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Geopolymers From DC plasma Treated APC Residues, Metakaolin, and GGBFS

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ABSTRACT

Air pollution control (APC) residues generated from cleaning gaseous emissions at energy from waste plants burning municipal solid waste are classified as hazardous waste and are a significant disposal issue in the UK. APC residues have been combined with glass forming additives and treated using DC plasma technology. This produces an inert glass (APC glass) that has potential to be reused. APC glass has been characterised and used to form geopolymers. Metakaolin and GGBFS geopolymers have also been prepared. The compressive strength, density, water absorption and porosity of APC glass geopolymers were evaluated. Samples were also characterised using XRD, SEM and FTIR. Results show that APC glass geopolymers have excellent mechanical properties compared to other geopolymer materials with high density, low porosity and particularly high compressive strength. This work demonstrated that plasma treated APC residues can be used to form geopolymers with properties suitable for a range of construction applications.

INTRODUCTION

APC residues are the fine particulate waste generated from air pollution abatement systems at EfW plants processing municipal solid waste (MSW). They are a mixture of fly ash, lime and carbon and contain significant levels of volatile heavy metals, soluble salts, particularly leachable chlorides, and trace organic compounds including dioxins and furans. APC residues are classified as a hazardous waste, with an absolute entry in the European Waste Catalogue (EWC 19 01 07*). Combustion of 1 tonne of MSW in a modern EfW plant typically produces about 40 kg of APC residues and approximately 170,000 tonnes of APC residues are generated each year in the UK.

The main disposal method for APC residues has been hazardous waste landfill, but this is problematic due to high levels of chloride leaching which exceed the waste acceptance criteria (WAC) limits for hazardous waste landfill. Alternative management options in the UK are limited [Amutha Rani et al. 2008a]. Thermal vitrification using DC plasma technology has been investigated as a potential treatment technology. DC plasma treatment of APC residues produces a stable, inert black glass that has potential to be re-used [Amutha Rani et al. 2008b].

Geopolymers are synthetic aluminosilicate materials consisting of Si and Al tetrahedra linked by shared oxygen atoms. They have comparable properties to cement based construction materials with the advantage of reduced greenhouse gas emissions compared to Portland cement [Duxson et al. 2007]. Depending on the composition of the raw materials, geopolymers can have high early compressive strengths, low shrinkage, rapid or slow setting, good acid resistance and fire resistance and low thermal conductivity [Davidovits 2008]. Raw materials for geopolymer production need to dissolve in alkaline solution and provide silica and alumina [Divya and Rubina 2007]. APC residue plasma derived glass is an aluminosilicate, and the aim of this research was to investigate the properties of geopolymers produced from APC glass. These have been compared to geopolymers made from metakaolin and ground granulated blast furnace slag (GGBFS) which are commonly used for geopolymer production.

MATERIALS AND METHODS

The glass produced from DC plasma treatment of APC residues was obtained from Tetronics Ltd [Tetronics 2008]. The material was supplied as < 2mm coarse particles. To form geopolymers the APC residue glass was dry milled to a fine powder (TEMA mill, TEMA Machinery Ltd). The particle size distributions of the raw materials are given in Figure 1. This shows that TEMA milled APC glass contains a much broader size range of particles compared to metakaolin and GGBFS.

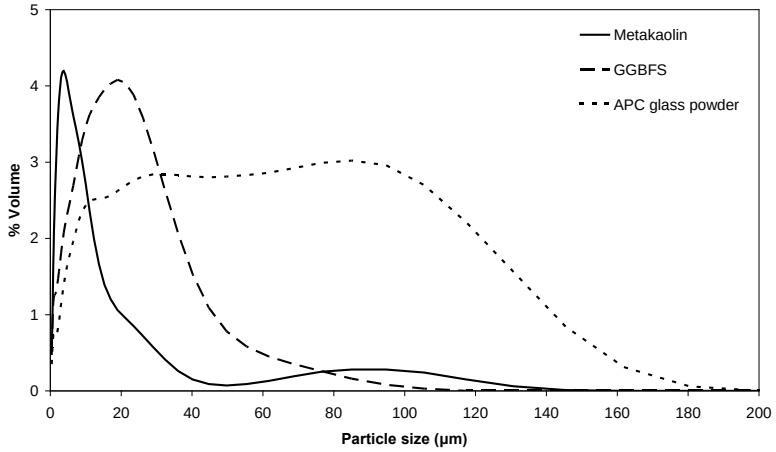


Fig. 1. Particle Size Distribution of APC Glass, Metakaolin and GGBFS

The chemical composition of APC glass, metakaolin and GGBFS are given in Table 1. The major oxides present are SiO_2, Al_2O_3 and CaO.

Table 1. Oxide Composition of APC glass, Metakaolin and GGBFS

	Composition weight %		
Oxide	APC glass	Metakaolin	GGBFS
Na_2O	2.9	ND	0.2
MgO	2.3	0.5	9.2
Al_2O_3	14.8	34.0	13.9
SiO_2	41.1	59.5	34.7
P_2O_5	0.8	ND	ND
K_2O	<0.1	1.9	0.3
CaO	32.6	0.6	38.8
TiO_2	1.2	0.2	1.0
Fe_2O_3	4.1	0.7	0.5
SO_3	ND	1.1	<0.1

ND – Not detected

X-ray diffraction (XRD) data provides information on the mineralogical composition of the raw materials and this is given in the Figure 2. APC glass is amorphous as indicated by the high background around 30˚ and lack of sharp peaks in the XRD data. GGBFS is predominantly amorphous with low intensity peaks indicating the presence of calcite. Metakaolin usually is mostly amorphous but XRD shows there is some quartz and muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$).

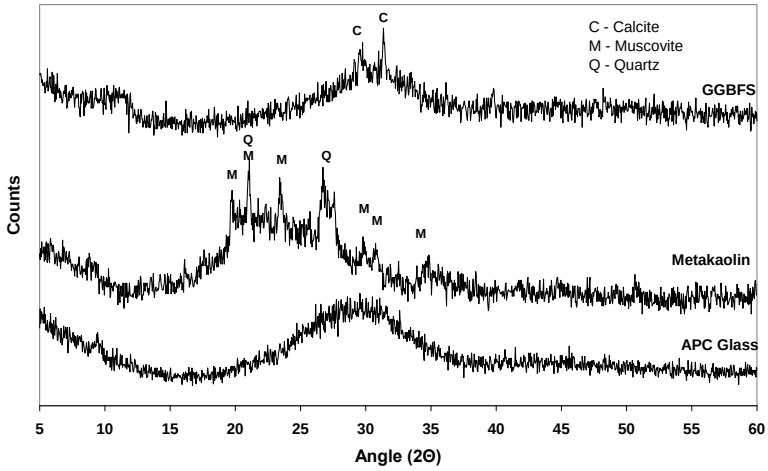


Fig. 2. XRD Analysis of APC Glass, Metakaolin and GGBFS

Sodium silicate solution (VWR International) and sodium hydroxide pellets (Fisher Scientific UK Ltd.) were used to form the activating solution, with distilled water used in all experiments. The parameters used to prepare samples for each mix and more specifically silicon to aluminium ratio in each mix (Si/Al), solid to liquid ratio in each mix (S/L), sodium hydroxide concentration

in the activating solution ([NaOH]) and silicon concentration in the activating solution ([Si]) are presented in Table 2.

Table 2. Composition Parameters of APC Glass, Metakaolin and GGBFS Samples

Mixes	Si/Al (mol)	S/L	[NaOH] (M)	[Si] (M)
APC glass geopolymer	2.6	3.4	6	2.5
Metakaolin geopolymer	2.87	1	6	2.5
Alkali-activated GGBFS	3.05	0.8	6	2.5

The optimum silica and sodium hydroxide concentrations in the activating solution were determined for APC glass geopolymers in previous experiments, and the same concentrations were used to prepare metakaolin and GGBFS geopolymers, although different S/L ratios were used in order to form castable pastes.

The preparation of geopolymers involves mixing the solid components (APC glass powder, metakaolin or GGBFS) with a highly alkaline sodium silicate activating solution. The activating solution was prepared by first dissolving sodium hydroxide pellets in water. This was left to cool to room temperature before the required amount of sodium silicate solution was added. The activating solution was thoroughly mixed with the solid component of the mix, either APC glass powder, metakaolin or GGBFS, for 10 minutes using a 5lt mortar mixer. The paste was then poured into rectangular moulds (80 x 25 x 25 mm^3) on a vibrating table. The moulds were covered with glass slips and the samples were de-moulded after 24 hours. The samples were wrapped in cling film and left to cure at room temperature.

All samples were characterised for compressive strength and APC glass geopolymers were further characterised for density, water absorption and porosity. The mineralogical composition of the samples was determined (XRD, Philips PW1700 series). Scanning electron microscopy (SEM, JEOL JSM 5610LV) was used to examine the microstructure of samples polished to a 1μm surface finish. FTIR analysis (Magna-IR 560 Spectrometer E.S.P., Nicolet) was used to provide information on the chemical bonding present.

RESULTS

Compressive strength data is presented in Figure 3, with three samples tested for each mix. The compressive strengths of the samples were similar after 7 days curing (13-28 MPa), but there were significant differences after 28 and 92 days. At 28 days APC glass geopolymers had compressive strengths that were 3 times higher then the other samples. This strength increase continued with samples reaching 133 MPa after 92 days. Similar strength changes were not observed for the other geopolymer samples tested, where strengths at 28 and 92 day were similar to those at 7 days. The data shows that APC glass geopolymer can have significantly higher final compressive strength than metakaolin and GGBFS geopolymers, with densities of 2300 kg/m^3, porosity of ~5.5% and low water absorption. The compressive strength of APC glass geopolymers is comparable to the compressive strength of geopolymer cements which is reported to be >90MPa [Davidovits 2008].

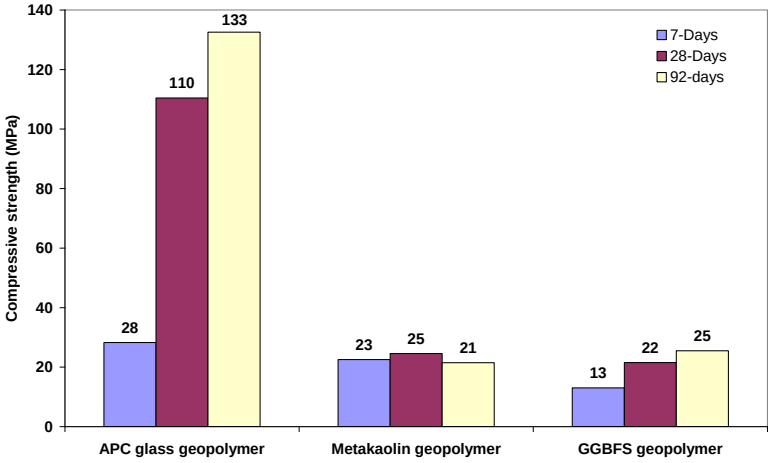
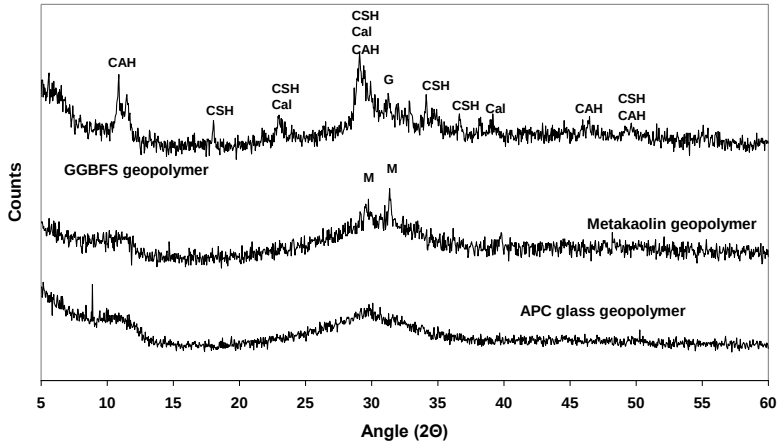


Fig. 3. Compressive Strength Data at 7 28 and 92 Days for APC Glass, Metakaolin and GGBFS Geopolymers

Figure 4 shows XRD data of geopolymers prepared with APC glass, metakaolin and GGBFS.



CSH - Calcium silicate hydrate, Cal - Calcite, CAH - Calcium aluminium oxide hydrate, M - Muscovite, G - Gypsum

Fig. 4. XRD Analysis of APC Glass, Metakaolin and GGBFS Geopolymers

The APC glass geopolymer is amorphous. Metakaolin geopolymers show a characteristic high background between 20˚ and 40˚ 2θ with a decrease in the crystalline peaks associated with the initial material. Peaks for quartz and muscovite have almost disappeared indicating a high degree of geopolymerisation. XRD data of the GGBFS geopolymer also indicates a broad amorphous background around 30˚ 2θ, but several new crystalline phases seem to have formed, due to hydration reactions, including calcite and CAH.

Figure 5a-c shows polished surfaces of the geopolymer samples prepared from APC glass, metakaolin and GGBFS.

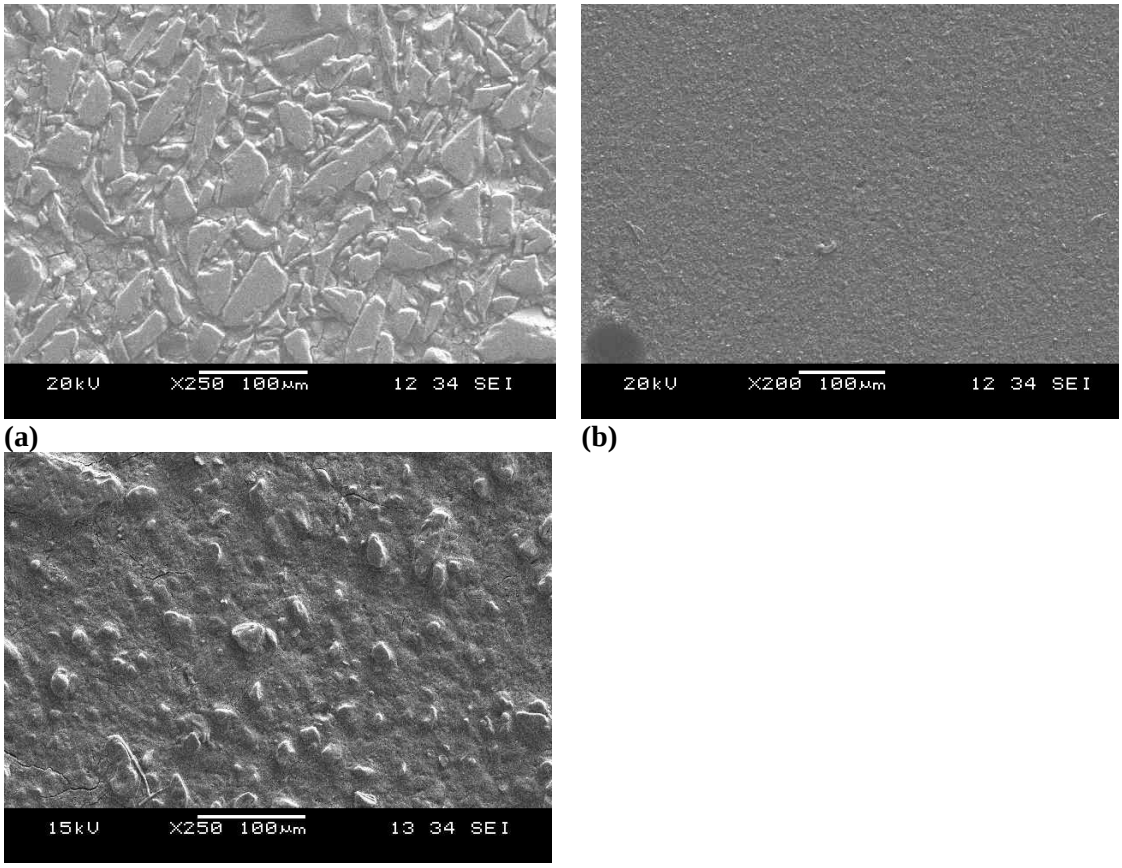


Fig. 5. SEM Images Showing the Microstructure of: (a) APC Glass Geopolymer, (b) Metakaolin Geopolymer, (c) GGBFS Geopolymer

The geopolymer made from metakaolin has a very homogenous matrix containing no coarse unreacted material. The SEM images of APC glass and GGBFS geopolymers show more heterogeneous microstructures that contain unreacted particles surrounded by a binder phase. A particularly high volume of unreacted particles is observed in the APC glass geopolymer.

Figures 6 shows FTIR spectra for the three types of geopolymers. It can observed that the infrared spectra are similar, having analogous absorption bands. All samples show bands around 3440 cm^{-1} and 1650 cm^{-1} which can be attributed OH stretching vibration and HOH bending vibration respectively. The bands visible between 1400-1450 cm^{-1} are due to CO_2 stretching vibration in carbonates. The bands are more clearly defined in the APC glass and GGBFS geopolymers and this indicates that metakaolin based geopolymers are less sensitive to atmospheric carbonation.

The main band in all samples is at 1000 cm^{-1} and this corresponds to Si-O stretching vibrations either due to the geopolymer network or C-S-H. The metakaolin geopolymer, which can be considered as a pure geopolymer, developed a main peak in the region between 1025-1045 cm^{-1} while in APC glass geopolymer this was at 976 cm^{-1} with a shoulder around 1060 cm^{-1}. GGBFS geopolymers show a double peak observed at 958 cm^{-1} and 1022 cm^{-1}.

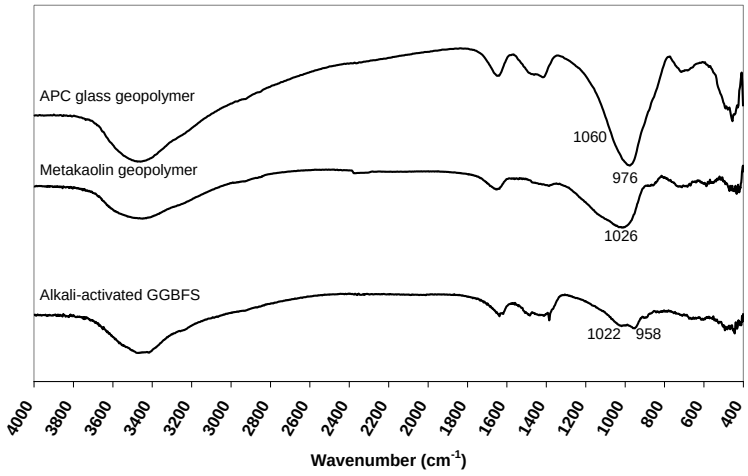


Fig. 6. FTIR Analysis of APC Glass, Metakaolin and GGBFS Geopolymers

Between 500-800 cm^{-1} metakaolin geopolymer develops two peaks. The first is at 721 cm^{-1} and the second less developed peak is at 597 cm^{-1}. In the same region GGBFS geopolymer has one broad peak centered around 660 cm^{-1}. In that region APC glass geopolymer has a broad band centered around 714 cm^{-1}. This is very similar to the one observed in metakaolin geopolymers. There is also a very broad band between 400 and 600 cm^{-1} which indicates a degree of overlapping in this region. All samples developed a band around 450 cm^{-1}, which can be assigned to Si-O bond bending.

DISCUSSION

APC glass geopolymers exhibit much higher compressive strengths than metakaolin or GGBFS geopolymers prepared with the same alkali and silica concentrations in the activating solution. The 7-day compressive strengths are similar for all materials. However, a significant difference is observed after 28 and 92 days, with APC glass geopolymer developing much greater strengths. Early compressive strength is highly dependent on factors such as the particle size distribution, mineral composition of the starting material and type and concentration of activator [Fernández-Jiménez et al. 2005]. Metakaolin and GGBFS particles are much finer than APC glass powder which means that with the same concentration of activator the dissolution process will be more rapid. Although APC glass is coarser in terms of particle size, it develops similar early strengths. This may be due to the presence of calcium in the system which is reported to have a positive effect on geopolymer compressive strength [Xu and Van Deventer 2002b; Yip et al. 2005]. This is because it provides additional nucleation sites for precipitation of dissolved species [Van Deventer et al. 2007].

Calcium and unreacted APC glass are likely to be responsible for the high compressive strength of APC glass geopolymers. Apart from geopolymer network there is possibly the formation of amorphous Ca-Al-Si or aluminium modified C-S-H gel which results in a decrease in porosity and higher compressive strength [Yip and Van Deventer 2001; Xu and Van Deventer 2002a]. SEM shows that APC glass geopolymer is heterogeneous, consisting of a binder phase and unreacted APC glass particles. The unreacted APC glass particles are believed to act 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 expected to occur in APC glass geopolymers [Monette and Anderson 1993 ; Boccaccini et al. 1997].

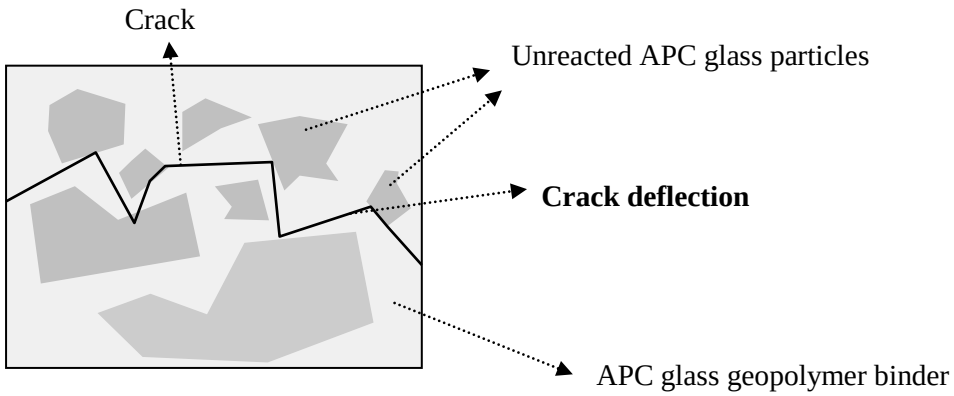


Fig. 7. Schematic Diagram Showing the Crack Deflection Mechanism in APC Glass Geopolymers

A similar heterogeneous structure was observed in the GGBFS geopolymer but with much less unreacted material. Metakaolin geopolymers have a highly homogeneous microstructure with no unreacted phases present [Lecomte et al. 2006].

XRD analysis indicated that APC glass geopolymers are completely amorphous while metakaolin geopolymers are mostly amorphous with some crystalline peaks resulting from unreacted initial material. The amorphous XRD pattern of the APC glass geopolymer does not exclude the presence of amorphous CSH gel in the structure. The GGBFS geopolymer contained several new crystalline phases that formed due to hydration reactions. These included C-S-H gel, calcite and calcium aluminate hydrates.

FTIR analysis provides information on the molecular structure of materials. The comparison of the spectra revealed similarities between APC glass geopolymer and the other materials. The band observed in APC glass geopolymer at ~700 cm^{-1} is almost identical to the band developed in metakaolin geopolymer. The main peak is observed at 976 cm^{-1} but it has a shoulder around

1060 cm^{-1} which is the area that geopolymers develop their main peak. Similarly the GGBFS geopolymer had a broad band with peaks at 958 cm^{-1} and 1022 cm^{-1}.

The APC glass geopolymer is not a pure geopolymer because it is likely to contain both aluminosilicate gel and hydration products such as C-S-H gel or aluminium modified C-S-H gel. The coexistence of both geopolymer and C-S-H phases has previously been reported [Alonso and Palomo 2001; Yip and Van Deventer 2003; Yip et al. 2005] and these phases contribute significantly to the final physical properties of the material..

CONCLUSIONS

1. The aluminosilicate glass derived from DC plasma treatment of APC residues is a potential raw material for the production of geopolymers.
2. The broad particle size range in the milled glass results in geopolymer glass composites in which unreacted APC glass particles are embedded in a geopolymer binder.
3. The high calcium content of APC glass means that the geopolymer may also contain an amorphous C-S-H gel phase.
4. Geopolymers with very high strength (~130 MPa), high density (2300 kg/m^3) and low porosity (~5.5%) can be formed.
5. This research, when combined with previous work on DC plasma treatment, represents a effective way of managing APC residues generated at EfW facilities that minimises waste and maximises resource efficiency.

ACKNOWLEDGEMENTS

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