EVALUATION OF NEW USES OF VOLCANIC ASHES AND PALEO-SOILS COMING FROM MT. ETNA VOLCANO IN THE GEOPOLYMER PRODUCTION

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ENVIRONMENTAL AND TECHNOLOGICAL STATE OF ART

Mt. Etna volcano (Sicily, Italy) offers large quantity of pyroclastic deposits around its flanks, which contribute to make them fertile and unique in all the world over the centuries. Moreover, the historical architecture of Etnean area has been strongly influenced by the local geological setting, which provided stone materials and aggregates to apply in building field. Unfortunately, despite the abundance of pyroclastic materials, they are considered a waste material according to the current legislation due to the possible interactions with other matrices (*e.g.*, smog caused by engines of cars) which can modify their natural origin. Therefore, they are stocked in disposal areas with a high-cost management, instead of to be treated and used. Moreover, worth of note is that the use of pyroclastic rocks in the mortars is restricted to the old leached deposits since the fresh volcanic products have an excessively high chlorides and sulphates content due to their interaction with the volcanic gasses (Barone *et al.*, 2016). Therefore, the thick pyroclastic deposits produced by the recent frequent explosive activity of Mt. Etna, stocked in dedicated disposal areas, cannot be used in the traditional cement industry.

In the last decades, a new class of innovative material was proposed as alternative to traditional Ordinary Portland Cement (OPC), whose general name is geopolymer, belonging to alkali activated material class. Up to now, concrete industry is contributing for nearly 8% of the world's total carbon dioxide discharge into the environment. Most of CO_2 pollution is linked to the carbonation of calcium carbonate and clinker production (Provis & Bernal, 2014).

The interest to develop a new class of environmentally friendly construction materials which are, low-energy-consuming and cost-efficient, as well as the attention to a sustainable management of waste materials, increased exponentially in the last decades. In this scenario, alkali activated materials (AAMs) and geopolymers (GP) are good alternatives, enclosing all features requested by industrial community (Provis & Bernal, 2014). This class of solid materials is synthesised by the reaction of a finely milled aluminosilicate powder with alkaline solution. In detail, the term "geopolymer", coined in the 1970s by Prof. Davidovits and patented in 1982 (Davidovits, 1982), recalls a look like an artificial rock, having better properties (mechanical properties, resistance against temperature, acid or external sulphate attack) than the traditional Portland cement (Duxson *et al.*, 2007). These materials are based on an amorphous alumino-silicate network, made of tetrahedral units alternately linked by sharing oxygen atoms and balanced by cations come from alkaline solutions, such as Na^+ or K^+ (Davidovits, 1991). Their formation process is not fully understood until now. This latter, proposed by Glukhovsky (1959) for the first time, was further developed by other scientists, outlining the transformation of aluminosilicate precursors into a synthetic gel. This model can be divided into three main reaction stages which occur rapidly making them of difficult distinguish (Palomo *et al.*, 1999; Xu & Van Deventer, 2000): *i*) dissolution of aluminosilicate source in high pH solution to form reactive precursor of silica and alumina hydroxyl group; *ii*) rearrangement of aluminosilicate structure to more stable states through condensation (Fernández-Jiménez *et al.*, 2006; Provis *et al.*, 2005); *iii*) polymerisation in 3D polymeric chain and ring structure consisting of Si-O-Al-O bonds (polycondensation) (Autef *et al.*, 2013).

In this scenario, this work has foreseen to valorise two volcanic materials, which continue to influence (or have influenced in the previous centuries) in different way the Cultural and Social Heritage of Catania town (Italy). On one hand, the volcanic ash deposits widespread in Mt. Etna area, and on the other hand, the "*ghiara*" paleo-soils, widely used as aggregates in the architecture of Catania old town, were used through the alkaline activation process with the aim to find an eco-friendly alternative to the traditional building materials, favouring the circular economy. In detail, mortars and plasters, used in many important monuments, are characterized by a peculiar dark grey colour even thought, especially in the nearby of Catania town and ancient time, the use of mortars with brick-red colour was common. These latter are produced with the use of the so-called "*ghiara*". This material is a paleo-soils characterized by a reddish hue due to the oxidising conditions reached in contact with the overlying lava flow (Belfiore *et al*., 2010). Therefore, the final aim is to use both volcanic raw materials in production of AAMs from an industrial point of view for restoration interventions of historical buildings located in Etnean area.

RAW MATERIALS

Once sampled volcanic raw materials on the southern-eastern flank of Mt. Etna volcano, a cleaning step was performed to easily remove organic particles. Once the moisture has dried and removed after a drying at 105 °C into the oven, both materials were dry milled and sieved to obtain a grain size < 75 µm, considered suitable for the alkaline activation process (Lancellotti *et al.*, 2013). Chemical and mineralogical characterization were carried out following the measurement set-up are reported in Barone *et al*. (2020a). The chemical compositions of both raw materials are quite similar but "*ghiara*" has a higher Al_2O_3 abundance and a lower CaO than volcanic ashes (Barone *et al*., 2020a). Volcanic materials are also richer in iron, magnesium and calcium elements. In general, they showed more than 50% of amorphous phase (volcanic glass), in particular in volcanic ash, value reached almost 75%, so perfectly suitable to be used in alkali synthesis (Barone *et al*., 2020a). Moreover, volcanic ash evidenced the typical mineralogical phases of Mt. Etna basaltic rocks, such as calcium plagioclase, pyroxene and olivine (± magnetite), as also reported by Barone *et al*. (2016) and Corsaro & Métrich (2016), whereas "*ghiara*" paleo-soil highlighted, in addition to the aforementioned phases, iron oxides and hydroxides (goethite and hematite) and, in some cases, calcite (Barone *et al*., 2020a). Therefore, chemical and mineralogical composition of Mt. Etna lavas are similar to other volcanic deposits used in literature for geopolymer productions, make them suitable for alkaline activation (Tchakoute *et al*., 2013; Djobo *et al*., 2017; Barone *et al*., 2020b; Occhipinti *et al*., 2020). Indeed, volcanic precursor is one of the most suitable aluminosilicate sources for AAMs production thanks to high amorphous content generated by the rapid quenching during a volcanic explosion which prevail on crystallinity grade.

CASE STUDY: EVALUATION OF POLYCONDENSATION REACTION

Considering the complexity of geopolymerization process and the need to confirm the alkaline nature of some formulation developed, a continuous monitoring of fresh pastes from early stage was carried out by means of FT-IR spectroscopy.

Materials

Four formulations for each volcanic raw material were tested using the addition of 10 and 20 wt.% of metakaolin, known as ARGICAL™ M1000 (Gharzouni *et al*., 2014), and two different alkaline activators based on Na or K alkaline cation (Finocchiaro *et al*., 2020). The same formulation protocol was followed: preparation of solutions and following addition of the powders; mixing with mechanical mixer for few minutes; filling the cylindrical plastic pots and vibration to remove air bubbles.

The sample labels take into account the nature of volcanic precursor (indicating with the letter "V", the samples with volcanic ash, whereas with the "G", the samples with "*ghiara*"), the type of activating solution (prefix Na- for sodium solution and prefix K- for potassium solution) and the amount of metakaolin added (M-10 or M-20 respectively for 10 and 20 wt.%) (Finocchiaro *et al*., 2020).

Methods

A Thermo Fisher Scientific 380 infrared spectrometer (Nicolet) was used for continuous measurements on fresh alkaline pastes with the aim to observe the structural changes in time after the alkaline reaction. In detail, a micro diamond cell was used on all fresh pastes to progressive analysis in time from 0 to 8 hours with collection every 10 min (Finocchiaro *et al.*, 2020). In detail, once mixed the aluminosilicate sources with both alkaline solutions, a drop of each formulation was deposited onto diamond substrate of FTIR apparatus in the ATR mode to monitor the structural development of the synthesized mixtures (Finocchiaro *et al.*, 2020). In this scenario, the solid mixture dissolution and the geopolymerization process can be observed, thus highlighting the kinetic variations of samples activated respectively with both alkaline solutions.

Results and discussion

In situ ATR-FTIR spectroscopy was used for the first time to monitor the kinetics of geopolymer gel formation on slurries based on fly ash (Rees *et al.*, 2007). This approach is used to evaluate the effects of solid and liquid reactants on structural evolution which reflects the network reorganization due to a geopolymerization reaction. The main feature of polycondensation reaction occurrence is the shift toward lower wavenumbers over time of Si-O-M (Autef *et al.*, 2013). Once mixed the volcanic precursors through alkaline solutions, the fresh slurries were monitored by *in situ* FTIR spectroscopy to record the structural evolution. The final result is plotted in the trend of Fig. 1, showing the overlapping of each acquisition and the progressive shift toward low wavenumbers, better emphasized in the main position of Si-O-M.

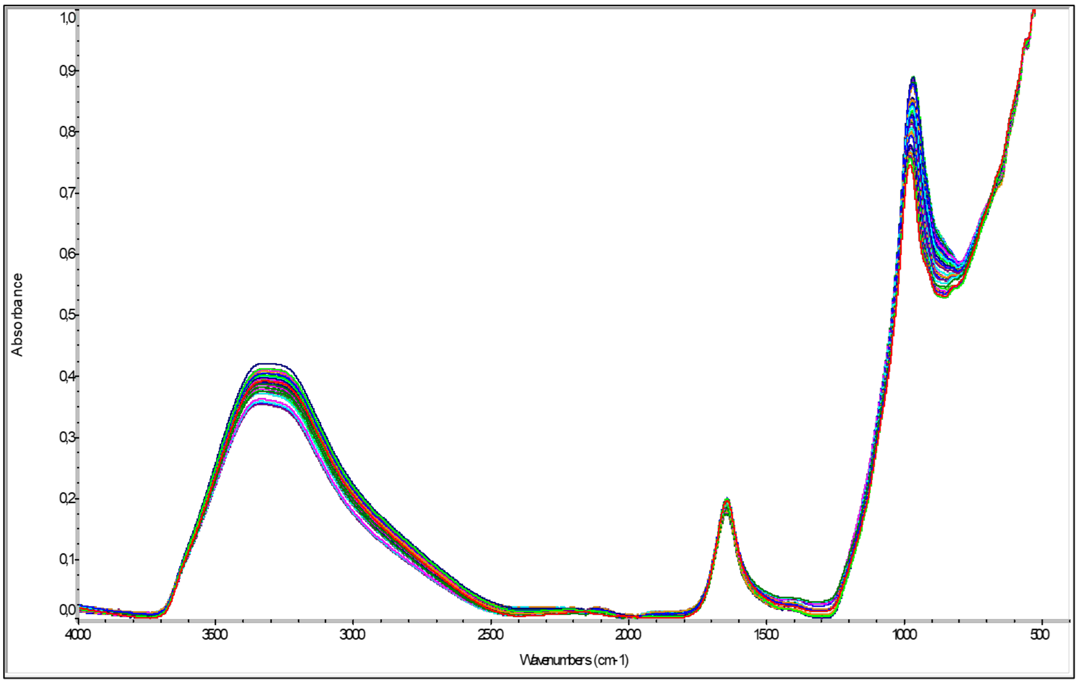

Fig. 1 - Demonstrative example of a polycondensation reaction occurrence through the progressive shift of *in situ* FTIR spectra over time (a spectrum represents the acquisition each 10 minutes up to 8 hours).

Whatever the sample, a continuous and progressive shift of the Si-O-M band position in time toward lower wavenumbers was evidenced. This behaviour suggests the replacement of Si-O-Si by Si-O-Al bonds which reflects a polycondensation reaction (Gharzouni *et al.*, 2016). Both sample sets showed the same behaviour regardless of the different quantity of metakaolin added in the mixture, whose shift reaches values ranging 12-18 cm^{-1}. In detail, the Na-set highlighted higher wavelengths then that ones with K solution (Finocchiaro *et al.*, 2020). Therefore, FT-IR analysis *in situ* on the slurries were useful to demonstrate the occurrences of polycondensation reactions

(Finocchiaro *et al*., 2020). Moreover, the obtained shift values are characteristic of aluminosilicate network formation, although are lower than other formulations based on metakaolin (Gharzouni *et al*., 2014).

FURTHER RESULTS AND DISCUSSION

A multidisciplinary approach on these materials was performed, whose measurement setting and results are reported in Barone *et al*. (2020a), Finocchiaro *et al*. (2020), Caggiani *et al*. (2021). XRD results showed an amorphous composition combined with the mineralogical phases of volcanic precursors (Barone *et al*., 2020a). The combination of the spectroscopic techniques has allowed to observe aluminosilicate structures (Caggiani *et al*., 2021) with a more or less contribution of carbonates which decreases at increasing metakaolin content in the mixture (Finocchiaro *et al*., 2020) or due to the much time at air exposure generating efflorescence phenomena (Barone *et al*., 2020a). Moreover, the metakaolin used as additive component demonstrates the positive influence on mechanical performance as well as a better network organization (Finocchiaro *et al*., 2021). The compressive strengths showed also after one-week high value, whose average values are: 17 MPa for Na-V/GM-10 and 45 MPa for Na-V/GM-20 for Na-set whereas 25 MPa K-V/GM-10 and 75 MPa K-V/GM-20 for K-set, with a general increase of 15% after 21 curing days (Finocchiaro *et al*., 2020).

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