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Investigation of Volcanic Ash Based Geopolymers as Potential Building Materials

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Abstract

Volcanic ash powders from Etna (Italy) and Cameroon were used as the principal source of aluminosilicate to produce geopolymers with the potential for making building products. The volcanic ash was ball milled and reacted with concentrated alkaline solutions for polymerisation and subsequent curing at 75–400 °C for 12–48 h.

It was found that the gel was more viscous than a similar gel formed from metakaolin. Geopolymers made from both ashes had bulk densities of 1.7–2.0 g/cm³ and water

absorption values of 20–25 %. Their compressive strength values were 25–35 MPa and the bi-axial four-point flexural strength values ranged from 14–20 MPa. These values increased by 20 % when cured for 21 d after 90 d storage. It was also found that by curing at 200–400 °C the mechanical properties increased.

Scanning electron micrographs showed that with thermal curing microcrystalline phases were present along with undissolved crystalline phases. These phases remained bound to the matrix and acted as a filler for strengthening the materials. The Ca, Mg and Fe present as impurities in the volcanic ash formed some of these crystalline phases and did not form any deleterious hydroxide or carbonate phases.

Keywords: geopolymer, volcanic ash, dissolution, polycondensation, building materials

1 Introduction

Alumino-silicate polymers, referred to as geopolymers, are materials with excellent mechanical and chemical properties compared to ordinary Portland cement based materials. Potential applications for geopolymers include pre-cast structures, non-structural materials, such as pavements, products for containment and immobilization of toxic, hazardous and radioactive wastes, advanced structural tooling, refractories, fire resistant composites used in buildings, airplanes, ship structures, racing cars, and the nuclear power industry.

Geopolymerisation involves mechanisms such as the dissolution of aluminium and silicon species in high pH alkaline solutions followed by room temperature polymerisation of active surface groups and soluble species to form a gel, then subsequently polycondensation to form hardened geopolymer structures. The rate of dissolution of the aluminium and silicon species is directly dependent on the amorphous nature of the starting materials as well as the fineness of the particles. The smaller the particle size of the starting materials, the higher the reactivity and the geopolymerisation rate. The synthesis of geopolymers relies on the same reaction mechanism as reported by others [1–3].

Ghukhovsky [3] assumed that, since the geological transformation of some volcanic rocks into zeolites takes place during the formation of sedimentary rocks at low temperatures and pressures, it might be possible to transfer this process to cementitious systems. A direct synthesis of alkaline alumino-silicate minerals in the phase composition of such cementitious systems **may ensure strength and durability in the artificial stones formed. Therefore, (delete)** The complex geopolymer structure consists of chains, sheet-like and three dimensional networks made of various three-dimensional structural unit types of connected SiO₄ and AlO₄ tetrahedra [4].

The amorphous nature of volcanic ash due to its high non-crystalline silica content accounts for the dissolution of this material in alkaline solution. This led to the idea of using volcanic ash for the development of strengthened structural materials by dissolution, polymerisation and polycondensation. It is reasonable to assume that volcanic ash, which is an amorphous alumino-silicate, will form geopolymers similar to metakaolin or fly ash. The present work investigated volcanic ash as an alternative raw material for geopolymer structural products. Among the raw materials investigated up to now for geopolymerisation, metakaolin has been identified as the alumino-silicate with the highest release per weight of both silicate and aluminate even after only a few hours in alkaline solution [1, 2]. This might be ascribed to the purity of the material, which is essentially composed of SiO₂ and Al₂O₃. The high stability of the glassy phase of fly ash, slags, and others alumino-silicate wastes with high temperature thermal history as well as volcanic ash can be explained by their slow dissolution in alkaline solution. But even though the dissolution of these wastes takes time, they have been found to be very suitable for the geopolymerisation concept [5]. Therefore our objective was to investigate the alkaline activation of volcanic ash firstly in geopolymer building products. The difference with volcanic ash comes from the amount of aluminate monomers released, which will be lower since the alumina content is lower than **in** the metakaolin **content**. On the other hand, volcanic ash has the advantage that it can be directly

dissolved in alkaline solution without any thermal pretreatment and is thus more energy-efficient and environmentally friendly since it requires just sieving or at most grinding. The other advantage comes from the chemical composition of volcanic ash which, with its high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and high alkali content, can be activated with lower amounts of alkaline solution than metakaolin. The complexity of the chemical composition of volcanic ash will complicate the understanding of its geopolymerisation mechanism since the geopolymer solids formed by alkali-activation of aluminosilicate have been shown to be pH dependent. Further, a mixture of geopolymer gel, calcium silicate hydrate phases, etc. will be difficult to monitor. Applications for geopolymeric products made from volcanic ash are primarily centred on, but by no means limited to, the building industry, where their durability, strength and fire resistance provide many advantages.

Volcanic ash is composed of small jagged pieces of rock (Fig. 1), minerals and volcanic glass the size of sand and silt (less than 2 mm in diameter) erupted from volcanoes. Such volcanoes exist throughout the world, for example Mount St. Helens in the USA, Etna in Italy, Mount Pinatubo in the Philippines, Tarawera in New Zealand, Santiaguito and Pacaya in Guatemala, Fuego in Costa Rica and Fako in Cameroon. This means millions of tonnes of volcanic ash are available. Studies [7–9] have investigated the utilization of volcanic ash in cements and ceramic production but it is still under-exploited. In the work reported here we used volcanic ash from two deposits (Mount Etna in Italy and Foubot in Cameroon) in geopolymerisation applications.

From the chemical point of view, geopolymers for structural applications constitute a three dimensional framework formed by SiO_4 and AlO_4 tetrahedra linked by shared oxygen atoms, with alkali cations (Na^+ , K^+ , Ca^{2+} , etc.) from the activator solution present to balance the negative charge of tetrahedrally coordinated Al^{3+} . The principle of geopolymerisation is based on the assumption of Glukhovskiy, which considered a directed synthesis of alkaline aluminosilicates minerals in the phase composition of cementitious systems on the

basis of the geological process of transformation of some volcanic rocks into zeolites at low temperatures and pressures [3]. Although opinions differ regarding the exact mechanism responsible for the geopolymerisation reactions, it is apparent that in many cases where materials such as alumina silicates with a thermal history are used, the dissolution, polymerisation and polycondensation are intermediate steps and the dissolution of the starting materials seems to not be completed before the final hardened structure is formed [6]. In the case of volcanic ash, the dissolution was found to be very slow. This is due to the high stability of the glassy phase of volcanic ash compared to, for example, metakaolin. The influence of temperature on the final properties of volcanic ash based geopolymers indicated that some elements still need to be activated to take part in the process.

2 Experimental

2.1 Materials

The volcanic ash samples used for the synthesis of geopolymers were from Mount Etna (Italy) for PZI and Foubot (Cameroon) for PZC. Their characterization by means of traditional chemical analysis gave the chemical composition summarized in Table 1. The sodium hydroxide (8M) and sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 3$) solutions used were laboratory reagent grade.

2.2 Geopolymerisation process

The two volcanic ash samples were ball milled to particles less than 250 μm in size. A mixture of solutions of 50 % NaOH and 50 % Na_2SiO_3 was prepared with around 15 % in total volume of water added. Volcanic ash powder was then added gradually to make a highly viscous paste which was slip cast in plastic moulds. Cylindrical specimens (4 cm \times 7 cm) were prepared from both volcanic ash samples. The specimens obtained were transferred to an oven after 24 h for thermal curing at 25, 75, 100, 200 and 400 °C. The samples were cured for 48 h at 25, 75, 100 and 200 °C and 12 h at 400 °C. The specimens were removed and characterized. The labelling followed the ash designations, i.e. GPZI indicates the geopolymer produced with PZI.

2.3 Characterization of geopolymer products

Specimens obtained after thermal treatment were characterized progressively after 21 and 90 d. The characterization included bulk density, porosity, water absorption and mechanical properties evaluated following the ASTM C20-00, ASTM F394-78 and ASTM C62 and C216. The mineralogy of geopolymers was studied using XRD analysis with a goniometer PW3050/60 theta/theta. A SEM (PHILIPS XL40) operating at 25kV was used for microstructure investigations of as-fractured surfaces of samples. Fractured surfaces were gold coated and secondary electron images (SEI) were collected.

3 Densification behaviour, mechanical properties and microstructure of volcanic ash based geopolymers

The geopolymers obtained after curing exhibited very low shrinkage of less than 2 % for all the specimens. As is seen in Fig. 2, the bulk density varies from 1.7 g/cm^3 for GPZI and GPZC at room temperature curing to 1.8 g/cm^3 and 2.0 for GPZC and GPZI in specimens treated at 400 °C. This indicated the influence of the curing temperature on the densification of volcanic ash based geopolymers. This influence was directly correlated to the mechanical behaviour. The bi-axial four point flexural strength which was about 14 MPa for the two materials increases linearly with temperature up to 20 MPa at 400 °C, while the compressive strength goes from 28 MPa for GPZC and 36 MPa for GPZI at room temperature to 52 and 56 MPa respectively (Fig. 3). These observations contrast with observations by Cioffi et al. [10]. In fact, densification of metakaolin based geopolymers was found to be negatively influenced by the temperature development within a wider range. However, it is clear that geopolymerisation reactions are exothermic during which the heat produced is used for the evaporation of water, leading to the formation of micro cavities. Therefore the use of temperature for volcanic ash based geopolymer curing processes should be advantageous since volcanic ash is described as a mix of aggregates with particles of glassy phases in which nucleoids and microcrystalline

minerals are bound. The temperature should then be an activation factor. It has been shown [2, 5, 6] that temperature is an important parameter in the polymerization and polycondensation of fly ash activated with alkaline solution. Fly ash and volcanic ash are materials of a glassy nature with complex chemical compositions and they are not expected to behave in the same manner as metakaolin. The volcanic ash from Mount Etna was found to develop better characteristics in geopolymer applications. More dense and more resistant products produced from this raw material also presented lower porosity and water absorption as indicated in Fig. 4. The porosity decreases linearly with increasing temperature, which partly explains our assumption that temperature is here considered as an activation factor which contributes to the welding of complex phases developed during the dissolution and polymerisation of volcanic ash. The total porosity, which was more than 30 % for room temperature curing, decreases gradually to less than 25 % for GPZI and lower for GPZC, where the porosity goes from 35 % to 29 % in the same interval. The lower porosity of GPZI is assumed to result from the coexistence of polysialates and CSH phases which, in the case of GPZI, should be more important as regards the Ca^{2+} content. The densification behaviour, the mechanical properties and the porosity can be compared to that of traditional porous ceramics. Quite a range of civil engineering applications are suited for volcanic ash based geopolymer systems, considering that the present materials are produced at lower temperatures than conventional ceramics. The values of compressive strength (>20 MPa) and water absorption (≤ 20 %) comply with the ASTM standards C62 (SW) and C216 (SW) respectively for building and facing bricks. In Fig. 5, it can be seen that, like conventional metakaolin geopolymer materials, volcanic ash based geopolymer materials have a mainly crystalline character. The peaks of various phases are observed in room temperature cured geopolymer together with traces of amorphous material visible as a large shoulder which causes a lack of flatness in the base line. When cured at 400 °C, the

already identified peaks of initial polycrystalline phases [7, 8] decrease in intensity while new peaks develop. The newly formed crystalline phases were more pronounced in the GPZI than GPZC, confirming the different behaviour in the densification mechanism and hence in the mechanical properties. From the micrographs in Fig. 6 it is clear that the difference in the densification behaviour of the two volcanic ash materials results in different microstructures. GPZI samples present compact structures with polysialates and unreacted grains homogeneously dispersed in the geopolymer matrixes and well interconnected for a relatively low porosity. The interconnection was similar for GPZC but porosity was more extended. With high magnification (Fig. 6 b), the relatively lower densification of GPZC compared to GPZI is more evident: this difference can be directly attributed to the difference in the chemical composition of the two materials. The Si/Al ratio was 3 for GPZI while it was 4 for GPZC; 3 and 3.5 for Si/Na ratio and 2 and 1 for Al/Na. The sample GPZI contains a high percentage of ions Ca^{2+} , resulting in the increase in new nucleoid sites and growth of calcium silicate hydrates, CSH, gel which, in turn, contributes to enhanced densification. The formation of precipitates containing Ca in the initial stages of geopolymerisation will provide a large number of potential nucleation sites at the solid-liquid boundaries thus formed. The formation of calcium silicate hydrates will remove a proportion of the excess silicate from the microstructure.

The iron concentration in volcanic ash indicates an appreciable amount of Fe in various forms, either as a network former or network modifier in the glassy phases, or as discrete oxide phases such as maghemite or magnetite [11, 12]. Network-forming Fe^{3+} under the geopolymerisation process will show reprecipitation of Fe as faster than Si and Al. $\text{Fe}(\text{OH})_2$ will be formed as $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ in the case of Ca^{2+} and Mg^{2+} . These are chemical parameters to be taken into consideration when studying volcanic ash based geopolymer materials. However, volcanic ash has the advantage that it does not contain carbonates, which are in many

cases sources of porosity and detrimental to the mechanical properties.

The polymerisation mechanism of volcanic ash involves encapsulation of undissolved crystalline phases present in the form of nucleoids or micro particles [7, 8] which cannot be dissolved by alkaline solution. This encapsulation is believed to be either physical or chemical when these particles are taken into the geopolymer network and possibly bound into the structure with charge balancing roles, or remain physically trapped by the surrounding network. The alkaline solution not only dissolves alumina and silica precursors but also hydrolyses the surface of particles, allowing reactions to occur between already dissolved silicate and aluminate species and the particle surface. In many cases, a surface reaction is responsible for bonding the undissolved particles into the final geopolymer structure. The thermal history of volcanic ash, which is different from that of metakaolin, should explain the low dissolution rate. This low dissolution rate and slow hardening behaviour still require investigation in relation to the dissolution of calcium, iron and magnesium ions during the geopolymerisation of volcanic ash. These ions might have mainly remained in nucleoids and crystalline microphases acting as fillers to strengthen the structure of volcanic ash based geopolymers. However, when dissolved in geopolymer gel, they cause the formation of $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ and $\text{Fe}(\text{OH})_2$, which can be expected to be detrimental to the strength and the long term stability of the geopolymers even though Ca^{2+} in geopolymer materials is considered as a source of new sites of nucleation and the formation of C-S-H gel boosts the strength.

Perera et al. [13], studying Fe speciation in geopolymers with a Si/Al molar ratio of ~2, observed that Fe was present in octahedral sites, either as isolated ions in the geopolymer matrix or as oxyhydroxide aggregates which had not reacted with the starting materials' geopolymer components. Thus, apart from the iron remaining in the structures of various microcrystalline phases present in the raw volcanic ash, iron ions present in the volcanic ash geopolymer gel should have occupied specific sites instead

of forming $\text{Fe}(\text{OH})_2$, giving the geopolymer a homogeneously coloured structure.

4 Conclusion

Volcanic ash is a natural material rich in alumina and silica and an ideal raw material for geopolymerisation.

- Glassy and dehydroxylated aluminosilicates which characterize volcanic ash can be dissolved in alkaline solution into silicate and aluminate monomers prior to polycondensation into geopolymer structural materials: dissolution and hardening time can be longer compared to conventional standard metakaolin geopolymer but thermal curing (200–400 °C) can be applied as an activation factor.
- Volcanic ash activated by alkaline solution and thermal curing is transformed to microcrystalline/semi-crystalline phases as shown in the SEM micrographs.
- The presence of Ca^{2+} ions induced the formation of precipitates containing Ca and a potential number of nucleation sites at solid-liquid interfaces. The formation of calcium silicate hydrates will contribute to enhancing the densification and microstructure.
- Various crystalline phases present in volcanic ash will not be dissolved during dissolution, polymerisation and polycondensation, but will remain bound to the matrix and act as fillers, strengthening the material.
- Geopolymerisation of volcanic ash provides an opportunity whereby a valuable product may be derived from this currently under-utilised material.
- The good densification behaviour, good mechanical properties and lower porosity of volcanic ash based geopolymer materials indicate that these materials seem to be suitable for building applications.
- The strength of volcanic ash based geopolymer is believed to originate from the strong chemical bondings in the aluminosilicate gel formed, as well as the physical and chemical reactions occurring between the geopolymer gel, non or partially reacted phases, and particulate aggregates. The high mechanical properties achieved by volcanic ash based

geopolymer materials indicate that unreacted crystalline particles have a positive effect on the strength behaviour of these materials.

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References

- [1] Xu, H., Van Deventer, J.S.J.: The geopolymerisation of aluminosilicate minerals. *International Journal of Mineral Processing*. **59** (2000) 247–266
- [2] Kostas Komnitsas, Dimitra Zaharakis: Geopolymerisation: A review and prospects for the minerals industry. *Minerals Engineering* **20** (2007) 1261–1277
- [3] Glukhovskiy, V.D.: Soil silicates: their properties, technology and manufacturing and fields of application. *Doct. Tech. Sc. Degree Thesis*, Civil Engineering Institute, Kiev Ukraine, 1965
- [4] Singh, P.S., Bastow, T., Trigg, M.: Structural studies of geopolymers by ^{29}Si and ^{27}Al MAS-NMR. *J. of Mater. Sci.* **40** (2005) 3951–3961
- [5] Van Deventer, J.S.J., Provis, J.L., Duxson, P., Luckey, G.C.: Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products. *J. of Hazardous Mater.* **A139** (2007) 506–513
- [6] Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Lucky, G.C.: The characterization of source materials in fly ash-based geopolymers. *Mater. letters* **57** 1272–1280
- [7] Leonelli, C., Kamseu, E., Boccaccini, D.N., Melo, U.C., Rizzuti, A., Billong, N., Miselli, P.: Volcanic ash as alternative raw materials for traditional vitrified ceramic products. *Advances*

in *Applied Ceramics* **106** (2007) [3] 135–141

- [8] Kamseu, E., Boccaccini, D.N., Sola, A., Rizzuti, A., Leonelli, C., Melo, U.C., Billong, N.: Sintering behaviour, microstructure and mechanical properties of low quartz content vitrified ceramics using volcanic ash, pp. 19–26, *Advances in Applied Ceramics* **107** (2008) [1] 19–26
- [9] Melo, U.C., Billong, N.: Activité pouzzolanique des déchets de briques et tuiles cuites. *African J. of Sci. and Technol.* **5** (2004) [1] 92–100
- [10] Cioffo, R., Maffucci, L., Santoro, L.: Optimisation of geopolymer synthesis by calcination and polycondensation of kaolinitic residue. *Resources conservation and Recycling* **40** (2003) 27–38
- [11] Lee, W.K.W., Van Deventer, J.S.J.: The effect of ionic contaminants on the early-age properties of alkali-activated fly ash-based cements. *cem. Conc. Res.* **32** (2002.) 577–584
- [12] Yip, C.K.: PhD thesis, University of Melbourne, 389p, 2004
- [13] Perera, D.S., Cashion, J.D., Blackford, M.G., Zhang, Z., Vance, E.R.: Fe speciation in geopolymers with Si/Al molar of ~2. *J. of the Europ. Ceram. Soc.* **27** (2007) 2697–2703

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Captions

Fig. 1 Ash particle, 1980 Mount St. Helens eruption (200 x)

Fig. 2 Bulk density (g/cm^3) of volcanic ash-based geopolymers (GPZI and GPZC) as a function of curing temperature

Author please add these corrections to your Fig. 2:
Horizontal axis: Temperature / °C
Vertical axis: Bulk density / g/cm^3

Fig. 3 Bi-axial flexural and compressive strength (MPa) of volcanic ash based geopolymers (GPZI and GPZC) as a function of curing temperature

Author please add these corrections to your Fig. 3:
Horizontal axis: Temperature / °C
Vertical axis: Bi-axial flexural and compressive strength MPa

Fig. 4 Water absorption (w) and total porosity (p) of volcanic ash based geopolymers (GPZI and GPZC) as a function of curing temperature

Author please add these corrections to your Fig. 4:
 Horizontal axis: Temperature / °C
 Vertical axis: Water absorption (w) and total porosity

Fig. 5 XRD of geopolymer specimens: GPZC1 and GPZI1 (25 °C), GPZC1 and GPZI1 (400 °C)

Author please add these corrections to your Fig. 5:
 Horizontal axis: 2θ / °

Fig. 6 a Micrographs of geopolymer specimens showing high densification for PZI (a and b) compared to PZC (c and d) with high relative porosity

Fig. 6 b: Micrographs of geopolymer specimens showing well interconnected grains and polysialates for PZI (e and f) and relative segregations and low cohesion for PZC (g and h)

Author: Please note the corrections to the caption of Fig. 6. (marked green)

Sample	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	TiO ₂	SO ₃	P ₂ O ₅	MnO	LOI	Total
PZI	49	15	5.9	3.44	3.99	2.17	9.91	2.17	1.3	0	0.19	0.9	94
PZC	49.5	15.9	10	3.94	1.35	1.71	11.88	1.82	0.5	0	0.67	1.08	98.43

Trace elements: As, Sr, Co, Cr, Cu, Hg, Li, Mo, Ni, Pb, Sn, V, Zn, Ga, Nb, Rb, Ba, Y, Th

Fig. 1

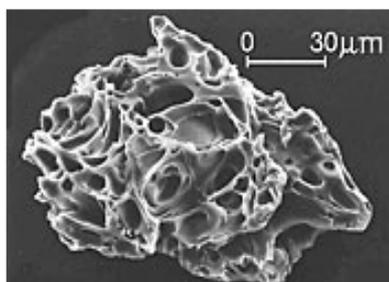


Fig. 2

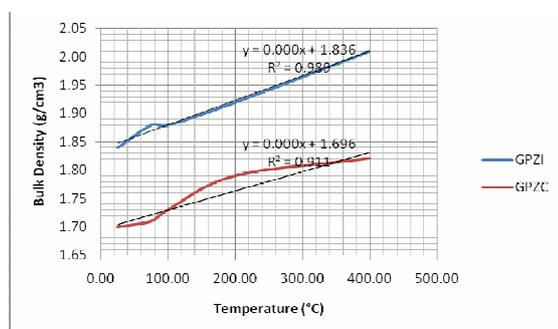


Fig. 3

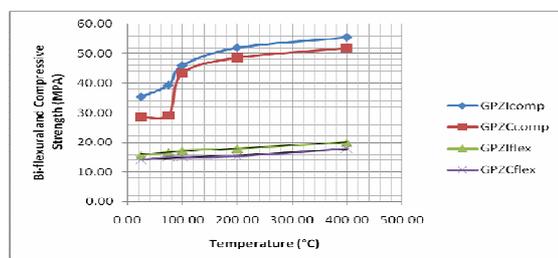


Fig. 4

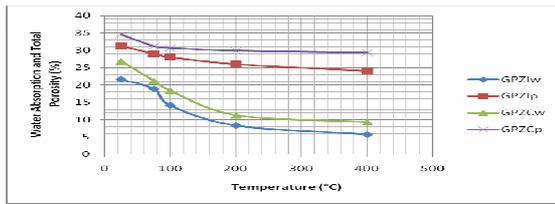


Fig. 5

