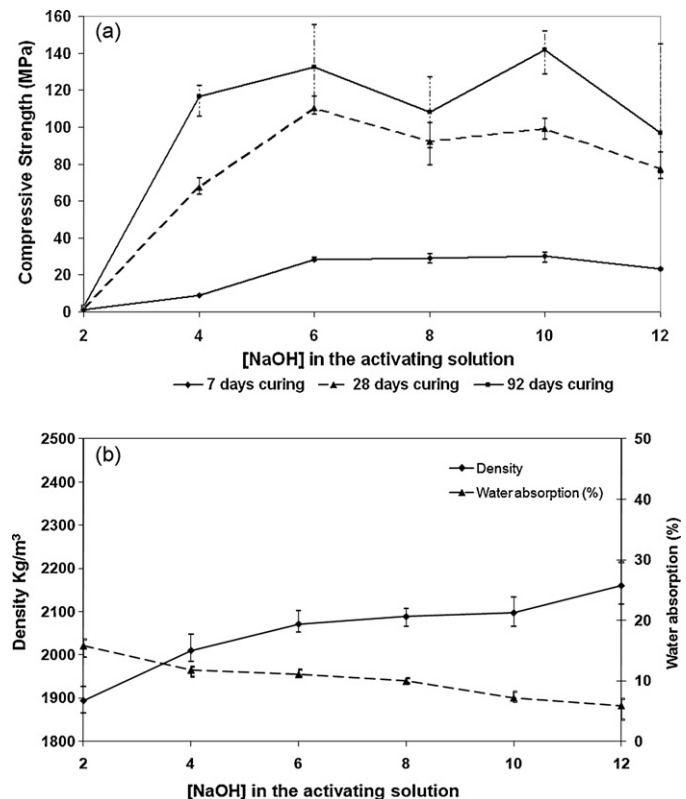

Fig. 4. Effect of sodium hydroxide concentration in the activating solution on APCDG geopolymers: (a) compressive strength and (b) density and water absorption.

The dissolution of the alumino-silicate species in samples prepared with lower sodium hydroxide concentrations in the activating solution is limited, and relatively low amounts of silicate and aluminate species are available for geopolymerisation. This results in lower compressive strengths in the final material. With increasing sodium hydroxide concentration, the dissolution of alumino-silicate species increases and the amount of monomers available for geopolymerisation is higher, resulting in increased compressive strength. It was observed that for sodium hydroxide concentrations greater than 10 M the compressive strength of the final material reduced, which is in accordance with previous studies [19,31]. The high compressive strengths and high density of APCDG geopolymers can also be attributed in the presence of calcium in the system, as previous research has shown that calcium has a positive effect on geopolymerisation and on the compressive strength of the materials formed [21,28].

3.2.2. Microstructural characterisation

XRD data are presented in Fig. 5. All the geopolymers are amorphous as indicated by the high background between 20° and 40° 2θ.
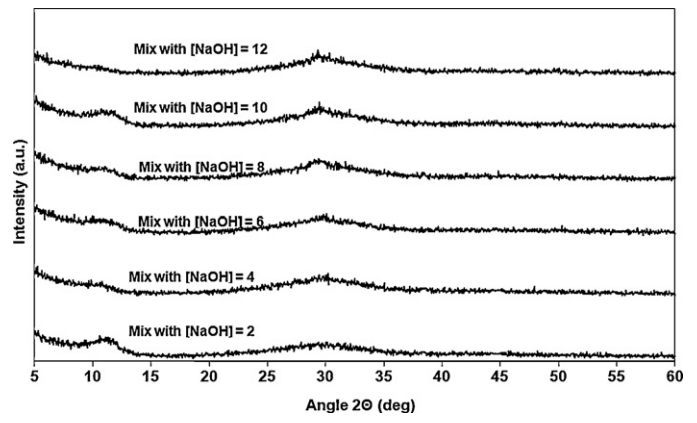
Fig. 5. XRD analysis of geopolymer samples with different sodium hydroxide concentration of the activating solution.
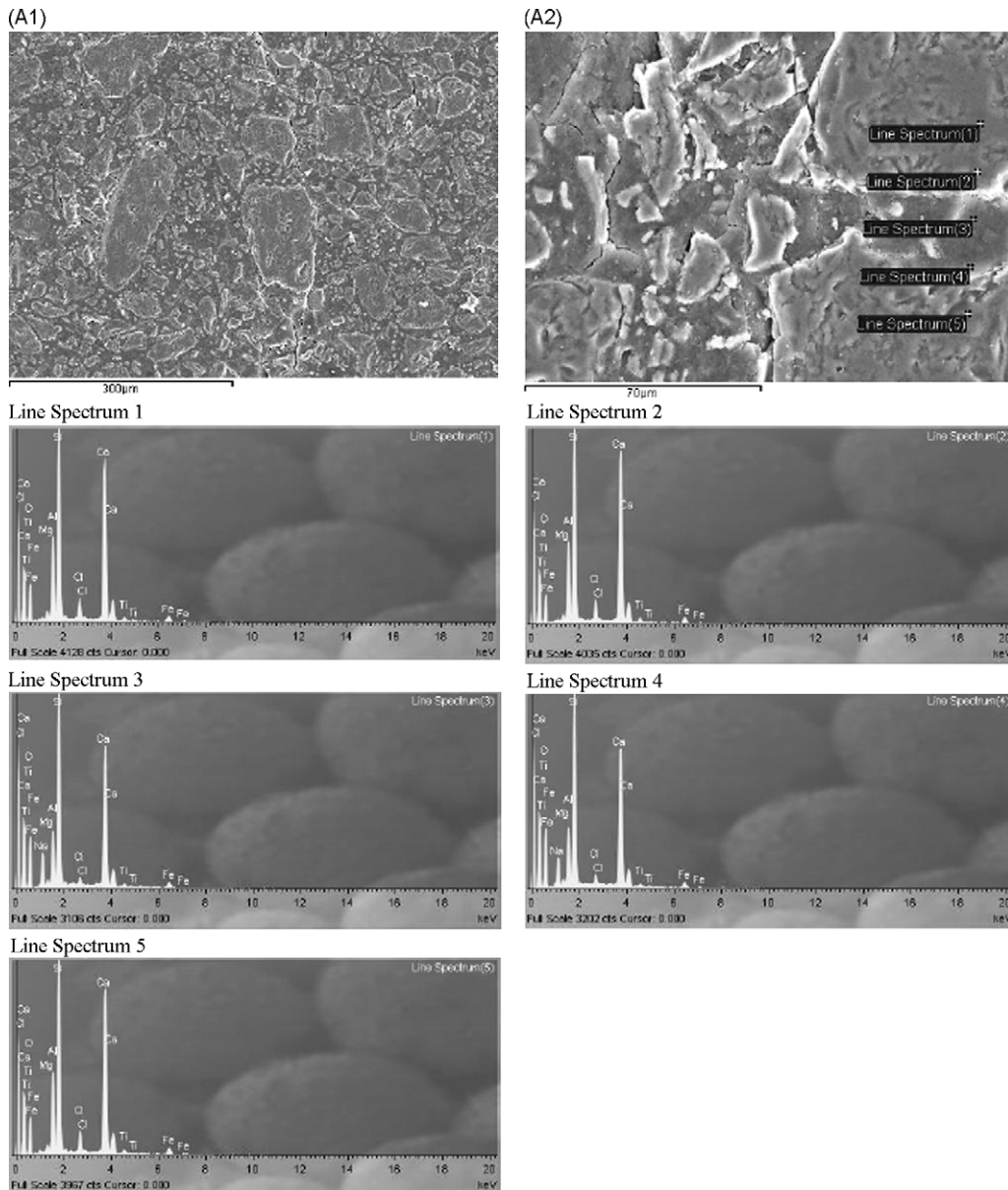
Fig. 6. SEM–EDS analysis of optimum APCDG geopolymer.

Table 2
Chemical composition of optimum APCDG geopolymer by SEM–EDS analysis.

Spectrum	Weight%								
	O	Na	Mg	Al	Si	Cl	Ca	Ti	Fe
Line spectrum (1)	35.58		0.91	8.37	20.98	3.06	27.68	0.9	2.52
Line spectrum (2)	30.37		0.89	8.66	22.58	3.19	30.3	1.06	2.95
Line spectrum (3)	39.73	5.94	0.7	5.87	21.45	0.78	22.47	0.65	2.41
Line spectrum (4)	42.47	5	0.71	5.77	19.83	1.2	22.16	0.51	2.34
Line spectrum (5)	34.89		0.77	8.27	21.15	2.98	28	1.05	2.9

There are no crystalline peaks associated with the alkali activation of APCDG, indicating that crystalline C-S-H is not formed. XRD indicates no, or very low, calcium hydroxide levels [22]. The data do not exclude the possibility of the formation of amorphous C-S-H and/or calcium hydroxide.

SEM–EDS images of the microstructure of optimum samples and corresponding spot analysis data are presented in Fig. 6. A1 and A2 show that a significant volume of unreacted APCDG remains in the material, with the geopolymerisation derived matrix phase chemically bonding these into the microstructure. This geopolymer–glass composite structure results in a high strength material that is expected to have high fracture surface energy and toughness (K_{1C}) because they can employ toughening mechanisms, such as crack deflection, typical of particle reinforced ceramics [32]. The SEM images reveal that the optimum APCDG geopolymer has very low porosity. Table 2 shows that the major elements present are O, Ca, Si, Al, Cl, Na, Fe, Mg and Ti. Sodium is detected in the binding phase as it is in the activating solution. The elemental analysis does not indicate a clear distinction between a geopolymer phase and a phase containing C-S-H hydration products. There is also no evidence of calcium hydroxide precipitates. The high level of calcium in the APCDG means that the binding phase is probably a mixture of geopolymeric gel (M or Ca geopolymer) combined with the types of hydration products observed in geopolymers prepared from metakaolin and other high calcium materials such as ground granulated blast furnace slag (GGBS) [23].

Micrographs of the optimum geopolymer sample prepared showed a heterogeneous microstructure containing unreacted APCDG particles of various sizes and shapes surrounded by a geopolymer binder phase. It seems that the small particles react completely during processing to form geopolymer, while larger particles are only partially reacted. The result is a material composed of unreacted APCDG particles in a binder phase resembling the microstructure of a particle reinforced composite [32]. This is in agreement with previous research with GGBS and metakaolin [33,34]. The unreacted glass particles act effectively as rigid inclusions in the matrix and have a strengthening and toughening effect. Toughening mechanisms such as crack deflection and crack bowing, which are typical in particle reinforced ceramic matrix composites, are able to occur [32,35]. Cracks developed during compressive strength tests are observed in the binder phase between the unreacted APCDG particles. From the examination of fracture surfaces it is apparent that cracks change direction as they encounter the APCDG grains and do not to pass through them, indicating a toughening mechanism based on crack deflection. Quantitative experiments are required to assess the contribution of the glass particle inclusions to the final mechanical properties of these materials. Nevertheless, the results have shown the possibility of designing the initial composition to obtain materials with "composite" microstructures and enhanced mechanical properties.

4. Conclusions

The alumino-silicate glass derived from the DC plasma treatment of APC residues is a potential raw material for the production of geopolymers. The broad particle size range of the milled glass results in geopolymer–glass composites in which unreacted APC residue glass particles are embedded in a geopolymer binder phase. The high calcium content of APCDG means that the geopolymer may also contain an amorphous C-S-H gel phase. The sodium hydroxide concentration in the activating solution significantly affects the geopolymer process. Concentrations up to 10 M allow the formation of geopolymers. An activating solution with a sodium hydroxide concentration of 6 M produces material with a high strength (~130 MPa), high density (2070 kg/m^3) and low water absorption (~10%). This work has demonstrated that APCDG can be used as the raw material for the production of novel geopolymer–glass composites with excellent mechanical and physical properties. Further research is required to develop viable commercial applications for this material. When combined with previous work on DC plasma treatment of APC residues, the research represents an effective way of managing APC residues generated at EfW facilities that minimises waste and maximises resource efficiency.

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