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GEOPOLYMERS FOR TILE INDUSTRY

Presentata da: Lorenzo Valeriani

Coordinatore Dottorato

Prof. Luca Vittuari

Supervisore Universitario

Prof.ssa Maria Chiara Bignozzi

Supervisore Aziendale

Dott. Claudio Beneventi

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‘A tutte le persone che mi sono state d’esempio e d’ispirazione fino ad oggi,

e a tutte quelle che lo devono ancora essere’

ABSTRACT

The large amount of waste yearly disposed to landfill, the global impoverishing of natural resources and the emergency of carbon dioxide emissions are among the motivations that have driven this research within the last three years.

This project aims to develop energy-saving methods for manufacturing tiles by using geopolymerization as an innovative processing technique. In fact, classical ceramic tiles are usually produced by sintering at temperatures ranging between 1100-1250 °C depending on natural raw materials selected for the mixture. Geopolymers, instead, are amorphous aluminosilicate inorganic polymers obtained by mixing alkali-silicate solutions with reactive aluminosilicate precursors, and geopolymerization may occur at room temperature or at temperature lower than 150 °C, and several types of waste may be used as geopolymer precursors. The possibility to obtain geopolymer tiles with properties comparable with those of ceramic tiles is extremely challenging, but geopolymerization would represent a huge energy-saving in the consolidation process as well as in natural raw materials exploitation.

The main target of this research is then looking for an effective way to move towards sustainable solutions for tile industry. Geopolymer-based tile may eliminate the main energy intensive processing step, namely the high temperature firing process. Moreover, the idea is to reach the substitution of natural raw materials with waste from the ceramic processes.

The research started with an accurate physico-chemical characterization of wastes produced during the ceramic cycle. Granulometry studies were carried out to select an optimized grain size distribution of the investigated precursors. At first several innovative mix designs were tested in order to determine the waste capability to be alkali-activated. Casting and pressing methods were used for shaping the samples, and different curing conditions were tested to optimize the polymerization process and the final geopolymer properties. Thermal characterization by DTA-TG analysis, optical dilatometer and heating microscope as well as microstructure analysis with XRD and SEM techniques have been carried out on final products.

The synthetized geopolymer tiles exhibit interesting properties comparable with those usually shown by BIIa ceramic tiles. In particular, the geopolymer tiles exhibited value of water absorption less than 1.2% and a mechanical strength higher than 26 N/mm^2. Results show that the dry waste powder, activated by potassium hydroxide and K-silicate reactants, are the most promising reagents to develop geopolymer formulation, since they minimize water absorption and maximize mechanical strength of the final hardened product.

The macro-porosity of pressed geopolymers is lower than that of casted samples, in which air remains trapped. The thermal characteristics of geopolymers are very different compared to those of ceramic tiles, since a very pronounced thermal expansion occurs after 500 °C, thus preventing decoration with

firing. Different decoration methods were tested and the most promising one is UV curing decoration, which does not require thermal sintering processes in order to obtain the specific characteristics of surface resistance.

Some surface treatments were also tested to protect the decorated geopolymers from usury, chemical aggression and stains. Also, in this case the most promising treatment was the hardening UV coating.

The geopolymerization approach can be used to obtain tiles according to the requirements reported in UNI EN ISO 10545 standard. Nevertheless, the obtained geopolymer tiles can be considered potentially appealing for floor and wall covering applications, while an improvement is necessary if technological features comparable to porcelain tiles (BIa) are desired.

Table of Contents

1. INTRODUCTION

AIM AND OBJECTIVE

The aim of this project is the development of energy-saving methods for manufacturing tiles through the use of geopolymerization as innovative processing technique. Ceramic tiles are usually produced by sintering at temperatures ranging between 1100-1250 °C; this sintering process gives specific technological features to the ceramic material, such as very low porosity and consequently low water absorption and high mechanical resistance. Geopolymers, instead are amorphous inorganic aluminosilicate polymers obtained by mixing alkali-silicate solutions with reactive aluminosilicate precursors at low temperatures. The possibility to obtain geopolymer tiles with technological properties comparable to ceramic tiles is extremely challenging, and the idea of this research is to obtain a geopolymer material with low porosity and consequently low water absorption and high mechanical resistance. Recreating an amorphous structure without resorting to sintering process at high T is extremely challenging and underlines the extreme complexity of research and development of this research project.

Nowadays, geopolymer have been largely investigated. Their structure, mainly amorphous, is usually obtained by alkali-activated polymerization of alumina-silicate sources such as calcined clays and feldspar or wastes (Davidovits, 1976; 2017).

The alkali activation is a singular procedure, in which an aluminosilicate material (raw materials or industrial by-products) is mixed with an alkaline activator; the resulting paste is then cured at specific conditions producing hardened materials. In previous researches, it has been found that the main reaction product formed in such systems is an amorphous aluminosilicate gel with short-range order in its three-dimensional structure. Testing a lot of raw materials and processing conditions, the purpose of the research in this field is to obtain new materials that can exhibit a controlled range of properties and characteristics such as flexural strength, water absorption, shrinkage, time of setting, chemical resistance, fire resistance and hardness. However, these properties are not necessarily inherent to all type of formulations, and it is very difficult to obtain all the above-reported properties in the same formulation (Kara *et al.*, 2010).

Most of the papers in the literature deals with metakaolin and fly ashes as precursors, (industrial by-product of thermal power stations that use coal like fuel) (Palomo, A., M. Grutzeck, 1999; Fernández-Jiménez *et al.*, 2008).

Commercially available metakaolin is a highly technical product obtained by several cleaning steps of originally raw kaolin in order to reach a definite colourless degree for its use for example as filler in plastics. On the other hand, pure metakaolin is an expensive material; hence production of ceramic materials based on it is not realistic.

Also wastes can become interesting raw materials for geopolymerization, such as ceramic sludge and ceramic wastes, that promise high ecological benefits and lower costs (Bignozzi, 2011), but their use leads to difficulties in handling and, especially, in the final product quality. The search for alternative low-cost and/or highly available materials able to improve product quality may lead, among other things, to "normal clays" or other low-cost raw materials (Fernández-Jiménez *et al.*, 2008). These materials are widely available all over the World and may show certain reactivity after a thermal activation process (Davidovits, 2002; Barbosa and MacKenzie, 2003).

Several types of industrial wastes are rich in silica and alumina thus fulfilling the first requirement necessary for geopolymerization (Xu and Van Deventer, 2000; Bignozzi *et al.*, 2013). The leaching ability of Al and Si follows the descending order: Metakaolin > Zeolite > Slag > Fly Ash > Pozzolana >Kaolin (Panagiotopoulou *et al.*, 2007).

This project wants to start an investigation on ceramic wastes and sludges as unconventional source of aluminosilicate. Tests have been currently running, highlighting how the geopolymerization process can successfully occur in this type of materials. Wastes from ceramic processes have been activated using different substances (KOH, NaOH and Na,K-Silicate) to investigate the best reaction conditions for their geopolymerization process.

With the aim to further increase the type of wastes to be used as precursor and to promote a new recycling route, alkali-activated materials based on partial substitution of metakaolin and others raw materials are currently under investigation. The research aims also to solve the problem of disposing certain types of waste to landfill, such as fired ceramic waste, making tiles production more competitive, sustainable and respectful of the environment.

Below are listed the main benefits foreseen from this research:

- preserve natural stocks of virgin rocks and important minerals in Europe such as clay, limestone and feldspar; reduce import of minerals for ceramic mixture from overseas; considering that naval transport used for raw materials is the most important pollution factor regarding CO_2 emissions and fine dust;
- widening of the tile market by including more sustainable products in substitution to other materials such as stone, marble and wood that determine stronger environmental impacts; the project will not only minimize the environmental impact of the extraction of natural materials in quarry and the felling of trees, but it will also divert waste from landfill and stimulate reuse of industrial waste;

- reduction of processes energy consumption (electricity and methane have the highest impact factor on the tiles production cost).

These innovative tiles can be considered as common demolition waste products at the end of their life (after an average use of 20 years). Geopolymer wastes can be recycled into useful products such as drainage materials, rock base for driveways and paths or as composite material for aggregates. But the most important point is that this type of material can be reused to produce tiles using again the geopolymerization process. By recycling or reusing these ceramic-like materials, large amounts of waste will be diverted from landfill and this will help reducing the demand for natural resource.

In the ceramic production process, not only a high amount of CO_2 is emitted (around 0.2 kg CO_2/kg final product or alternatively 3 kg CO_2/m^2 final product), but also a substantial quantity of energy is required that increases the total production costs of around 25-30%. On the other hand, geopolymers require much lower temperature around 25-150 °C to obtain the desired strength. As a result, geopolymer-based tile processing will allow to save substantial amount of energy, minimize costs and deeply reduce CO_2 emissions (Kara *et al.*, 2010).

RESEARCH SCOPE

Scope of this research is the achievement of low-porosity and high-mechanical strength geopolymers.
This research presents an inclusive study in developing cured geopolymeric materials able to possess superior strength and low porosity than those shown by typical geopolymeric ones. The main raw material here studied was ceramic waste, which is a low-cost aluminosilicate waste generated in huge quantities worldwide from ceramic industry. With the development of efficient techniques for cured geopolymers, there is a huge potential to increase the commercial viability of geopolymers also as construction materials in construction industry, by eliminating heating processes and preparation of alkaline reactant.
Thus, the significance of the scope of this thesis can be summarised as follows:

- Innovations

- Create a low porosity amorphous material using geopolymerization as a cold sintering process.
- Identify a decorating system that do not need a heating process.
- Realize an innovative prototype line that can allow the creation of the geopolymers.

- Waste recover

- Convert aluminosilicate ceramic wastes from ceramic industrial processes into new raw materials for geopolymer material production.

- Industry progress

- Simplify the processes for ceramic production.

- Reduction of energy consumption and costs.

- Environment safety

- Reduction of greenhouse gas emissions.

- Sustainable waste management.

STRUCTURE OF THE THESIS

All chapters of this thesis are based on a systematic experimental work and they can be briefly summarised as follows:

- Chapter 2 provides an introduction to the ceramic tile process and a description of the main wastes produced during the industrial process.
- Chapter 3 provides a literature review of geopolymeric materials and the use of the classic row materials in geopolymer technology. The contents mainly focus on the fundamental of geopolymers, geopolymerization reaction and its chemistry, together with the role of the factors affecting the properties and mechanisms of geopolymerization. One important point is the background of research, where previous works about geopolymers, already applied in the tile sector, are reported.
- Chapter 4 provides an accurate description of materials and methods in the experimental work of this thesis. Typical materials used in laboratory are presented with general properties and specific characterizations. Details of testing equipment and preparation process of samples are described. The heart of the chapter is the study of the mix design and the evolution of formulations.
- Chapter 5 describes testing techniques for the investigation of technological properties of the obtained materials. The effect of different manufacturing and curing procedures and curing on the mechanical properties and mechanisms, such as flexural strength, water absorption and micro-structure of each manufacturing procedure, are the key results to identify the appropriate method to fulfil the development of the geopolymeric materials.

- Chapter 6 deals with all the tests made to improve and find the best decoration methodology for geopolymeric materials.
- Chapter 7 describes all the quality tests made to characterize the surface of the geopolymeric tiles obtained following the standard requirements.
- Chapter 8 describes and illustrates the production technologies identified for the industrialization of the studied geopolymeric materials.
- Chapter 9 summarizes the economic and industrial feasibility of the materials, taking into account the environmental sustainability factor.

2. CERAMIC PROCESS

CLASSIFICATION OF CERAMIC TILES

The specification of ceramic tiles is a viable alternative for any commercial application with its low maintenance quality and versatility.

International recognized standard ISO 13006 defines ceramic tiles as: “thin slabs made from clays and/or other inorganic raw materials, generally used as coverings for floors and walls”. It further divides ceramic tiles into groups according to their method of shaping and their water absorption.
We will look at the range and variety of product types that can be included in the classification of ceramic tile for floors and walls. The range of technical and aesthetic features and of the performances by the different types is vast.

The table below indicates the potential classes and the associated product standards. The greater the water absorption of the tile, the greater will be its expansion in damp or wet conditions.

Water absorption W (% by mass)				
Shaping	Group I W ≤ 3%	Group IIa 3% ≤ W ≤ 6%	Group IIb 6% ≤ W < 10%	Group III W > 10%
A – Extruded *	Group AI	Group AIIa-1 Group AIIa-2	Group AIIb-1 Group AIIb-2	Group AIII
B - Dry Pressed+	Group BIa E ≤ 0.5% Group BIb 0.5% ≤ E ≤ 3%	Group BIIa	Group BIIb	Group BIII
C – Tiles made by other processes++	Group CI	Group CIIa	Group CIIb	Group CIII

Notes:

* Groups AIIa and AIIb are divided into two parts (Part 1 and Part 2) with different product specifications.

+ Group BIII covers glazed tiles only. There is a low quantity of dry pressed unglazed tiles produced with water absorption greater than 10% that is not covered by this product group.

++ These tiles are not covered by ISO 13006.

Porcelain (fully vitrified):

Either unglazed or glazed and characterised by a low water absorption of less than 0.5% (BIa), porcelain tiles are normally dry pressed.

Vitrified and semi vitrified:

These can either be unglazed or glazed and made by dry pressing or extruding. Such tiles fall into two main categories based on the water absorption of the tile body measured as a percentage. Vitrified tiles Class BIb (dry pressed) and Class AI (extruded) have a water absorption of between 0.5% to 3%. Semi-vitrified tiles Class BIIa (dry pressed) and AIIa (extruded) have a water absorption of between 3% to 6%.

Glazed porous body

The majority of standard wall tiles have glazed porous bodies with a water absorption between 10% and 20% and are classified BIII. When the face of such tiles is covered with a vitreous glazing either gloss or satin, they are suitable for a wide variety of internal applications. Such tiles are not frost resistant and should only be used in internal conditions above subzero temperatures.

Glazed vitrified

The porcelain vitrified and semi-vitrified tiles possess similar technical properties when glazed and can be used for internal cladding applications. Only vitrified and porcelain tiles with a water absorption value lower than 3% should be used for external cladding applications in conditions that are subject to frost.

CERAMIC CYCLE

The ceramic process (Figure 2.1) is divided into several specific productive steps:

- milling process, where the raw materials are dosed and milled together with water and deflocculant, forming a liquid slip.

- spray drying process, where the slip is dried with a spray dryer creating a powder with humidity of about 6%.

- pressing process, where the previous mixture is shaped with an industrial presses and variable molds according to the final format to be obtained.

- drying process, where the new formed tile is dried.

- decoration process, where the tiles are decorated with digital printers and covered with glaze in order to obtain the final surface.

- firing process, the most critical step since tiles reach the sintering temperature and at the end of the heating, they reach more than 60% of glass phase, which permits to obtain low water absorption and high mechanical strength materials.

- rectifying process, where a diamond disc wheels gradually abrade the sides of the tiles producing a fine powder, the dry rectifying powder, in order to obtain extremely straight tiles.

Marazzi Group has a complete ceramic cycle (Figure 2.2), differently from other tile manufacturers. Most of the wastes produced in the ceramic process are internally recycled together with wastes from other ceramics plants. The only exception is given by the rectifying powder, which is not easily reintroduced in the cycle due to the high volatility and the risk of decreasing the quality of the final product.

Figure 2.1 – Ceramic process scheme.

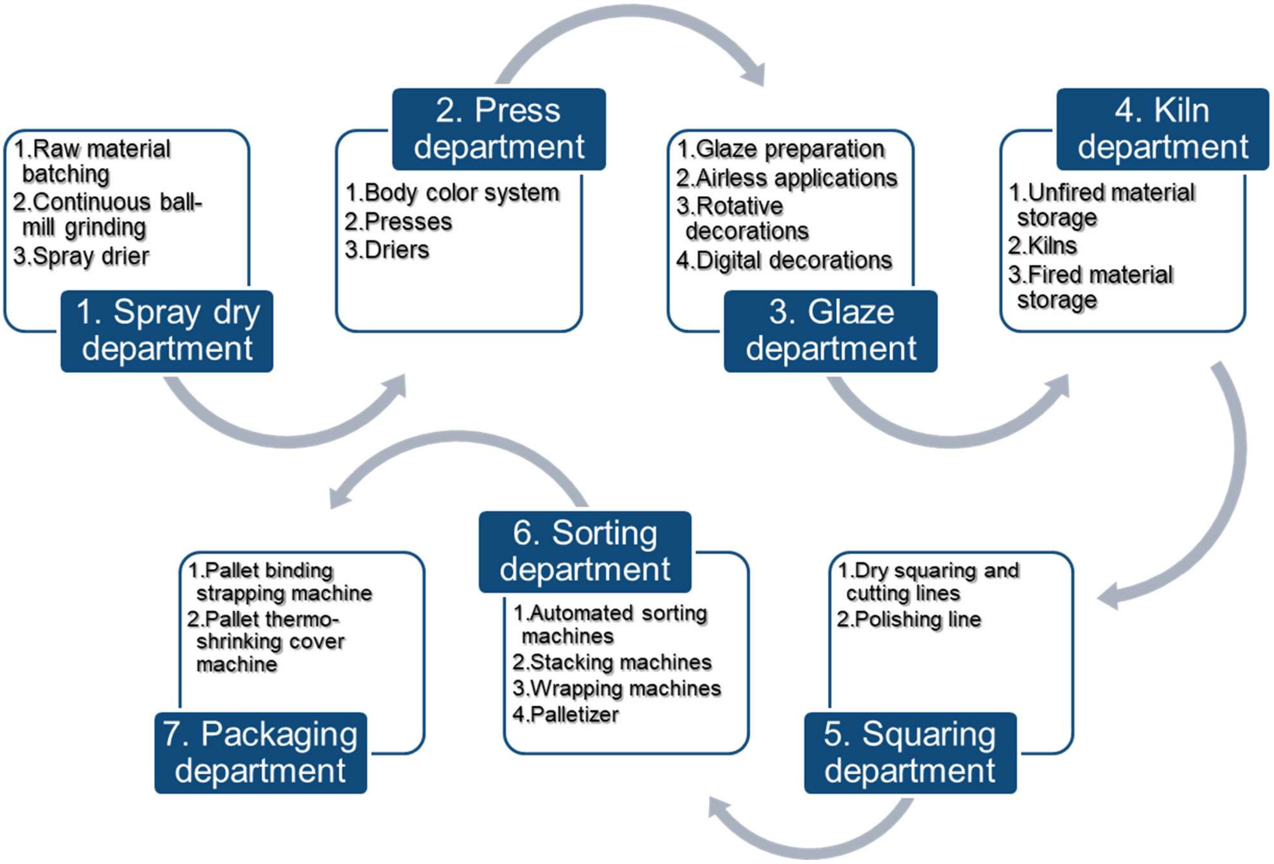


Figure 2.2 – Complete ceramic cycle at Marazzi Group.

For many ceramic products, including tile, the body composition is determined by the amount and type of raw materials. The raw materials also determine the colour of the tile body, which can be red or white, depending on the amount of iron-containing raw materials used. Therefore, it is important to mix them in the right amounts in order to achieve the desired properties. Batch calculations are thus required, which must take into consideration both physical properties and chemical compositions of the raw materials. Once the appropriate weight of each raw material is determined, the raw materials can be mixed together, ready for the milling process.

Mill and Spray drier department:

- Continuous ball-mill (Figure 2.3)

A batch of raw materials is continuously charged in a ball-mill: here, thanks to the falling and rubbing, the raw materials are mixed with water (becoming slip) and grinded to a target granulometry, important for the next parts of the process.

Figure 2.3 – Continuous ball mill.

- Spray drier (Figure 2.4)

The mix of water and raw material is pumped in a cylinder, where the slip is sprayed through a hot airflow. Droplets of the slip are dried as they are heated by a rising hot air column, forming small, free flowing granules that result in a powder suitable for forming. The spray-dried blend is stored in silos, awaiting to be used.

Tile bodies can be also be prepared by dry grinding followed by granulation. This last uses a machine in which the mixture of previously dry-grinded material is mixed with water in order to compact the particles into granules, which again form a powder ready for forming.

Figure 2.4 – Spray drier scheme.

Presses & dryers:

- Industrial Hydraulic presses (Figure 2.5)

Most tiles are formed by dry pressing. In this method, the free-flowing powder containing a low percentage of moisture, flows from a hopper into the forming die. The material is compressed in a steel cavity by steel plungers and is then ejected by the bottom plunger. Automated presses are used with high operating pressures.

Several other methods are also used where the tile body is in a wetter, more moldable form. Extrusion plus punching is used to produce irregularly-shaped tile and thinner tile in a faster and more economical way. This involves compacting a plastic mass in a high-pressure cylinder and forcing the material to flow out of the cylinder into short slugs. These slugs are then punched into one or more tiles using hydraulic or pneumatic punching presses.

Figure 2.5 – hydraulic ceramic press.

- Dryer (Figure 2.6)

Ceramic tiles usually must be dried after forming, especially if a wet method is used. Drying removes the water at a rate slow enough to prevent shrinkage cracks. Continuous or tunnel driers are used, which are heated using gas or oil, infrared lamps, or microwave energy. Infrared drying is better suited for thin tile, whereas microwave drying works better for thicker tile. Another method, impulse drying, uses pulses of hot air flowing in the transverse direction instead of a continuous flow in the material moving direction. Anyway, the most applied method is using burners with methane. After drying, pieces are ready to be glazed.

Figure 2.6 – Ceramic Dryer.

- Glazing lines (Figure 2.7):

To prepare the glaze, a batch formulation is calculated, and the raw materials are weighed, mixed and dry or wet milled. The milled glazes are then applied using one of the different methods available. In centrifugal glazing or dishing, the glaze is fed through a rotating disc that flings or throws the glaze onto the tile. In the bell/waterfall method, a stream of glaze falls onto the tile as it passes underneath on a conveyor. Sometimes, the glaze is simply sprayed on with an airless method. For multiple glaze applications, screen printing on, under, or between tile that have been wet glazed is used. In this process, glaze is forced through a screen by a rubber squeegee or other devices. Dry glazing is also being used. This involves the application of powders, crushed frits (glass materials), and granulated glazes onto a wet-glazed tile surface. Nowadays glazing lines at Marazzi Group have multiple decoration applications that can decorate a wide range of sizes and products. Each glazing line has an ink-jet digital printer (Fig 2.8): the product is decorated contactless, allowing both uniform distribution of the color across even structured surfaces, and decorative effects such as wood, stone and marble-looks, which can now be produced with up to 40 surface variants to provide very natural effects. All the glazing processes are under supervision of a programmable electric board: LCD monitors show failures in the lines and monitor the performances to reduce material and time wastes.

Figures 2.7 and 2.8 – ceramic glazing line and ceramic digital printer

Kiln & in-process automated storage:

A single-layer kiln (Figure 2.9) guarantees a high degree of technical and geometrical stability to the product thanks to studied firing cycle. Inside, the temperature peak is reached gradually (up to 1200°C), improving dimensional stability of the products. There are three firing step, warming of the tile, sintering of the tile and cooling of the fired final product.

Automated storage (Figure 2.10): unfired and fired tiles are stored in a system of boxes and platforms. Thanks to PC supervisions and laser guided vehicles, materials can be moved inside the building in total automation.

For tiles requiring a single firing, usually the ones that is prepared by wet milling, roller kilns are generally used. These kilns move the wares on a roller conveyor and do not require kiln furniture such as batts or saggers. Firing times in roller kilns can be as low as 30 minutes, with firing temperatures around 1100-1250 °C.

Figures 2.9 and 2.10 – ceramic kiln and automated storage system.

Rectifying, Lapping & Sorting lines:

- Cutting and Rectifying line (Figure 2.11) provide cutting of the tiles to their final sizes, squaring all the materials fired in the kiln, to produce perfectly right-angled slabs and edges, and finally checking the working precision, with a variance of 0.1 mm. All the processes are supervised by sensors that correct the working parameters just-in-time.
- Lapping is the process of using a loose abrasive between two surfaces that rub together, thus abrading the part. Typically, lapping is used to achieve a surface roughness and flatness beyond the capabilities of standard grinding
- Sorting lines (Figure 2.12), using automated check-vision and laser sensors, are able to check caliber, shades and flatness of the tiles. After this, the machine stacks the graded tiles and conveys them to the product boxing and labelling process, carried out using innovative, highly-flexible systems. Then, the boxed tiles are palletized depending on their quality.

Figures 2.11 and 2.12 - Cutting and rectifying line and Sorting line.

Pallet thermo-shrinking line and automated stocking:

- Thermo-shrinking line (Figure 2.13): the full pallet is brought to another line in order to be prepared for the external warehouse, where the pallets are strapped in both direction (horizontal and vertical), capped with shrinkable plastic film and sent to the kiln that fits the plastic film to cover the pallet.
- Automated stocking (Figure 2.14): when pallets are completed in the palletizer, Laser Guided Vehicles (LGVs) take them out fully automatically. LGVs also provides to feed the thermo-shrinking line and store the pallet to the final indoor storage.

Figures 2.13 and 2.14 - Thermo-shrinking line and automated stocking.

WASTES FROM CERAMIC PROCESS

During the industrial production of ceramic tiles, numerous types of waste, deriving from specific processes, are produced (Table 2.1).

Table 2.1 – Ceramic processes and their consequent ceramic wastes.

PROCESS	WASTE
SPRAY DRY	NOT FIRED CERAMIC SLUDGE (NFCS)
PRESS	NOT FIRED PRESS POWDER (NFPP)
GLAZING	NOT FIRED GLAZE SLUDGE (NFGS)
RECTIFYING	FIRED CERAMIC POWDER (FCP) FIRED CERAMIC SLUDGE (FCS)
LAPPING	FIRED GLAZE SLUDGE (FGS)
SORTING	FIRED CERAMIC WASTE (FCW)

The ceramic wastes characterized in this research are all the fired ones because all the unfired wastes are currently reintroduced in the cycle. The main fired wastes produced are:

- Sludge resulting from rectifying process (RS);
- Sludge resulting from lapping process (LS);
- Sludge resulting from combined lapping and rectifying process (LRS);
- Fired ceramic waste (FCW);
- Powder from process (RP).

Nowadays all the sludges are recovered by inserting them in the wet milling cycle, while the dry fired ceramic wastes are disposed to landfill. In fact, dry fired wastes are dangerous inside the ceramic mixtures because they decrease the quality of the body and are also responsible for variation in piroplasticity during the firing process. The piroplasticity is important because it defines the deformation of the material during the heating at high temperature, when the mixture becomes plastic during the sintering process.

Marazzi Group produces about 45.000 ton/year of Rectifying Waste, where the 80% is made during the dry process, and most of this powder has to be disposed to landfills for an extra cost of 1.440.000 euros/year. The amount of dry rectifying powder amount produced in the entire ceramic district consists of about 500.000 ton/year.

RS: it is a sludge stored in large tanks after being collected from the production lines. This waste is formed during the squaring process, and it is composed of metal abrasives and water that abrade the edges of the tiles while making make straight edges. This material needs to be dried in order to be used for geopolymerization tests.

LS: it is a sludge stored in large tanks after being collected from the lapping lines. This material is made of resin abrasives and water that abrade the surface of the tiles while making polished surfaces. It needs to be dried in order to be used for geopolymerization tests.

LRS: it is a sludge stored in large tanks after being collected from a combined lapping and rectifying production lines. This material is composed of resin abrasives and water that abrade the surface of the tiles when making the surface polished and it also contains metal abrasives that abrade the edges of the tiles. It needs to be dried prior to be used for geopolymerization tests.

FCW: fired ceramic wastes resulting from production line after the firing process.

RP: Powder obtained during the rectifying process, mainly formed by metal abrasives that abrade the edges of the tiles when making straight edges.

3. LITERATURE REVIEW

GEOPOLYMER TECHNOLOGY

Victor Glukhovsky, who firstly assumed the geological process of geopolymerization systems, described that the formation of the zeolitic material starting from volcanic rocks or sedimentary rocks under low temperature and pressure. After the zeolitic materials were combined with strong alkaline solutions, the binder called 'Alkaline activated material' was formed with distinguish high pH values. In 1940, the important event of alkaline activated binder was recorded by activating blast furnace slag with sodium hydroxide solution. Later, in 1950, a synthesis of alkaline alumina-silicate minerals was developed in Ukraine as a mixed of C-S-H (Ca-Si-H) and alumina-silicate phases and also recorded for tall building use in Russia (Komnitsas & Zaharaki, 2007). In 1978, Joseph Davidovits firstly established the term of Geopolymers to describe a kind of alkaline activated alumina-silicate with an amorphous-to-crystalline system, which could form at low temperature in a short time. They consist of chain or network of mineral molecules linked with covalent bonds (Davidovits, 2017).

A geopolymer is a mineral macromolecule having a well-defined size and molecular structure. (Na,K)-poly(sialate) and (Na,K)-poly (sialate-siloxo) type geopolymers consisted of individual elementary nanoparticles of 5 to 40 nm in size (50 to 400 A°) separated by a nano porosity ranging from 3 to 10 nm (Davidovits, 2017). This microstructure is formed at ambient temperature and is still stable at temperatures well above 1000 °C. This nanoparticulate microstructure measuring 5 to 40 nm in size is also found in fly-ash-based geopolymer cement. It is therefore an essential characteristic of silico-aluminate geopolymers (Davidovits, 2017). It is the result of a very precise chemical mechanism involving covalent bonding and promoting the formation and production of ceramic-like materials. Yet it is the arrangement of these nanoparticulates that forms the geopolymer matrix. It governs the chemical, physical and mechanical properties of ceramic-like materials found in a wide variety of uses (Davidovits, 2017).

In terms of chemical composition, the alkali activation process can be applied to aluminosilicate sources with (SiO_2 + Al_2O_3) content > 80% (in this case the resultant products are known as geopolymers) or to precursors based on both aluminosilicate and Ca containing amorphous or crystalline phases (known as Inorganic Polymers (IP) and/or alkali activated materials (AAM)) (Bignozzi, Manzi, *et al.*, 2014). Depending on the chemical composition of the precursor, different binding phases can occur in these systems. The main binding phase of hydrated Portland cement is a partially Al-substituted calcium silicate hydrate (C–(A)–S–H) gel, whereas the main product in alkali activated systems is alkali (usually sodium) aluminosilicate hydrate (N–A–S–H) gel. In AAM, the role of calcium remains unclear and phase separation between C–A–S–H and N–A–S–H gels leads to a partial replacement of sodium with calcium to form (N,C)–A–S–H gel, showing a positive effect on the mechanical properties of the geopolymeric binder (Fernández-Jiménez, Palomo and Criado, 2005). It is clear that the choice of the source material plays a crucial role in AAM, being the origin of the binding strength (Bignozzi, Manzi, *et al.*, 2014).

The alkaline activated material is typically represented by zeolitic materials containing alkaline activators, the formation of which requires a relatively high setting temperature in the range of 20 to 180 °C. On the other hand, geopolymer material requires such from low temperature to less than 90 °C (Figure 3.1).

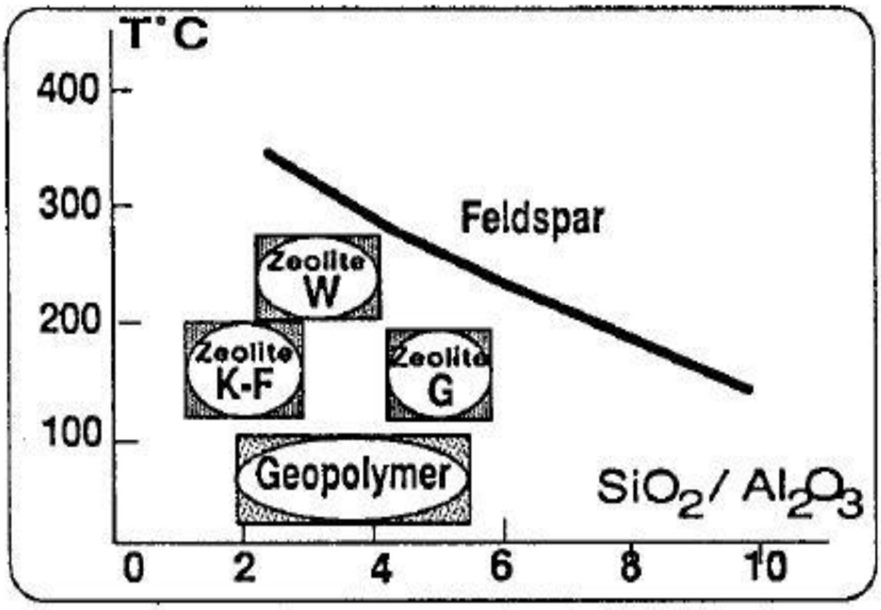


Figure 3.1 Crystallization temperature against Si/Al ratio of zeolite and geopolymers (Davidovits, 1991).

For geopolymer, main components of silicon oxide (SiO_2) and aluminium oxide (Al_2O_3) from any of prime materials (e.g. metakaolin, fly ash and blast furnace slag) are dissolved from their original sources in strong alkaline solutions (e.g. potassium/sodium hydroxide and potassium/sodium silicate) (Duxson, *et al.*, 2007a), forming chain rings polymer of silicon-oxygen-aluminate (Si-O-Al; Sialate chain) (Davidovits, 1991). Even though different terminologies have been stated by many researchers (e.g. alkaline activated material, hydroceramic, geomaterial, inorganic polymer concrete, and low-temperature aluminosilicate glass), the term Geopolymers is still widely used to represent this consolidating technology (Davidovits, 2011; Petermann, *et al.*, 2010).

To produce alumina-silicate based geopolymer material, the alkaline hydroxide and/or alkaline silicate solutions are initially mixed with raw prime materials to form the homogenous slurry. As geopolymers is able to poly-condense at the temperature below 90°C, the higher curing temperature is therefore no longer needed like ceramics (Davidovits, 1991). As heat is still a vital factor to accelerate geopolymeric reaction, the geopolymer mixture is hence cured in a temperature-controlled chamber (e.g. oven) at temperature around 40 to 90°C for a period of 6 to 48 hours (Chindaprasirt, *et al.*, 2007; Komnitsas & Zaharaki, 2007). The pre-cured geopolymer material will continually be kept at room temperature for further handling or until reach the testing ages. The curing can also be at room temperature without heating (Bignozzi *et al.*, 2014; Bignozzi *et al.*, 2010).

Geopolymer production is generally carried out as process shown in Figure 3.2. At present, geopolymers become a well-known material due to its terrific properties and applications. It tends to be an alternative choice for the construction industrial sector, although some obstacles have been raised for the development in real use.

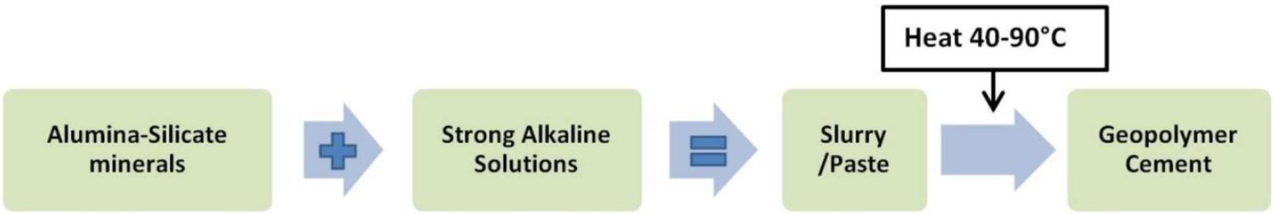


Figure 3.2 - Typical geopolymer synthesis process.

GEOPOLYMERIZATION REACTION AND ITS CHEMISTRY

As said before, Ceramic material sintering is totally different from Geopolymerization of the geopolymer formation process. In geopolymerization, when the silicate and aluminate oxide (Si^{4+} and Al^{3+} in IV-fold coordination) extend their bonding/cross-link to sialate (Si-O-Al) and poly-sialates, the ring chain of polymer silicate (Si) and aluminate (Al) was suggested in the formation of amorphous to semi-crystalline phases. It could be categorised into 3 types, namely (i) Poly-(sialate) type (-Si-O-Al-O-), (ii) Poly-(sialate-siloxo) type (-Si-O-Al-O-Si-O-), and (iii) Poly-(sialate-disiloxo) type (-Si-O-Al-O-Si-O-Si-O-) with a structure model as shown in Figure 3.3 (Davidovits, 2002). The empirical formula of geopolymer resultant product is:

$$M_n\,[-(SiO_2)_z - AlO_2 -]_n \cdot wH_2O$$

where M is the alkaline element such as potassium (K^+) or sodium (Na^+), n is the degree of polymerisation, z is Si/Al ratio which varies from 1, 2, 3 or higher, and "–" indicates the presence of bonding (Davidovits, 1991). The ratio of Si/Al results in different geopolymer properties, however, the low ratio of Si/Al ≤ 3 has been widely used to obtain three-dimensional cross-link networks as material and ceramics (Duxson, *et al.*, 2007a). Although there are many chemical types of geopolymers (e.g. Phosphate-based, High-molecular phosphate-based, Silicone-based or Humic-acid based geopolymer), the most common name is Alumina-silicate based geopolymers (Davidovits, 2011).

A distinction is made between two synthesis routes: alkaline medium (Na+, K+, Li+, Ca++, Cs+ and the like) and acidic milieu (phosphoric acid, organic carboxylic acids). The alkaline route is the most important, so far. The geopolymerization mechanism starts with polycondensation of oligomers into small ribbon-like molecules. This intermediary stage involves several Si-OH groups together with H_2O molecules. It is referred to as N-A-S-H or K-A-S-H by some cement scientists and generalized to the final geopolymer structure. The poly(sialate) final structure consists of well-polymerized individual elementary nanoparticles of 5 to 40 nm in size (Figure 3.5) (Davidovits, 2017).

Geopolymers chemically react within two different synthesis routes:

– in alkaline medium with (Na, K) hydroxides and soluble alkali-silicates, yielding poly(silicates), poly(siloxo), poly(silico-aluminates), poly(sialate) types and,

– in acidic medium (here with phosphoric acid), yielding poly(alumino-phospho) types.

Geopolymers comprise the following molecular units (or chemical groups) presently studied and implemented in several industrial developments (Davidovits, 2017):

- Si-O-Si-O- siloxo, poly(siloxo)
- Si-O-Al-O- sialate, poly(sialate)
- Si-O-Al-O-Si-O- sialate-siloxo, poly(sialate-siloxo)
- Si-O-Al-O-Si-O-Si-O- sialate-disiloxo, poly(sialatedisiloxo)
- (R)-Si-O-Si-O-(R) organo-siloxo, poly-silicone
- Al-O-P-O- alumino-phospho, poly(alumino-phospho)
- Fe-O-Si-O-Al-O-Si-O- ferro-sialate, poly(ferro-sialate)

Principally, geopolymer material consists of two main components: any prime material containing silica and alumina, and alkaline activators (Pacheco-Torgal, *et al.*, 2008b, 2014). Due to the complexity of various factors affecting geopolymerization during synthesis, the definite mechanism is not yet fully understood. However, many researchers agree that its mechanism consists of three-stage model which are dissolution after alkaline hydrolysis (destruction), transportation of cations (re-orientation), and poly-condensation of free silicate and aluminate species (hardening/solidification reactions) as shown in Figure 3.4 (Pacheco-Torgal, *et al.*, 2008a; Rangan, *et al.*, 2005). Figure 3.4 appears to have an error on the 3rd reaction of breakdown of Si-O-Si; it should be Si-O-Al. Somehow, it is also noted that the overlapping can occur during each stage, causing the difficulty to specify every single stage individually (Glukhovsky, 1967).

Dissolution, hydrolysis and condensation reactions of metakaolin in alkaline conditions (with high and low Si/Al ratios) have been discussed in detail by number of authors. The dissolution and hydrolysis reactions can be written as (Silva, Sagoe-Crenstil and Sirivivatnanon, 2007):

$Al_2O_3 + 3H_2O + 2OH^{-} \rightarrow 2[Al(OH)_4]^{-}$

$SiO_2 + H_2O + OH^{-} \rightarrow [SiO(OH)_3]^{-}$

$SiO_2 + 2OH^{-} \rightarrow [SiO_2(OH)_2]^{2-}$

The presence of $[SiO_2(OH)_2]^{2-}$ ions is preferred to $[SiO(OH)_3]^{-}$ in very high alkaline conditions. Condensation can occur between aluminate and silicate species or silicate species themselves, depending on the concentration of Si in the system. With mixtures with low Si/Al ratios (=1), condensation predominantly occurs between aluminate and silicate species, resulting in mainly poly(sialate) polymer structures. Likewise, when the Si/Al ratio increases (N1), the silicate species formed as a result of the hydrolysis of SiO_2, tend to condense among themselves to form oligomeric silicates. These oligomeric silicates in turn condense with $Al(OH)_4^{4-}$, forming a rigid 3D network of polymer structures (Silva, Sagoe-Crenstil and Sirivivatnanon, 2007).

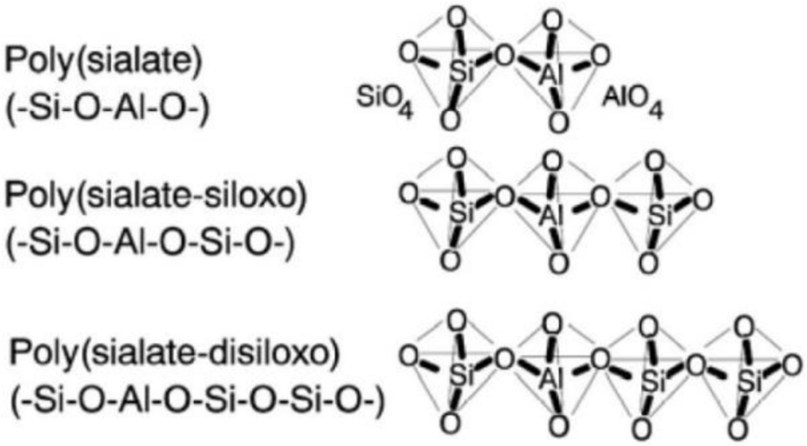


Figure - 3.3 Type of poly-sialates structures (Davidovits, 2002).

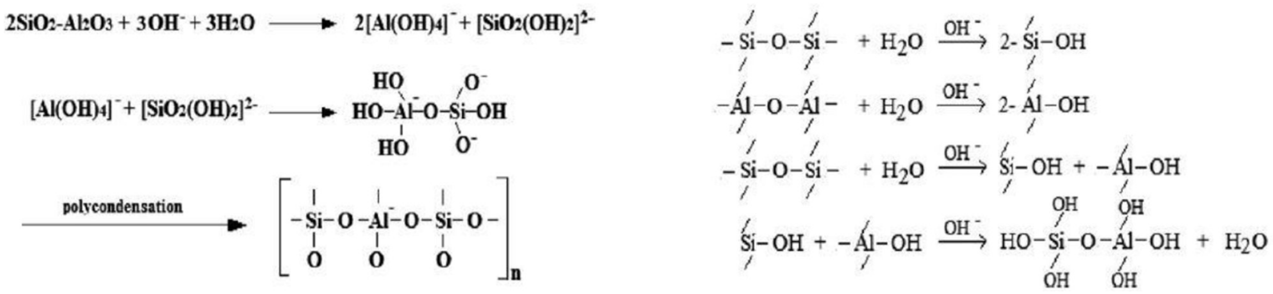


Figure 3.4 - A reaction pathway involving the poly-condensation (Pacheco-Torgal, *et al.*, 2008a)

More explanation of geopolymerization was illustrated by Duxson, et al. (2007a) in the schematic formation (Figure 3.6). Dissolution of alumina-silicate sources by alkaline solution produces reactive silica and alumina ion species. A complex mixture of those species is thereby settled to speciation equilibrium. After that, the gelation of oligomers starts forming, while some of H_2O is released in this stage as only nominal water was used in dissolution process. The gelation is then re-arranged and re-oriented to connect together as a gel network of three-dimensional structure under exothermic process (Rangan, *et al.*, 2005). The cross-linked SiO_4 and AlO_4 tetrahedral are formed when the negative charge on Al^{3+} in IV-fold coordination is balanced with positive charge of alkaline ions (Na^+, K^+) (Rovnaník, 2010). At the final setting stage, the polymerization process provides the formation of amorphous to semi-crystalline alumina-silicate network with excellent physical properties (Shi, et al., 2011). The final reaction products of those systems can be C-S-H (Ca + Si), zeolite/polymers (Si + Al) or C, N-A-S-H (Ca,Na + Al + Si) which mainly depend on the characteristics of raw starting materials and alkaline activators (Pacheco-Torgal, *et al.*, 2008a).

The reaction alumino-silicates with NaOH proceeded as describe at first, the amorphous glass, quartz, and mullite components partially dissolved in NaOH solution (Reaction (1) and (2)), and the produced Na^+, $Al(OH)_4^-$ and $H_2SiO_4^{2-}$ ions reacted to precipitate new solid phases (Reaction (3) and (4)) (Luo, Zheng, *et al.*, 2017).

$$SiO_{2(\text{quartz or glass})} + NaOH_{(aq)} = Na_2SiO_{3(aq)} + H_2O_{(l)} \tag{1}$$

$$3Al_2O_3{\cdot}2SiO_{2(s)} + 10NaOH_{(aq)} = 6NaAlO_{2(aq)} + 2Na2SiO_{3(aq)} + 5H_2O_{(l)} \tag{2}$$

$$6Na^+_{(aq)} + 6Al(OH)_4{}^-{}_{(aq)} + 10H_2SiO_4{}^{2-}{}_{(aq)} = Na_6Al_6Si_{10}O_{32}{\cdot}12H_2O_{(s)}(\text{P zeolite}) + 20OH^-{}_{(aq)} \tag{3}$$

$$8Na^+_{(aq)} + 6Al(OH)_4{}^-{}_{(aq)} + 6H_2SiO_4{}^{2-}{}_{(aq)} = Na_8Al_6Si_6O_{24}(OH)2{\cdot}4H_2O_{(s)}(\text{zeolite}) + 10H_2O_{(l)} + 10OH^-{}_{(aq)} \tag{4}$$

Mechanisms of Reaction

In general, it is admitted that several stages are produced during the synthesis of zeolites from alkaline leached silicates. In the first one, the aluminosilicate mineral is dissolved in the alkali solution, which favours the formation of different zeolite precursors from dissolved species (nucleation). In the second stage, different nuclei reach the critical size and the crystal growth starts. During the nucleation period, both thermodynamic and kinetic parameters have a big influence. In our particular case, the first stage can be divided in two parts:

1. Destruction–coagulation: in this substage, the Me-O, Si-O-Si, Al-O-Al, and Al-O-Si bonds of the initial starting material are broken. Parallel to this process, complexes and polymerized species (-Si-O-Na, -Si-O-Ca-OH, $Al(OH)_4$, $Al(OH)_5$ and $Al(OH)_{6)}$, are formed in the solution.

2. Coagulation–condensation: in this substage, dissolved species react, forming a coagulated structure.

Taking into account the experimental conditions used, the crystal growth from the zeolitic nuclei formed is extremely slow. Therefore, an amorphous materialitious matrix (aluminosilicate gel or zeolite precursor) is preferentially formed, although small amounts of zeolites are also detected (Fernández-Jiménez and Palomo, 2005; Fernández-Jiménez, Palomo and Criado, 2005).

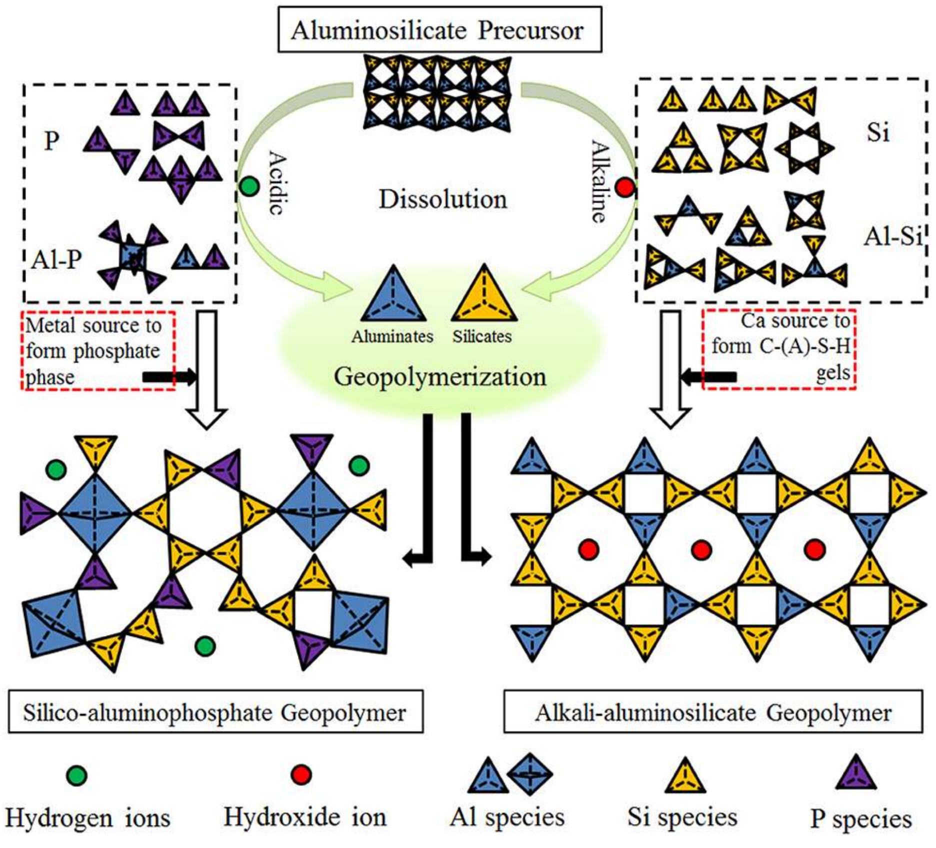


Figure 3.5 – Aluminosilicate precursors and final structure.

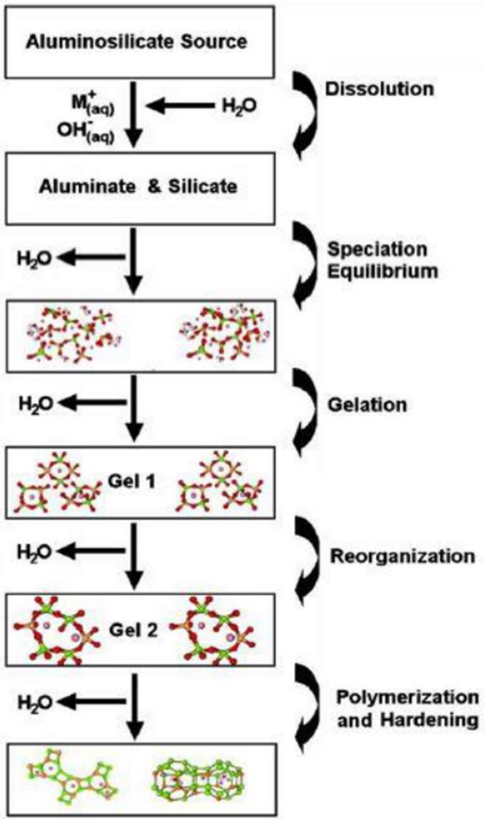


Figure 3.6 Model of geopolymerization (Duxson, *et al.*, 2007a)

GEOPOLYMER BINDER CONSTITUENTS

Main raw materials involved in geopolymer synthesis.

Alkaline activation requires two main components, namely the solid precursor, rich in silica and alumina (with the highest possible amorphization degree); and the activator solution, based on an alkali metal (usually sodium or potassium) or an alkali earth metal (usually calcium). It constitutes an excellent solution to enhance the properties of most industrial residues. The target of the ongoing research dealing with the application of this technique to different engineering applications is twofold: maximise the mechanical behaviour and to minimise the porosity. Alumina-silicate mineral, a kind of pozzolanic material, could be found everywhere especially as by-products. Therefore, producing geopolymers is not only an alternative choice for recycling a large amount of wastes but could also achieve some specific properties of that ceramic-like material. The main raw materials for geopolymer synthesis, which have normally been used in research studies, can be classified in three major categories, namely (i) Industrial wastes, (ii) General wastes and recycle materials, and (iii) Natural materials. The specific characters of those raw materials in previous studies are further summarised as follows:

Raw material from industrial wastes: A huge number of industrial wastes are annually produced worldwide from several types of production processes such as combustion ash (Bignozzi, Manzi, *et al.*, 2014), slag (Bignozzi *et al.*, 2013), ceramic waste (Bignozzi, Fusco, *et al.*, 2014), mine waste or agricultural waste (Sujatha, *et al.*, 2012). Some of these are currently used in cement material production or as additives to improve the properties and to utilize the massive amount of those by-products. However, most of these wastes will be disposal-stored or landfilled (Komnitsas, *et al.*, 2004; Nuruddin, *et al.*, 2011b). Some of the industrial wastes, for example, are fly ash, bottom ash, rice husk ash (RHA), granulated blast-furnace slag (GBFS), silica fume, steel slag, mine tailing and material kiln dust (CKD).

Raw material from general wastes and recycled materials: the general wastes or recycled materials are produced everywhere worldwide. Although these materials sometimes are less in volume than industrial wastes, the value-added conversion has utterly attracted much interest in addition to reducing unnecessary waste and pollution. Some of the general wastes, for example, are waste paper sludge ash (WPSA), water sludge and construction wastes. Raw material from natural materials: some of raw prime materials for geopolymer synthesis can be obtained or produced from natural sources such as kaolin (kaolinite or china clay), metakaolin (calcined kaolin), silty clay, diatomite (microscopic shells of diatoms), volcanic rock, etc (Panagiotopoulou *et al.*, 2007). However, those natural materials are available in some specific geological areas with limited quantities.

Briefly, as geopolymeric formation occurs when alumina-silicate sources react with strong alkaline solution, any material which contains silica and alumina can be used in the synthesis of geopolymers. The overview of raw materials involved in geopolymer synthesis can be categorised into three types, namely industrial waste (IW), general waste (GW) and natural mineral (NM). It was found that the calcium-contained materials could provide similar or better mechanical strength than that of the typical one due to the cross-linkage of calcium silicate hydrate (C-S-H) and geopolymeric gel in the single binder. In literature it can be seen that the industrial waste (e.g. fly ash, mine tailing and GBFS) achieved the highest strength followed by natural mineral (metakaolin and natural pozzolan), while general waste (construction waste) seems to produce the lowest mechanical strength. However, other factors, e.g. Si/Al ratio, type of sample, testing age, type of alkaline activator, curing conditions and sample size, also need to be considered on the compressive strength of the final products. Table 3.1 summarises the chemical composition of each raw material (as a representative) such as fly ash, high calcium fly ash, GBFS and so on. The main values presented are the contents of SiO_2, Al_2O_3, CaO and SiO_2-to-Al_2O_3, together with (Si/Al) ratios, which significantly influence the geopolymerization of the material. Noticeably, the widely used materials, such as fly ash and metakaolin, contain high percentages in SiO_2 and Al_2O_3 (overall amount of SiO_2 and Al_2O_3 is over 70 % or equal to 1.0 to 3.0 of Si/Al ratio).

Table 3.1 - A representation of chemical composition using in geopolymer synthesis by raw prime materials.

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	FeO	Si/Al	% Si+Al	References
1. Industrial & General waste												
Low calcium Fly ash	50.00	28.25	13.50	1.79	0.89	0.32	0.46	0.38	-	1.77	78.25	(Nath & Sarker, 2012)
High calcium Fly ash	39.70	20.00	14.10	17.30	1.40	1.40	2.70	2.60	-	1.99	59.70	(Rattanasak, et al., 2011)
GBFS	32.46	14.30	0.61	43.10	3.94	0.24	0.33	4.58	-	2.27	46.76	(Nath & Sarker, 2012)
Silica Fume	92.00	0.46	1.60	0.29	0.28	0.51	0.61	0.19	-	200.00	92.46	(Dutta, et al., 2010)
Steel Slag	15.00	6.70	15.40	44.20	10.90	0.20	0.10	0.70	-	2.24	21.70	(Hu, et al., 2008)
Ferronickel Slag	32.74	8.32	0.76	-	2.76	-	-	-	38.80	3.94	41.06	(Komnitsas & Zaharaki, 2007)
Tungsten mine waste	53.48	16.66	12.33	-	1.27	0.62	7.65	-	-	3.21	70.14	(Pacheco-Torgal, et al., 2007)
Cement Kiln Dust	11.00	3.90	2.00	42.00	3.60	-	0.60	-	-	2.82	14.90	(Khater, 2012)
Waste paper sludge ash	26.25	17.50	4.40	23.40	0.90	0.10	0.20	4.63	-	1.50	43.75	(Anuar, et al., 2011)
Water Sludge	70.40	15.40	5.30	1.53	0.96	0.90	3.66	0.31	-	4.57	85.80	(Kongkaew, 2007)
Demolished Wall	76.42	1.88	1.28	9.84	0.26	0.22	0.08	2.09	-	40.65	78.30	(Khater, 2011)
Waste Concrete	71.53	2.14	2.43	12.76	0.39	1.04	1.13	0.33	-	33.43	73.67	(Khater, 2011)
2. Metakaolin	54.78	40.42	0.76	0.10	0.41	0.07	2.72	-	-	1.36	95.20	(Yip, et al., 2005)
3. Kaolin	48.10	36.90	0.26	0.20	0.17	0.20	1.90	-	-	1.30	85.00	(Hounsi, et al., 2013)
4. Rice husk ash (RHA)	86.10	0.17	2.87	1.03	0.84	-	4.65	0.41	-	506.47	86.27	(Nuruddin, et al., 2011b)
5. Silty Clay	20.10	7.55	32.89	26.15	0.47	-	3.17	4.92	-	2.66	27.65	(Sukmak, et al., 2013)
6. Diatomite	59.30	10.00	18.50	1.20	-	-	-	2.74	-	5.93	69.30	(Phoo-ngernkham & Sinsiri, 2011)
7. Volcanic Mud	38.50	14.20	23.76	5.62	-	-	4.31	0.78	-	2.71	52.70	(Al Bakri, et al., 2012)

Type of alkaline activators involved in geopolymer synthesis

Geopolymer material, the alumina-silicate minerals, has major component of SiO_2 (silicon dioxide) and Al_2O_3 (aluminium oxide) which dissolved from their original source in strong alkaline solution, which are, in fact, in the first two columns (group I and II) of the periodic table of the elements, called alkaline metals and alkaline earth metals respectively. The alkaline metals (i.e. Lithium, Sodium, Potassium, Rubidium, Cesium, and Francium) have one electron in their outer shell and are active in bonding with other elements. The alkaline earth metals (i.e. Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium) have two valence electrons and are one of the reactive elements in nature (Halka & Nordstrom, 2010). The alkaline metals as alkaline activators of geopolymer material (group I) are more reactive and more often used than the alkaline earth. There are many alkaline activators which were used in geopolymer synthesis e.g. potassium/sodium hydroxide (KOH/NaOH), potassium/sodium silicate (K_2SiO_3/Na_2SiO_3), sodium carbonate (Na_2CO_3), calcium hydroxide ($Ca(OH)_2$) or the combinations of any alkaline solutions together (Fernández-Jiménez & Palomo, 2005; Panagiotopoulou, *et al.*, 2007). However, the most widely used alkaline activators in geopolymer synthesis can be summarised as follows:

- Sodium hydroxide solution (NaOH): NaOH solution is normally used to produce geopolymer material due to its widely available and cheaper than other alkaline solutions (Hardjito, *et al.*, 2008). Its main role is to provide an alkaline environment of hydroxide ion (OH^-) dissolving alumina-silicate minerals from their origins. It is reported that, in sulphate immersion, the fly ash-based geopolymer synthesized with only sodium hydroxide solution achieved higher strength than those of sodium silicate solution or a combination of sodium and potassium hydroxide solution (Bakharev, 2005a).
- Sodium silicate solution (Na_2SiO_3): Na_2SiO_3 solution or water glass is normally used in geopolymer synthesis as an alkaline activator and another source of Silica (Si). It is also cheaper than potassium silicate solution (K_2SiO_3) when produced in large quantity (Dimas, *et al.*, 2009). Similar to other alkaline activators, the strength of geopolymers increases with an increase in concentration. Nevertheless, using sodium silicate solution alone could not achieve the same strength level of those NaOH or KOH solutions. The reason is probably due to the fact that using of Na_2SiO_3 solution achieves less dissolution rate than that of using OH^- compound (Rashad & Zeedan, 2011).
- Sodium hydroxide and Sodium silicate solution (NaOH and Na_2SiO_3): A combination of sodium hydroxide and sodium silicate solution is one of the most widely used alkaline activators for geopolymer synthesis. It is known that soluble hydroxide dissolves alumina-silicate minerals from origin sources while soluble silicate improves the poly-condensation of geopolymer

material and also controls the amount of silicate in mixtures as a binder. The optimum proportion of Na_2SiO_3 and NaOH is therefore an important factor in geopolymer synthesis. The fly ash-based geopolymers with Na_2SiO_3 and NaOH has been found performing better than only NaOH or Na_2SiO_3 solution alone (Fernández-Jiménez, *et al.*, 2007; Phoo-ngernkham & Sinsiri, 2011).

- Potassium hydroxide solution (KOH): KOH solution is also normally used to produce geopolymer material due to its widely available and cheaper than other alkaline solutions (Hardjito, *et al.*, 2008). Its main role is to provide an alkaline environment of hydroxide ion (OH^-) dissolving alumina-silicate minerals from their origins.
- Potassium silicate solution (K_2SiO_3): K_2SiO_3 solution or water glass is normally used in geopolymer synthesis as an alkaline activator and another source of Silica (Si). Similar to other alkaline activators, the strength of geopolymers increases with an increase in concentration. Nevertheless, using potassium silicate solution alone could not achieve the same strength level of those NaOH or KOH solutions. The reason is probably due to the fact that using of K_2SiO_3 solution achieves less dissolution rate than that of using OH^- compound (Rashad & Zeedan, 2011).
- Potassium hydroxide and Potassium silicate solution (KOH and K_2SiO_3): A combination of potassium hydroxide and potassium silicate solution is one of the most widely used alkaline activators for geopolymer synthesis. It is known that soluble hydroxide dissolves alumina-silicate minerals from origin sources while soluble silicate improves the poly-condensation of geopolymer material and also controls the amount of silicate in mixtures as a binder. The optimum proportion of K_2SiO_3 and KOH is therefore an important factor in geopolymer synthesis.

Theoretically, alkaline metals in periodic table groups I and II can be used as an activator, but the most widely used ones are Sodium (Na) and Potassium (K) due to their strong alkaline properties and global availability. However, with more economical saving aspect, sodium soluble is therefore more extensively used than that of potassium soluble (Hardjito, *et al.*, 2008). For geopolymerization, it was reported that alkaline cations control almost all reactions in geopolymeric hardening and could provide significant effect on strength development (Van Jaarsveld, 2000). Eventually, most of alkaline activators used in fly ash and metakaolin-based geopolymers are sodium and potassium hydroxide (Na-KOH) and sodium and potassium silicate (Na-K_2SiO_3) solutions due to its roles in dissolving of alumina-silicate minerals, being the additional sources of Si and Na-K, and providing initiate formation. Heat applying for curing purpose would stimulate and enhance poly-condensation afterwards (Komnitsas & Zaharaki, 2007). The types of alkaline activators used (listed by the compressive strength achievement) are presented in Table 3.2.

Design of geopolymer constituents - Alkaline activators' concentration and ratio:

Compressive strength of geopolymer generally increases with the increase in specific concentration of alkaline activators (Hardjito & Fung, 2010; Xu & Van Deventer, 2000). A higher concentration gives rise to a stronger ion-pair formation, provides more complete and faster poly-condensation process of particle interface and enhances the dissolution of the alumina-silicate materials in the presence of activators (Mishra, *et al.*, 2008). Nevertheless, too high concentration could lead to an increase of coagulated structure (Alonso & Palomo, 2001), causing less flow ability with fast setting behaviour. Although, the dissolution and hydrolysis were accelerated, an incomplete poly-condensation of the system was also found (Phoo-ngernkham & Sinsiri, 2011). The optimum alkaline concentration could also vary by a large number of conditions and factors such as specific properties of prime materials, Alkaline activator-to-Prime material ratio, Na-K_2SiO_3 to Na-KOH ratio, curing temperature or even the age of testing. In addition, the Na-KOH solution concentration between 10 and 15 molars (M), and 30 to 50% w/w of Na-K_2SiO_3 solution are commonly used in geopolymer synthesis.

Alkaline activator-to-Prime material ratio by mass:

Mass ratio of alkaline solution and prime material is widely used in geopolymer synthesis in order to define both alkaline dosage and water content. In most cases, fly ash was used, and the ratio would probably be called Alkaline activator-to-Fly ash (A/FA) ratio. Barbosa, et al., (1999) and Hardjito, *et al.* (2008) have tested the effect of A/FA ratio on the strength development by using 10 M NaOH solution as an alkaline solution with the A/FA ratio of 0.34 to 0.46. It was observed that the compressive strength increased when the A/FA ratio increased until it reached the optimum at around 0.40. Too high A/FA ratio could cause the precipitation at early stage before geopolymerization and this would result in a strength decrease as more sodium carbonate was formed and obstructed the polymerization process. It must be noted that depending on the type of alumina-silicate materials, the recommended A/FA ratio could be between 0.35 and 0.50 to achieve both compressive strength and workability (Ma*, et al.*, 2012; Xie, *et al.*, 2009).

Table 3.2 - Compressive strength of various alkaline activators in geopolymer synthesis.

No	Alkaline		Sample Type	Comp. Strength		Starting Materials (% wt)	Additives (% wt)	Curing Condition		References
	Main (M)^a	Addition		MPa	Age (d)			C°	Hrs	
1	NaOH (12.5)	Na_2SiO_3	Paste	95.0	28	FA (100) class F^b	-	85	20	(Fernández-Jiménez, et al., 2007)
2	NaOH (75%)^c	KOH (25%)^c	Paste	95.0	28	MK (100)	-	40	20	(Duxson, et al., 2007c)
3	NaOH (15)	Na_2SiO_3	Paste	92.1	7	FA (100) class F	-	75	7 days	(Phoo-ngernkham & Sinsiri, 2011)
4	KOH (7)	Na_2SiO_3	Mortar	72.3	3	FA (100) class F	-	85	24	(Kong & Sanjayan, 2010)
5	KOH (7)	Na_2SiO_3	Paste	71.2	3	FA (100) class F	-	85	24	(Kong & Sanjayan, 2010)
6	NaOH (12)	-	Mortar	70.4	28	FA (100) class F	-	85	20	(Fernández-Jiménez & Palomo, 2005)
7	KOH (-)	Na_2SiO_3	Paste	70.0	28	MK (100)	-	40	20	(Duxson, et al., 2007c)
8	KOH (12)	K_2SiO_3	Paste	70.0	28	FA (90) class F	BA (10)	80	24	(Hardjito & Fung, 2010)
9	NaOH (-)	-	Paste	67.0	28	GBFS (100)	-	38	90 days	(Khater, 2012)
10	Na2SiO3 (-)	-	Paste	45.0	28	FA (100) class F	-	60	28 days	(Rashad & Zeedan, 2011)
11	NaOH (-)	Na_2CO_3	Mortar	36.0	-	FA (100) class F	-	85	20	(Fernández-Jiménez & Palomo, 2005)

^{a} M = Molarity, ^{b} FA class F = low calcium fly ash, ^{c} percentage by weight.

In addition, as water in the mixture is a vital factor for hardening process, the water-to-solid (w/s) ratio (the total mass of water is the sum of water in sodium hydroxide solution, sodium silicate solution and added water, while the total mass of solid is the sum of fly ash, sodium hydroxide solid, sodium silicate solid and other added solids such as sand or aggregates) is also considered (Hardjito, *et al.*, 2008). It was found that the w/s ratio should be in the ranges of 0.18 to 0.22 and 0.26 to 0.32 for fly ash-based geopolymer paste and concrete respectively (Chindaprasirt, *et al.*, 2010). Apart from that, the calculation of additional water required can also be carried out to compensate the evaporation in the mixture (Zhang, *et al.*, 2009).

Na-K_2SiO_3 to Na-KOH solution (S/H) ratio by mass:

The optimum of S and H is an important factor in geopolymer synthesis. It must be noted that the amounts of S and H are generally referred to the amount of alkaline solution (by mass) in A/FA ratio as well as the water content and pH level. Previous research studies revealed that low calcium fly ash-based geopolymers would achieve the optimum ratio of 1.0, 1.5 or 2.0, depending on the type of prime materials (Nath & Sarker, 2012) while optimum values of the high calcium fly ash based was in the range between 0.67 and 1.00 (Chindaprasirt, *et al.*, 2007).

Silica-to-Alumina (Si/Al) ratio of prime materials:

The ratio of Si/Al is a significant factor, which affects the degree of crystallinity and reaction when mixed with alkaline materials (Xu & Van Deventer, 2003), forming of amorphous to semi-crystalline phases. Both polysialate-siloxo (Si/Al = 2) and polysialate-diloxo (Si/Al = 3) provided good strength to geopolymers, even polysialate-siloxo (Si/Al = 2) seems to be formed faster and has a slight lower compressive strength than polysialate-diloxo (Si/Al = 3). The monomeric group of $[SiO(OH)_3]^-$, $[SiO_2(OH)_2]^{2-}$ and $[Al(OH)_4]^-$ normally form later than Si and Al species as small alumina-silicate oligomers can improve the geopolymeric formation (Weng & Sagoe-Crentsil, 2007). It has been reported that metakaolin-based geopolymers achieves a satisfactory strength with the Si/Al ratio of 1.90 to 3.0, while the appropriate ratio of fly ash-based geopolymers is approximately 2.0 to 4.0 (Andini, *et al.*, 2008; Duxson, *et al.*, 2007c). By this, it can be supposed that the effective Si/Al ratio, for both fly ash-based and metakaolin-based geopolymers, should be around 2.0 to 3.0.

Delay time of preparation process:

The delay time is the period of time that specimens were left at the room temperature for casting and wrapping, before placing in the oven. Chindaprasirt, *et al.* (2007) studied the delay time of 0, 1, 3 and 6 hours before putting the high calcium fly ash-based geopolymer samples in the oven at 60°C for a period of 24 hours. The results showed that, like those from Hardjito, *et al.* (2004), the delay time before oven curing can affect the compressive strength of geopolymers. The optimum delay time of any paste was suggested to be approximately half of its initial setting time. For example, the optimum delay time might be around 1 hour when the initial setting time is 2 hours. In addition, it can be suggested that an optimum delay time depend on starting material's characteristics, adopted from activator system and specific curing conditions (Chindaprasirt, *et al.*, 2010). However, it is noted that geopolymers gained approximately 70 percent of strength within 4 hours after curing in appropriate conditions. This is in contrast with well-known behaviour of cement in term of gaining strength over time and undergoing with hydration reaction (Khale & Chaudhary, 2007).

Curing procedures of geopolymers

In early 1940s, a combination of zeolitic materials and alkaline solutions was used to produce alkaline-activated material with specific cuing temperature and duration such as a record of mixing blast furnace slag with sodium hydroxide (Roy, 1999). Geopolymer material was positively reported with terrific mechanical properties, although the high curing temperature above low temperature and specific curing duration, including specific mix design, are required to raise probability of durability (Sofi, *et al.*, 2007). Curing geopolymers is normally carried out in electrical ovens, nevertheless, many alternative methods of geopolymer heating were observed for the best practical handling and resultant. Using microwave for preheating or full curing was found to reduce the duration of oven curing (Chatveera & Makul, 2012) as well as a preheating of alkaline solution before mixing was also studied to improve final strength of geopolymer concrete (Dutta, *et al.*, 2012). However, oven curing is the most widely used method for geopolymer production nowadays. Curing procedures on various temperatures and durations in geopolymers can be summarised as follows.

Effects of curing temperatures on geopolymer properties:

Many previous experiments on curing temperature of both geopolymer paste and mortar (between 30 and 90°C) showed that an increase at curing temperature gives an increase of chemical reaction and this enhances the mechanical strength in early stage of geopolymerization (Van Jaarsveld, *et al.*, 2002). Whist, too high curing temperature (e.g. over 90°C) would lead the samples to experience a substantial loss of moisture with porous structure, causing a negative effect on the final mechanical properties of geopolymeric products (Rovnaník, 2010). The optimum temperature for geopolymers cured in those tests was found to be around 60 to 75°C, which could appropriately improve the geopolymerization process and microstructure development (Chindaprasirt, *et al.*, 2010). Concrete produced by fly ash-based geopolymers has also been studied under different curing conditions. Demie, *et al.* (2011) and Reddy, *et al.*, (2012) found that a good compressive strength was gained when curing temperature was in the range of 60 to 70°C, while further curing at 80 to 90°C seemed to result in a decrease in strength.

It can be summarised that curing temperature is one of the important factors affecting the strength of geopolymers. Although, higher temperatures (above room temperature) give a higher strength, too high temperature could cause cracking, resulting in a decrease in its strength. The rapid loss of moisture could also lead to the formation of micro-cavities. The temperature range from 40 to 80°C clearly enhanced mechanical properties, but the optimum range from 40 to 60°C seems to be an appropriate curing condition, which matches all performance, environmental and economic aspects (Hounsi, *et al.*, 2013).

Effects of curing duration on geopolymer properties:

The curing duration could also affect the mechanical properties of geopolymers. At the most frequently used temperatures of 40 to 60°C, the curing duration was found in range from 4 to 96 hours (4 days), depending on the design of each experimental condition. However, the periods of 6, 12, 24, 48 and 72 hours were often used as controlled duration for trailing or studying other factors (Komnitsas, *et al.*, 2004). Chatveera and Makul (2012) studied the effect of curing duration of fly ash-based geopolymer material, reported that at the curing temperature of 85°C, 24 hours gave a higher strength than 48 hours (Chatveera & Makul, 2012), while Chindaprasirt, *et al.* (2007) studied the curing temperature of 60°C, found that a good strength was obtained at minimum heat curing of 48 hours (2 days) and a higher strength was obtained with 72 hours (3 days). However, both mentioned studies concluded that an increase in the curing time beyond the optimum limit did not enhance the strength of the geopolymeric specimens. This may be suggested that prolonging curing may result in excessive loss of moisture during curing process, which causes uncompleted formation and generates large pores in the structure (Zhang, *et al.*, 2009). These reasons could cause any failures in microstructures of the final products (Phoo-ngernkham & Sinsiri, 2011). In fact, a curing period of 12 to 24 hours seems to be the suitable duration with satisfied compressive strength and economic approach, although a shorter or longer curing duration than 24 hours might give rise to the different strength developments.

Summary of geopolymers curing procedures

For the curing regimes, there is a huge variable range of both curing duration and curing temperature to achieve mechanical properties of geopolymer material. As aforementioned, the optimum curing conditions mainly depended on prime material's properties, alkaline activators, water content, age of the samples and other ratios (Chindaprasirt, *et al.*, 2007). The curing regimes directly affect not only degree of geopolymerization but also evaporable water in gel structure which firstly fulfils the pores (Duxson, *et al.*, 2007b). When water or moisture is rapidly liberated from either too high temperature or prolonged curing, the remained micro-pores might shrink, deteriorating the geopolymers, e.g. their strength (Bakharev, 2005b). It can be drawn that, beside the aforementioned factors, the suitable curing temperature and period are within the range of 40 to 60°C and 8 to 24 hours respectively. However, in some cases, curing in low condition is able to provide an acceptable result with no external heat applied. Some of high strength fly ash-based geopolymer pastes (with sodium hydroxide and sodium silicate solution) under different curing conditions are presented in Table 3.3.

Table 3.3 Compressive strength for different curing regimes in geopolymer synthesis.

No	Curing Condition		Sample Type	Prime Materials (% wt.)	Comp. Strength		SS/SH	References
	Hrs	C°			MPa	Aged		
1	20	85	Paste	FA (100) class F^b	95.0	28 d	0.18	(Fernández-Jiménez, et al., 2007)
2	168 (7d)	75	Paste	FA (100)	92.1	7 d	2.00	(Phoo-ngernkham & Sinsiri, 2011)
3	24	40	Paste	FA (100) class F	77.0	28 d	-	(Ma, et al., 2012)
4	24	60	Paste	FA (100) class F	67.0	7 d	2.50	(Al Bakri, et al., 2011b)
5	8	75	Paste	FA (100) class C	63.0	28 d	-	(Guo & Shi, 2012)
6	Outdoor/Ambient curing		Paste	FA (100)	48.7	28 d	-	(Nuruddin, et al., 2011b)
7	48	65	Paste	FA (100)	42.0	28 d	-	(Sukmak, et al., 2013)
8	6	65	Paste	FA (100)	34.0	7 d	1.50	(Taebuanhuad, et al., 2012)
9	Indoor/Ambient curing		Paste	FA (100)	19.7	28 d	-	(Nuruddin, et al., 2011b)

Developing of mechanical strength during curing

It was revealed that less setting time of geopolymers requires higher curing temperature at above room temperature as well as high concentration of alkaline solution, which eventually accelerates the hardening and rate of geopolymerization of geopolymer material (Hardjito, et al., 2008; Rovnaník, 2010).

Mechanical strength is widely used to assess property of geopolymers, due to its representative, simplicity and low cost of testing (Komnitsas & Zaharaki, 2007). The compressive strength of fly ash based-geopolymer material could achieve up to 95 MPa at the age of 28 days (Fernández-Jiménez, et al., 2007), which is equivalent to ultra-high strength concrete (MacGregor, 1997). In addition, other measurements on strength were also tested and proved to be equal to or even better than those of mortars e.g. flexural strength (Fernández-Jiménez & Palomo, 2005), split tensile strength (Sofi, et al., 2007) and bond strength (Hu, et al., 2008). It can be drawn that the improvement in strength clearly refers to more completion of chemical dissolution and geopolymerization.

Drying shrinkage is the decrease in volume of geopolymer material with time and is independent of the external actions, which leads to cracking or dropping in load-carrying capacity because of a loss in volume. Alternatively, expansion can cause crackse when its parts fail to withstand the force or the repeated cycles of expansion. Previous research studies have indicated that geopolymers had superior shrinkage and expansion resistance (Fernández-Jiménez, et al., 2007), including thermal properties when exposed at elevated temperature (800 to 1,000°C).

Geopolymers has low water absorption due to its dense structure (Davidovits, 2002). Pores in structure partially depended on water content and also affect the porosity of geopolymers. It was also found that overheating leads to an increase of early strength with large pores while lower temperature leads to a decrease of early strength with smaller pores. By this, it means that the size of pores is directly related to aging, amount of water used and curing regimes in the processing, which dominate the final density of that geopolymers (Lizcano, et al., 2012).

It can be concluded that the mechanical strength of the material increases during formation of the gel in first stage of the alkaline activation (coating of particles with an Al-rich aluminosilicate gel, Gel 1), but increases further as a result of the Si enrichment of the materialitious materials (formation of the Si enriched aluminosilicate gel, Gel 2). In the case of the ash M with the highest "(Si/Al) Reactive" ratio, the lowest mechanical strength (see Figure 3.7) is obtained as a consequence of the smaller amount of Si incorporated into the aluminosilicate gel (low degree of reaction attained) (Fernández-Jiménez *et al.*, 2006). The presence of a proper amount of soluble Si in the activation solution contributes the development of the compressive strength, thus geopolymers activated by silicate solutions exhibited much higher compressive strength than those activated by hydroxide solutions. For the case of geopolymer blocks activated by the sodium silicate solution containing K^+, they exhibit a higher compressive strength, the stronger basicity of K^+, allow higher rates of silicate dissolution (Sun *et al.*, 2013).

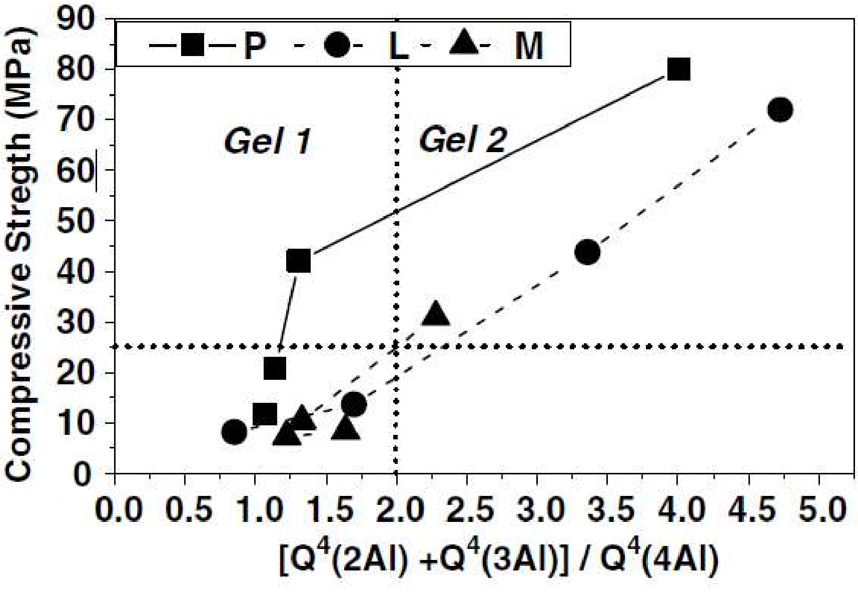


Figure 3.7 - Mechanical strength versus Q4(2Al) + Q4(3Al)/Q4(4Al) ratios deduced by NMR spectroscopy in the three fly ashes (Fernández-Jiménez *et al.*, 2006).

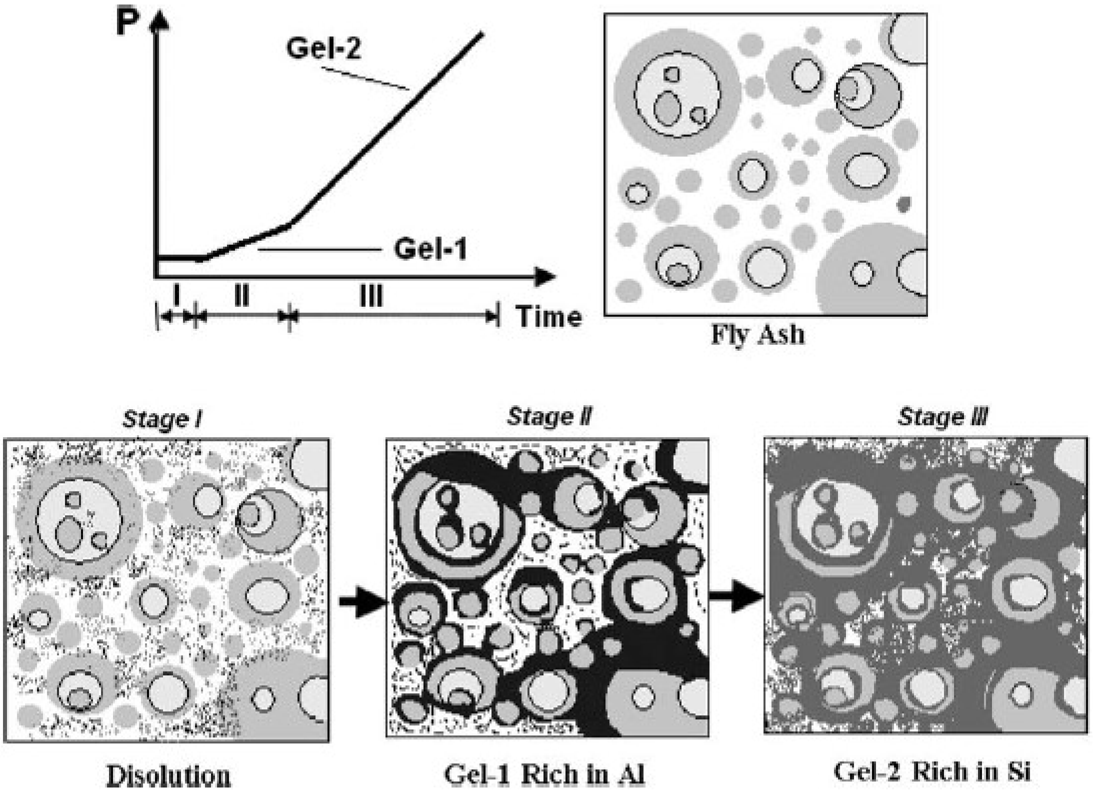


Figure 3.8 - Schematic description of mechanical properties evolution to the reaction time. Increment of mechanical performances is related to the Si/Al ratio in the gel (Fernández-Jiménez *et al.*, 2006).

Results of this investigation have clearly shown that the availability of dissolved Al and Si at a given moment highly influences the kinetics of the alkaline activation of fly ashes. Other variables, as concentration of the activator, curing temperature and curing time, play also a significant role in kinetics of gels formation. From a thermodynamic point of view the process of activation of fly ashes can be divided up to three main stages (see Figure 3.8) (Fernández-Jiménez *et al.*, 2006):

- Stage 1 (Dissolution stage): Most of the vitreous component of the fly ash is dissolved. No mechanical strength development is observed during the dissolution process (Fernández-Jiménez *et al.*, 2006).

- Stage 2 (Induction period): During the induction period a massive precipitation of a metastable Gel (named Gel 1) takes place, that produces the coating of unreacted fly ash particles. This gel displays the singular characteristic of incorporate (into the microstructural framework) a big part of the reactive aluminium existing in the ash, but not all the silicon. The beginning of this stage is associated to the initial setting of the paste. In this case a real degree of reaction 2 around 70–80% (the apparent degree of reaction 3 has been estimated about 30–40%), is obtain but the mechanical strength development of the material is not important (Fernández-Jiménez *et al.*, 2006).

- Stage 3 (Silicon incorporation stage): Finally, stage 3 corresponds to a period in which Gel 1 is transformed into Gel 2. This new gel is a Si-rich material since it accommodates into the structural framework that silicon which is more slowly dissolved in the alkaline medium (Fernández-Jiménez *et al.*, 2006).

Naturally, during the time in which Stage 3 is running the reaction degree continues advancing till reaching values >90% (real degree of reaction). At the same time, mechanical strength increases considerably. When the content of Gel 1 in the alkali activated fly ash is higher than the content of Gel 2, the mechanical strength development is low, 20–25MPa, however when the content of Gel 2 Gel 1, then the mechanical strength gain notably increases to 80 MPa (see Figure 8) (Fernández-Jiménez *et al.*, 2006).

The dissolution stage begins immediately after the alkali solution comes into contact with the fly ash. In this stage, the high OH^- concentration of the alkaline medium favours the break of covalent Si–O–Si, Si–O–Al and Al–O–Al bonds present in the vitreous phase of the ash, releasing the silicon and aluminium ions into the solution, where they form species with a high number of Si–OH and Al–OH groups. During the gelation stage, ionic species present in the solution (monosilicates and monoaluminates units) condense to form Si–O–Al and Si–O–Si bonds, giving rise to a three-dimensional aluminosilicate gel with alkaline cations compensating the deficit charges associated with Al for Si substitution. In these gels, the formation of Al–O–Al bonds between contiguous tetrahedra is not favoured. In the early stages of the reaction, the speed of formation of dissolved monomers is greater than the speed of precipitation of the gel (Fernández-Jiménez *et al.*, 2006).

The analysis of the mechanical strength, degree of reaction and microstructural characteristics of alkaline-activated ash pastes has shown that fly ashes that best perform under alkaline activation are: (i) ashes with a high reactive SiO_2 and Al_2O_3 contents and (ii) ashes with "(Si/Al) Reactive" ratios below 2. In all analysed cases an alkaline aluminosilicate gel is formed as the major reaction product regardless of the composition of the ash. For short reaction times, formed gels are constituted by an Al-rich phase, in which Si tetrahedra are surrounded by four Al tetrahedra (Q4(4Al) units). As the reaction progresses, this phase evolves into a more stable Si-rich phase, in which a higher amount of Si occupies Q4(3Al) and Q4(2Al) environments. In these materials, the increment of Si/Al ratios, improve considerably mechanical properties of aluminosilicate gels formed (Fernández-Jiménez *et al.*, 2006).

Key factors

The fundamentals of geopolymers and geopolymerization have been compiled together with most important factors affecting properties and characteristics of geopolymers, i.e. main binder constituents, alkaline activators and binder concentration, and the curing procedures. Any alumina-silicate material could be used to produce geopolymers. Three main categories of prime materials, Industrial Waste (IW), General Waste (GW) and Natural Mineral (NM), have been classified. The particle size and shape, chemical composition and amount of Silica (Si) and Alumina (Al) contents are the keys of achieving mechanical strength of geopolymers. Coal-fired fly ash seems to be the most studied raw material for the alkaline activated material due to its physical characteristics (small and spherical shape), chemical characteristics (rich in Si and Al) and eco-friendly origin (by-product). There are a variety of alkaline used in geopolymer synthesis, but in this study, the sodium and potassium hydroxide solutions and sodium and potassium silicate solutions seem to perform the most appropriate material for geopolymerization. The concentration of silicate soluble (in molarity and percentage), ratio of sodium-potassium silicate solution to sodium-potassium hydroxide solution by weight (S/H ratio), and alkaline solution to waste by weight (A/W) are also the important factors which need to be concerned. Curing regimes, temperature and duration, stimulating the formation of geopolymeric gel, should be optimised. Too high and too long curing lead to rapid loss of moisture content, which has an adverse effect on its mechanical properties. Whereas too low temperature or too short curing period obstructed the geopolymeric formation.

Most of geopolymer properties normally were comparable with ceramic material, even though its formation is totally different. Although the geopolymers has some limitations such as costly alkaline solution, risk associated with the high alkalinity of the activating solution or practical difficulties in curing process, it is still a new choice of construction material for the future with many advantages. Geopolymer material has been previously proven to have good physical and chemical properties. The benefits from being a waste treatment process and a low carbon-dioxide material are also highly concerned together with benefits in cost reduction. Main properties of the achieved geopolymer products with suitable manufacturing procedure and heat curing are also summarised in this chapter.

Overall, the future trend of geopolymers research shall focus on the understanding of polymerization mechanisms and this will standardise geopolymers for the commercial production. This might include the route of geopolymer synthesis with designable strength and properties, for example, the material with suitable activators and curing conditions, etc. Long-term assessment in both contamination and durability also need to be investigated before it becomes a new choice of innovative materials.

STATE OF THE ART FOR GEOPOLYMER TILES

In literature there are some research that have as objective the production of tiles obtained with a geopolymer process. Nobody talks about tiles made by geopolymeric process with a low porosity, low water absorption and high mechanical strength. Some authors reuse general ceramic waste, but no one try to geopolymerize sintered ceramic wastes from porcelain tiles.

Davidovits (2017) report that in the 1972, the French ceramicist team Jean Paul Latapie and Michel Davidovics, confirmed that water-resistant ceramic tiles could be fabricated at temperatures lower than 450 °C, without firing. They had found this technical information in a literature survey carried out by the French ceramic institution *Société Française de Céramique*. One component of clay, kaolinite, reacted with caustic soda at 150 °C (Davidovits, 2017).

Another known process to produce floor and wall tile using geopolymerization of alumino-silicate minerals is a method described in a French patent: Method for manufacturing floor and wall stone tiles with geopolymers, FR 2.528.818, 22/08/1982, and the inventors are Joseph Davidovits, Claude Boutterin. The process consisted of proportioning and blending of alumina-silicate minerals such as kaolinite, quartz, etc. in a highly alkaline medium followed by heat treatment in the range of 300 - 700 °C. The hitherto known process has the following limitations:

a) The production cost of tiles is relatively high when it uses costly raw materials such as pure silica, alumino-silicate minerals, talc, wollastonite, etc. as main ingredient.
b) The process of the raw materials is an energy intensive process need to be fired at a temperature arriving to 700 °C for a time in the range of 2 to 8 hours.
c) The tiles produced are in unglazed form. Glazing of the tiles is material intensive, cost intensive and energy intensive process.

Their invention referred to a manufacturing process of horizontal and vertical surface coatings obtained by geopolymerization. The invention uses a mineral polycondensation reaction of a silicon-aluminous alkaline mix. The reaction took place at temperatures lower than 120 ° C.

The second identified patent US4888311A was registered by Davidovits *et al.*, in the 1988 and the title is: Ceramic-ceramic composite material and production method. The invention referred to a ceramic-ceramic material composite having a fibrous reinforcing ceramic and a ceramic matrix made of a geopolymeric compound containing:

a) A poly(sialate) geopolymer Mn $(\text{--Si--O--Al--O--})_n$ and/or poly(sialate-siloxo) Mn $(\text{--Si--O--Al--O--Si--O--})_n$, M representing at least one alkaline cation, and n the degree of polymerization;

b) Ultrafine siliceous and/or aluminous and/or silico-aluminous constituents, of size smaller than 5 microns, preferably lower than 2 microns,

The geopolymeric compound being obtained by polycondensation at a temperature between 20 °C and 120 °C of an alkaline alumino-silicate reaction mixture, the composition of the principal constituents of the said geopolymeric compound expressed in terms of mole ratios of the oxides being between or equal to following values:

- $M_2O/SiO_2 = 0.10$ to 0.95;
- $SiO_2/Al_2O_3 = 2.50$ to 6.00;
- $M_2O/Al_2O_3 = 0.25$ to 5.70.

M_2O representing either Na_2O and/or K_2O, or a mixture of at least one alkaline oxide with CaO.

The fibrous reinforcing material consists of ceramic fibers such as SiC, Al_2O_3, SiO_2, glass, carbon. The addition of alkaline sulphides and alkaline sulphites enables glass fibers to be protected against chemical attack due to the alkalinity of the matrix.

The invention relates to the description and fabrication of composite, temperature-resistant materials based on fibrous ceramics, whose ceramic matrix is a geopolymeric alumino-silicate compound resulting from an inorganic polycondensation reaction mixtures based on alkaline and/or alkaline earth silico-aluminates. The principal object of this patent is the description of the various composite ceramic-ceramic materials, whose matrix is a geopolymeric alkaline and/or alkaline earth silico-aluminate compound. The second object of this invention is to describe the processes for obtaining these composite ceramic-ceramic materials. The polycondensation of the ceramic matrix is of the hydrothermal type. It is carried out at a temperature between 20 °C. and 120 °C and is similar to that by which minerals, such as synthetic zeolites, feldspars; or geopolymers of the type poly(sialate) or poly(sialate-siloxo), are obtained.

In the description of this invention, the term `composite material` designates a material composed of 2 or several constituents in intimate contact on a microscopic scale. In the case of composite materials with organic matrices, which are the most well-known, the constituents are:

a) an oriented or randomly disposed fibrous reinforcing material which confers its properties of strength and mechanical rigidity on the finished composite material.
b) a thermosetting or thermoplastic plastic material which can be allowed to set in the desired shape while the stresses are transmitted to the fibers.

In this invention, the fibrous reinforcing material is composed of fibrous ceramics. The plastic material is a thermosetting geopolymer and the matrix so obtained is of the ceramic type.

The notion of a ceramic-ceramic composite is defined in the work by Naslain, `Introduction to Composite Materials`, Editions du CNRS, Paris, 1985. In chapter XVIII of this work are described the various technologies used by workers in this field to carry out impregnation into the bulk of the fibrous material of the ceramic matrix. Three procedures are known: gas, liquid or solid procedures. These methods of impregnation all have in common the requirement of extremely high temperatures accompanied by techniques for avoiding the destruction at these temperatures of the fibrous reinforcing material. Liquid impregnation of a vitro-ceramic silico-aluminous matrix is generally carried out in four stages: (1) preparation of a pre-impregnate using slip, (2) making a composite preform, (3) compression between 6-10 MPa at high temperature 1200 - 1500 °C under controlled atmosphere, 4) curing at 900 - 1000 °C. This technique is analogous to that used for composite materials based on an organic matrix, with, however, an essential difference in the process temperature, 100 - 250 °C for organics compared with 1000 - 1500 °C for ceramics.

In contrast, the ceramic-ceramic composites of this invention are characterized by their ease of production at low temperature, their resistance to temperature and their mechanical strengths. These three qualities have up to now been irreconcilable. The ease of production could be found in organic plastic materials; resistance to temperature was the characteristic property of ceramics; mechanical strength could be obtained with composite materials. The composite materials of this invention reconcile these three properties. They can be transformed at low temperatures, between 20 °C and 120 °C with the same technologies as for organic plastics, remain stable up to 1200 – 1400 °C, and the presence of high-performance ceramic fibers confers on them excellent mechanical properties over a very wide temperature range. Another object of the invention is the description of manufacturing processes of several articles using the composite ceramic-ceramic material of the invention, in particular the making of small tooling and of items used in the casting of non-ferrous metals.

The third identified patent US20070221100 was filed by Kumar *et al.* in the 2007 with the title 'Process for the preparation of self-glazed geopolymer tile from fly ash and blast furnace slag'.

His invention provides a process for the preparation of self-glazed geopolymer tile using fly ash and granulated blast furnace slag. In the process of the present invention, the granulated blast furnace slag is fine grounded and/or mechanically activated in conventional grinding mills or high-energy mills. The fly ash, which is found in powder form and fine powder of granulated blast furnace slag, is thoroughly mixed to make a homogenous mixture. The alkaline solution is added into the mixture to initiate the geopolymerization. The ratio of water to powder is optimized to obtain a consistent paste to be used for vibration casting. During the casting, the consistent paste flows inside the mould and the particles settles at mirror finished surface of mould, giving rise to dense and smooth surface.

The self-glazed geopolymer tiles used have the following range of properties:

a) Compressive strength 20 - 50 MPa;
b) Fire resistance withstand 1000 °C;
c) Acid resistance: excellent;
d) Straightness of the side > 95 %;
e) Rectangularity > 95 %;
f) Surface finish glazed and free from defect;
g) Bulk density 1.5 – 2.5 gm/cc;
h) Water absorption 10 - 25%;
i) Hardness > 4 on Mohs Scale.

In this patent the cast tile is cured at room temperature during which geopolymerization reactions start. Two type of reaction occurs in the material, (a) The paste is cured at room temperature during which the dissolution of silica and alumina. After the initial dissolution, the paste is heat treated at the temperature in the range of 60 - 300 °C. In the enhanced curing condition dissolution of silico aluminate proceeds simultaneously with the gel formation and poly-condensation reactions and results into formation of polymeric Si—O—Al—O bonds called poly-sialate. Formation of poly-sialate results into setting and strength development of tiles, and (b) the latent hydraulic property of granulated blast furnace slag is enhanced at elevated temperature curing. During the hydration reactions, the CaO and SiO_2 present in slag reacts with water and form the C—S—H gel (C=CaO, S=SiO_2, H=H_2O), which is materialitious in nature. Formation of C—S—H gel accelerates the setting time at the earlier stage and also contribute towards strength development at later stage. The main advantages of the self-glazed geopolymer are:

1. Self-glazed geopolymer tile can be produced by the process invention, where glazing occurs automatically on tile surface, thereby no additional processing or cost for glazing is required.

2. The process utilizes very high proportion of abundantly available industrial waste (fly ash and granulated blast furnace slag) as major raw material to produce self-glazed geopolymer tile, thereby the cost of production is considerably reduced in comparison to the known process.

3. The process of the invention is helpful in resource conservation by replacing costly raw materials e.g. silica, kaolin, talc, wollastonite, etc. by the industrial wastes.

4. The process involves low temperature processing (50 – 300 °C), thereby helpful in energy conservation.

5. The process uses simple and easy steps and no CO_2 is emitted during processing.

The last patent found is the EP2727894A1, filed by Caballero Lopez *et al.,* in the 2012, and the title is: Forming of ceramic materials made with inorganic polymers. The invention is about a procedure for the forming of ceramic materials made with inorganic polymers, by the alkaline activation of thermally treated clays. The all procedure comprises a phase for the thermal treatment of clays, a phase for the mixing of, at least, thermally treated clays and an activating solution, an extrusion forming phase, a curing phase and a drying phase. As a result of this procedure, ceramic products presenting vastly superior mechanical properties, if compared to those of known materials with geopolymers, are obtained; allowing ceramic products to be obtained with very significant energy savings, because it avoids high-temperature firing processes. Moreover, the ceramic products obtained in this way possess better properties in terms of resistance to fire, heat, sound insulation and durability against external agents (ice, saline environments, humidity, etc) than those obtained through ceramic techniques. Extrusion forming phase is a development of the traditional formwork or compression method. The method involving extrusion with a de-airing chamber and Archimedes screw produces a linear product in a continuous manner, with a controlled cross-section, and which may be cut to a required length. Effective and efficient, this method comprises a first section with a mixing mill, which has two rows of blades assembled on two shafts that rotate in opposite directions, thereby providing an elevated cutting action that mixes the material efficiently, with the material being extruded between the blades. The mixing mill is supplied with the clay and activator premix. The mixing mill mixes the premix, making it homogeneous, maximizing its plasticity and expelling air by pushing the paste. By means of an Archimedes screw, used to transport the mixture, the mixture then passes through a perforated plate in the vacuum chamber. The material, in the form of pellets, is de-aired in a uniform manner by means of the application of a vacuum for eliminating as much air as possible. Finally, the mixture is pushed to the compacting chamber, where another Archimedes screw transports the material and pre-compacts it in order to remove any porosity before it passes through the die or rigid nozzle. The resulting product, which has a constant cross-section and is variable in length, is supported on trays and is cut to the required length by means of a cutting system. The advantage of this type of screw extruder is that, in a continuous manner, the mixing, de-airing, consolidation and the final shaping of the piece to be manufactured takes place in it. In addition, the factors of pressure, helix angle, and their rated ratio with respect to the fiction area of a nozzle with a constant section, make the end product an innovative piece of high technical quality.

Curing: In this context curing refers to the treatment of the sample at low temperatures (20 °C to 90 °C) and high relative humidity (40 % to 100 %) for a time period of between one hour and seven days, preferably between five and 24 hours, and more preferably between 20 and 24 hours.

The complete procedure is the following: the thermally treated clay or the mixture of thermally treated clay and clay is mixed with the components of the activating solution, which is preferably presented in the form of an MOH solution (M=Na, K) with a concentration between 2 and 12 M, containing sodium or potassium silicate in a percentage ranging between 0% and 20%, preferably 15%.

The mixing phase is performed by any of the methods well known in the industry, although the silico-aluminous material is preferably mixed in powder, generally the finer the better, with the liquid activating solution, with a ratio between the activating solution and the powdered materials (liquid/solid) ranging from 0.25 to 0.85, preferably from 0.40 to 0.60.

The mixing of silico-aluminous material with the components of the activating solution (sodium or potassium hydroxide, sodium or potassium silicate) in the form of powdered solids may optionally be carried out, with the subsequent addition of water prior to the start of the following phase. Mixing may be performed using the mixing, grinding, atomizing, flash drying methods etc. commonly employed in the industry. When the components are mixed, the extrusion process is performed by any of the methods commonly used in the ceramics industry (helical and piston extruders in the main, in any of their variants). Once the formed pieces have been obtained they are subjected to a curing process at low temperatures (20°C to 90°C) and high relative humidity (40% to 100%), for a time period of between one hour and seven days, preferably between five and 24 hours, and more preferably between 20 and 24 hours. Finally, the pieces are dried either at low temperature or at a temperature of up to 100°C. The resulting specimens presented the following information: Mechanical tensile and bending strength: 28.3 ± 3.1 MPa.

The EnerGeo project 'Insulating high strength-controlled porosity geopolymer floor tiles for the mitigation of global warming' developed by Ceramiche Gardenia Orchidea in collaboration with the University of Modena and Reggio Emilia started in the 2009. And the other project 'Ecofriendly ceramic tile development by geopolymerization' started in the 2010 and the involved project partners are Ceramic Research Center (SAM) from Turkey, Asociación de Investigación de las Industrias Cerámicas (ITC) from Spain and German Ceramic Society (DKG) from Germany. The research performers are SAM, ITC, Institut Für Gesteinshüttenkunde Aachen (GHI) and Bauhaus-Universität Weimar (BUW).

Gardenia Orchidea, through the implementation of the LIFE+ project "Energeo", implemented a pilot plant capable of demonstrating the feasibility of the application of geopolymers (class of materials based on synthetic aluminosilicates) on an industrial scale for the production of innovative flooring and coating tiles, with a production cycle which allows to reduce the emissions of greenhouse gases by more than 80% compared to the production of ceramic tiles or concrete products. The new products have been named "Geopolfloor". Thanks to the process and to the pilot plant realized, compared to a normal process of production of flooring materials of ceramic base, the environmental benefits are multiple:

- reduction of about 80% of overall CO_2 emissions;
- reduction of 60% of overall energy consumption;
- recycling of waste in the raw material mixtures of at least the 60% in weight;
- zero VOC emissions (Volatile Organic Compound).

The samples obtained by casting through the final pilot plant have the following characteristics:

- mechanical and thermal properties: flexural strength >7 MPa, resistance to 800 °C;
- thermal and acoustic insulation properties (mainly in the version Foam);
- no limits on tile dimensions (given a minimum thickness);
- greater ease to create complex structures (compared to stoneware/single firing);
- no intermediate drying of slurry (direct pouring in moulding);
- rapid manufacturing cycle (after 2 hours piece can be removed from the mould);
- no problems of dilatometric compatibility (cracks, crazing, bending, etc).

The technical and mechanical characterizations of the products obtained present in some cases lower values, especially from the point of view of the resistance to compression, compared to the porcelain stoneware, as it lacks the firing phase, which would also ensure greater resistance to the new products. It was not among the aims of the project, however, to find a perfect reply material of porcelain stoneware, very utopian, but to demonstrate the possibility of realizing products compatible with the use for floors or walls maximizing the benefits from the environmental point of view.

The aim of the project proposed in the framework of the 6th Joint CORNET, in the 2010: 'Ecofriendly ceramic tile development by geopolymerization' has the goal to develop low cost energy saving methods for manufacturing ceramic tile by using geopolymerization as a new ceramic processing technique (Kara *et al.*, 2010).

Two years later they shown the results of their research (Süzük *et al.*, 2012). The raw material used was a reagent material in the alkaline activation process (kaolin). The shaping methods used were a form and extrusion processes. This latter shaping method is new in the obtainment of alkaline inorganic polymers, since these materials have been studied from the outset by the traditional shaping method used in the material sector, namely by means of forms. The results show that the mechanical strength of the material obtained by alkaline activation was of the same magnitude as that of ceramic tiles and was closely related to the nature, microstructure, and chemical composition of the reaction products, as well as to the process variables. In every case, the main reaction product was an alkaline inorganic polymer (N-A-S-H gel), which was largely responsible for the mechanical properties of the material. In this work, extrusion has been studied as an alternative shaping method for this type of materials. The maximum tensile bending strength attained (16 MPa) exceeded the minimum required for earthenware tile (monoporosa) ($e < 7.5$ mm) and was much higher than that required for concrete tiles.

Another obtained characteristic of this project:

- Bulk density 1.4 g/cm3;
- Curing shrinkage < 0.05 %;
- Porosity ~ 30 %;
- Mohs Hardness 4-6.

Finally, they considered the possibility of decorating the pieces obtained. A glaze was selected from a literature search to find the fluxing compositions that might be used for this type of product. Based on the search results, three different composition systems were tested: '$BaO-B_2O_3-SiO_2$', '$ZnO-B_2O_3-Na_2O-SiO_2$', and '$Li_2O-B_2O_3-SiO_2$'. With a view to avoiding cracks and achieving good bonding between the substrate and the glaze, the coefficient of expansion of the substrate needed to be very similar to that of glaze. The foregoing compositions were therefore reformulated and a more appropriate frit for the needs of the product was prepared. The greatest problem posed by using a low-temperature frit, that need to be applied with the wet method, is the overlapping of organic matter in decomposition with the glaze sealing phase at the same temperature. The resulting piece (substrate obtained by alkaline activation + dry grit application) was then fired at 600 °C. So, this type of decoration needs an important thermic cycle.

The research study concerns the use of waste from glass bottles, fluorescent lamps and soda-lime window glass, used in its entirety as a raw material in the manufacture of tiles by applying the technique of alkaline activation to generate an alkaline cementitious material is the last paper found (Rivera *et al.*, 2018). The microstructure of alkali cement synthesized in this work from waste glass bottle (BG), in which a dense, compact matrix is seen with some small particles of glass embedded in the matrix, which indicates that dissolution of the precursor was satisfactory. It is known that a greater solubility of precursor materials produces a greater amount of cementitious gel, which is responsible for conferring the mechanical properties to the synthesized material. This result agrees with the results obtained for compressive strength (56 MPa). One factor that could contribute to greater solubility of BG as precursor of alkaline-activated mix, in addition to the amorphous nature, is the curing temperature, which was 70 °C for 24 h. In this respect, other authors note that an increase in the temperature of the alkaline activation process contributes to the dissolution of a greater quantity of glass particles when the particle size is less than 45 mm (Rivera *et al.*, 2018). The fabrication of tiles was performed using BG as precursor material was passed through 1.18 mm sieve after milling, and the retained material was discarded. To produce the mortar, a BG/WG ratio of 1/2.25 was used. This mixture was alkaline activated with a 4 M NaOH solution for subsequent fabrication of tiles that were moulded manually with dimensions of 20x20x2 cm. These parts were thermally cured in the mould for 24 h (70 °C, 80% RH, 24 h). The results of tests conducted on the tiles shown different types of tiles, type A and B, classified according to their mechanical properties. The tile fabricated with waste glass is classified according to ISO13006 standard as CIII high absorption tile, exhibited comparable physical-mechanical properties to and even exceeded some of the limits established in the Colombian standard (NTC1085) for type a cement floor tiles (compression and impact strength tests). About the maximum supported flexural load, the tile exhibited an intermediate value of 1006 N. It is worth noting that this value depends on the part geometry. In addition, although the tile fabrication process was a manual one, acceptable results were obtained, which suggests that an industrial process such as compaction or pressing moulding would contribute to densification of the piece. The results of the bending test would thus be greater, and the absorption would decrease. With the optimum mixture selected, it is possible to manually fabricate tiles that exhibits promising physical and mechanical properties: a compressive strength of 178 kg/cm2, a maximum supported flexural load of 1006 N, and an impact resistance from a height of 320 mm. These properties could be increased with a more technically process (Rivera *et al.*, 2018).

On internet there is another reference to a geopolymeric tile, an Italian company AGMA GEOPOLIMERI that promote a geopolymeric tile, but they don't describe any detail of their project. The description of their product is only the following phrase: 'The products are high-performance heat-resistant and insulating tiles, composed of waste and cold-produced materials, reducing about 80% energy costs and carbon dioxide emissions compared to the same parameters to produce classic tiles'. It's impossible to know others technological parameters and process parameters, but in the pictures that they show is clear that this type of tile is not decorated.

https://www.agmageopolimeri.com/portfolio/piastrella-geopolimerica/

In literature there are two works in which ceramic tiles are manufactured using geopolymeric materials as raw material, but these materials require a firing process (Luo, Ma, *et al.*, 2017; Luo, Zheng, *et al.*, 2017).

This project, unlike the works mentioned above, aims to obtain geopolymer tiles with low water absorption and high mechanical strength, using two shaping methods. The casting method has already been widely validated in the bibliography, by casting a slurry. The second shaping process is the pressing method, that has not yet been widely tested and validated in literature.

Of great importance is the material to be activated to achieve the research objectives, in fact it is different from all the mentioned projects, which use metakaolin, fly ash and blast furnace slag. In order to fulfill the objective of a closed ceramic cycle, was used fired ceramic waste.

4. MATERIALS AND METHODS

Geopolymerization require a good development of the key factors mentioned in table 4.1 and explained in the following chapter:

- Precursor’s characteristics;
- Activator nature and concentration;
- Processing.

KEY FACTORS IN GEOPOLYMERS

PRECURSOR’S CHARACTERISTIC	ACTIVATOR NATURE AND CONCENTRATION	PROCESSING
- PHYSICAL CHARACTERISTIC - CHEMICAL COMPOSITION - MINERALOGICA PROPERTIES	- NaOH, KOH - Sodium, Potassium, Lithium silicates	- % OF WATER - SHAPING METHODS - CURING CONDITIONS

Table 4.1 – Key Factors in geopolymerization.

PRECURSOR’S CHARACTERISTICS

Geopolymerization requires two main components, namely the solid precursor and the activators solution. The precursor must be rich in silica and alumina, in this project is the Ceramic Waste (with high amorphization degree); and the activators solution, is based on an alkali metal (usually sodium or potassium) or an alkali earth metal (usually calcium) hydroxides or silicates. They constitute an excellent solution to enhance the properties of most industrial residues.

The target of the ongoing research dealing with the application of this technique to different engineering applications is twofold: maximize the mechanical behavior and to minimize the porosity.

CERAMIC WASTES

In literature, the ceramic waste was activated by alkali hydroxides and/or sodium/potassium silicate solutions to synthesize geopolymer or alkali activated material; and the results indicate that waste ceramic could be a satisfying source material for thermostable geopolymer (Reig *et al.*, 2013; Sun *et al.*, 2013). But in one case the ceramic waste had high quantities of CaO and was formed CASH alkali activated material (Sun *et al.*, 2013). Also in the second work was tried to activate porcelain to reach a performing geopolymer, without success, and was added CaO to complete the reaction of geopolymerization (Reig *et al.*, 2013). Ceramic wastes are not only nonbiodegradable but also consume much space in landfill. A portion of this waste is often utilized for the excavation pit refilling. Thus, finding a new way to recycle this waste and subsequently using in the construction of infrastructures can be useful to preserve natural resources and the environment. Recent research (Huseien, Sam, *et al.*, 2018) revealed that ceramic wastes have pozzolanic properties, which can be used to make geopolymer with improved strength and durability. Using this waste to substituted conventional fine aggregates in geopolymeric mortars there is an effective lower water absorption performance, because the fine powder waste has a low porosity. In other two articles (Huseien, Sam, Shah, Asaad, *et al.*, 2019; Huseien, Sam, Shah, Mirza, *et al.*, 2019) was tried to alkali activated ceramic waste but only to obtain mortars with the addition of fly ash. The project started with the collection of all wastes produced during the ceramic cycle, destined to landfill, and also those intended for reintroduction into the production cycle. The first activity done has been a chemical-physical characterization of the precursors (Table 4.2, 4.3). The ceramic wastes characterized are:

- Sludge resulting from rectifying process (RS);
- Sludge resulting from lapping process (LS);
- Sludge resulting from combined lapping and rectifying process (LRS);
- Fired ceramic waste (FCW);
- Powder from process (RP).

Table 4.2 - Chemical composition by XRF (w.f. %).

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	ZnO	ZrO_2	BaO	SrO*	P_2O_5*	LOI	C**	S**
RS	70.8	18.3	0.7	0.6	1.1	0.2	2.0	4.7	0.0	0.1	0.1	0.0	0.2	0.6	0.1	0.0
LS	47.0	19.8	0.2	0.1	7.2	0.9	1.4	5.7	4.4	0.2	0.1	3.4	2.3	6.6	1.2	0.8
LRS	68.7	20.0	0.5	0.6	0.8	0.2	2.0	5.4	0.0	0.1	0.0	0.0	0.1	0.5	0.0	0.0
FCW	71.2	18.6	0.6	0.6	1.3	0.4	2.1	5.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0
RP	70.1	18.5	1.0	0.6	1.0	0.7	1.8	4.9	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0

* semiquantitative analysis - **Carbonium & Sulfur analysis

Table 4.3 - Mineralogical composition by XRD (w.f. %).

		RS	**LS**	**LRS**	**FCW**	**RP**
QUARTZ	%	11.44	1.30	17.15	19.53	12.50
MULLITE	%	5.84	-	6.05	6.98	6.95
ALBITE	%	7.98	4.26	6.54	5.74	3.54
CURUNDUM	%	-	2.22	-	-	-
ORTHOCLASE	%	-	-	0.85	0.96	-
NOT ORDERED PHASE	%	74.74	92.22	69.41	66.79	77.01

The mineralogical quantitative analysis was made using GSAS & EXPGUI software and Rietveld method.

The development of different alkali activated materials as environmentally friendly materials are rarely explored by using ceramic wastes. The low content of Al_2O_3 and CaO in chemical composition makes it very difficult to obtain activated materials based on waste ceramic at room temperatures (Huseien, Sam, Shah, Mirza, *et al.*, 2019). Consequently, the present study intends to develop environmentally friendly geopolymer materials with different way of applications of the ceramic waste using geopolymerization, activating the large quantity of amorphous ceramic glass available in these wastes.

The chemical and mineralogical characterization of the wastes give us very important information. The mineralogical analysis shows a high quantity of amorphous phase, a great material to be activated with reagents. But quartz and mullite don't react at high pH values.

The chemical analysis indicates that the available Si and Al permit to obtain a good activation. The relationship between silicon and aluminum indicates enough quantity of geopolymerizing material, but we have to consider that only the silicon and alumina present in the not ordered glassy phase is available to be activated, because the silicon and alumina present in the quartz and mullite minerals don't participate to the dissolving phase. The absence of calcium in the precursor allow to say that the materials obtained are geopolymers and not alkali activated materials.

These two ceramic processing wastes derive from the same source, the fired ceramic tile, for this reason they have very similar chemical analyzes. The mineralogical difference is due to the fact that RP derives from material with an higher sintering degree compared to FCW, this is visible from the quantity of amorphous phase present. Certainly, both could be raw materials for geopolymers but from what has

been verified during the tests, the material that reacts most to form the geopolymer phase is the one that contains the most amorphous phase, therefore, using FCW, reaction performance would be lost.
The LS waste is made up almost entirely of an amorphous phase which can facilitate the geopolymerization process, but the chemistry is characterized by a low SiO2 content prevents the formation of a high-density material. In fact, the SiO2/Al2O3 ratio moves away from the optimal ratio for the formation of geopolymer. Another detail that can be seen from the chemical analysis of the LS waste is that it has a high LOI. Inside this waste there is a resinoid material deriving from lapping wheel of the processing from which the waste is produced.
Analyzing these chemical and mineralogical observations the best usable waste is the dry waste powder, contain high not ordered glass phase and the lowest content of quartz and mullite.

REAGENTS

Alkaline solutions

A combination of sodium hydroxide, potassium hydroxide, sodium silicate and potassium silicate solutions were used as alkaline activators regarding the previous research literatures.

- Potassium silicate, anhydrous -48 mesh; SiO_2:K_2O 2.5:1 wt% - AlfaAesar – CAS: 1312-76-1; EINECS: 215-199-1;
- Sodium silicate, anhydrous -18 mesh; Na2SiO3 - 44.7-47.6% SiO2 - 49.1-51.7% Na2O – AlfaAesar- CAS: 6834-92-0;
- Potassium Hydroxide pellets 85%; KOH M=56.11 g/mol – PanReac AppliChem – CAS: 1310-58-3;
- Sodium Hydroxide anhydrous pellets; NaOH 97% - Carlo Erba Reagents – CAS: 1310-73-2.

The solutions were prepared by dissolving the pearl and powder in distilled water.

MIX-DESIGN – PROCESSING

SHAPING METHODS

In this project, unlike the works mentioned in the previous chapter, aims to obtain geopolymer tiles with low water absorption and high mechanical strength, using two shaping methods. The first is the casting method, already been widely validated in bibliography, by casting a mixed slurry.

The second shaping process is the pressing method, that has not yet been widely used and validated in literature for geopolymers but comparable to the shaping process for ceramic tiles.

The main difference between the two shaping method is the % of water used, high for casting and low for pressing. This difference has a very big influence during geopolymerization. Whit high amount of water, the fluid circulation is helped to reach all the waste particles. But with low amount of water the reactivity of the activator increases because is less diluted.

The second important difference is that during pressing, the mix of precursor and activators solution undergo to a very high pression, that compact the material.

CASTING METHOD

- Mixing for 10 minutes the milled powder with sodium or potassium hydroxide and sodium or potassium silicate;
- Adding of distilled water and mixing for 5 minutes;
- Casting the slurry in a mould (mould dimension 8*16 cm);
- Vibrating 5’ the mould for the elimination of all the bubbles of air formed during the mixing.

PRESSING METHOD

- Mixing of the milled powder with sodium or potassium hydroxide and sodium or potassium silicate;
- Spraying the distilled water determined in formulation;
- Sieving of the humid powder to obtain moisture uniformity;
- Pressing with a hydraulic laboratory press (mould dimension 8*16 cm) (Figure 4.1).

Figure 4.1 – Hydraulic lab press.

IDENTIFICATION OF THE BEST CERAMIC WASTE TO BE GEOPOLYMERIZED

Initially, the mixes were done considering the total amount of precursor like ceramic waste, for testing the capability to geopolymerize of these materials (Table 4.4). The samples shaping was done in two different methods: Casting method and pressing method. The first by transferring the slurry in a mould, the second by pressing the powder whit a lab press.

Preparation of geopolymer using the casting method:

The amount of dry ceramic waste and the activators were mixed according to the formulation below (Table 4.4). After 10 minutes of mixing of the waste powder and the activators, distilled water was added to reach the workability for an optimal mixing. After 5 minutes of mixing, the slurry was transferred in a mould for lab samples. During the filling procedure, the geopolymer mix was mechanically adjusted to remove the entrained air (5’ of vibration). Samples were cured for 24 h at room temperature closed in a plastic bag for create a relative humidity (R.H.) > 90%, then cured for 6 days at T = 60°C already closed in the plastic bag at R.H. > 90%.

The H_2O absorption is measured in according to the requirements reported in ISO 13006.

Table 4.4 – Mix design of the different ceramic precursor waste using casting method.

CASTING	**X**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1X	30	2	-	2	-	10	18.65
2X	30	-	2	2	-	10	dissolved
3X	30	2	-	-	2	10	20.50
4X	30	-	2	-	2	10	dissolved
5X	30	2	-	4	-	11	15.35
6X	30	4	-	4	-	12	11.86
7X	30	-	-	4	-	10	dissolved
8X	30	4	-	-	-	10	dissolved
CASTING	**Y**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1Y	30	2	-	2	-	10	dissolved
2Y	30	-	2	2	-	10	dissolved
3Y	30	2	-	-	2	10	dissolved
4Y	30	-	2	-	2	10	dissolved
5Y	30	2	-	4	-	11	dissolved
6Y	30	4	-	4	-	12	dissolved
7Y	30	-	-	4	-	10	dissolved
8Y	30	4	-	-	-	10	dissolved
CASTING	**Z**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1Z	30	2	-	2	-	10	dissolved
2Z	30	-	2	2	-	10	dissolved
3Z	30	2	-	-	2	10	dissolved
4Z	30	-	2	-	2	10	dissolved
5Z	30	2	-	4	-	11	dissolved
6Z	30	4	-	4	-	12	dissolved
7Z	30	-	-	4	-	10	dissolved
8Z	30	4	-	-	-	10	dissolved

CASTING	J	Reagent 1	Reagent 2	Reagent 3	Reagent 4	Reagent 5	H_2O absorption
	g	g	g	g	g	g	%
1J	30	2	-	2	-	10	17.50
2J	30	-	2	2	-	10	dissolved
3J	30	2	-	-	2	10	dissolved
4J	30	-	2	-	2	10	dissolved
5J	30	2	-	4	-	11	18.62
6J	30	4	-	4	-	12	13.65
7J	30	-	-	4	-	10	dissolved
8J	30	4	-	-	-	10	dissolved
CASTING	**K**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1K	30	2	-	2	-	10	15.71
2K	30	-	2	2	-	10	18.35
3K	30	2	-	-	2	10	19.20
4K	30	-	2	-	2	10	20.35
5K	30	2	-	4	-	11	14.00
6K	30	4	-	4	-	12	12.55
7K	30	-	-	4	-	10	dissolved
8K	30	4	-	-	-	10	dissolved

Preparation of geopolymer using the pressing method:

The amount of dry ceramic waste and the activator are mixed according to the formulation listed below. After 10 minutes of mixing, distilled water is added with an airbrush to reach the optimal humidity for pressing the powder (about 5-7%). The humid powder is then sieved for homogenize all the components and after is mixed for other 5 minutes. The next step is to weight 60 grams of wet powder and press it with a lab press to obtain a sample of 5x10 cm tile pressed at 300 kg/cm^2 of specific pressure.

Pressed samples were cured using the same procedure of casted samples: 24 h at room temperature closed in a plastic bag for create a relative humidity (R.H.) > 90%, then cured for 6 days at T = 60°C already closed in the plastic bag at R.H. > 90%.

Table 4.5 – Mix design of the different ceramic precursor waste using pressing method.

PRESSING	**X**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1X	30	2		2	-	5	11.65
2X	30	-	2	2	-	5	13.90
3X	30	2	-	-	2	5	15.65
4X	30	-	2	-	2	5	16.82
5X	30	2	-	4	-	5	10.55
6X	30	4	-	4	-	5	9.23
7X	30	-	-	4	-	5	dissolved
8X	30	4	-	-	-	5	dissolved
PRESSING	**Y**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1Y	30	2	-	2	-	5	dissolved
2Y	30	-	2	2	-	5	dissolved
3Y	30	2	-	-	2	5	dissolved
4Y	30	-	2	-	2	5	dissolved
5Y	30	2	-	4	-	5	dissolved
6Y	30	4	-	4	-	5	dissolved
7Y	30	-	-	4	-	5	dissolved
8Y	30	4	-	-	-	5	dissolved
PRESSING	**Z**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1Z	30	2	-	2	-	5	14.55
2Z	30	-	2	2	-	5	13.25
3Z	30	2	-	-	2	5	15.88
4Z	30	-	2	-	2	5	14.35
5Z	30	2	-	4	-	5	12.15
6Z	30	4	-	4	-	5	11.99
7Z	30	-	-	4	-	5	dissolved
8Z	30	4	-	-	-	5	dissolved

PRESSING	**J**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1J	30	2	-	2	-	5	15.23
2J	30	-	2	2	-	5	11.33
3J	30	2	-	-	2	5	16.15
4J	30	-	2	-	2	5	17.19
5J	30	2	-	4	-	5	13.25
6J	30	4	-	4	-	5	10.65
7J	30	-	-	4	-	5	dissolved
8J	30	4	-	-	-	5	dissolved
PRESSING	**K**	**Reagent 1**	**Reagent 2**	**Reagent 3**	**Reagent 4**	**Reagent 5**	**H_2O absorption**
	g	g	g	g	g	g	%
1K	30	2	-	2	-	5	14.21
2K	30	-	2	2	-	5	12.01
3K	30	2	-	-	2	5	15.44
4K	30	-	2	-	2	5	12.55
5K	30	2	-	4	-	5	9.98
6K	30	4	-	4	-	5	8.58
7K	30	-	-	4	-	5	dissolved
8K	30	4	-	-	-	5	dissolved

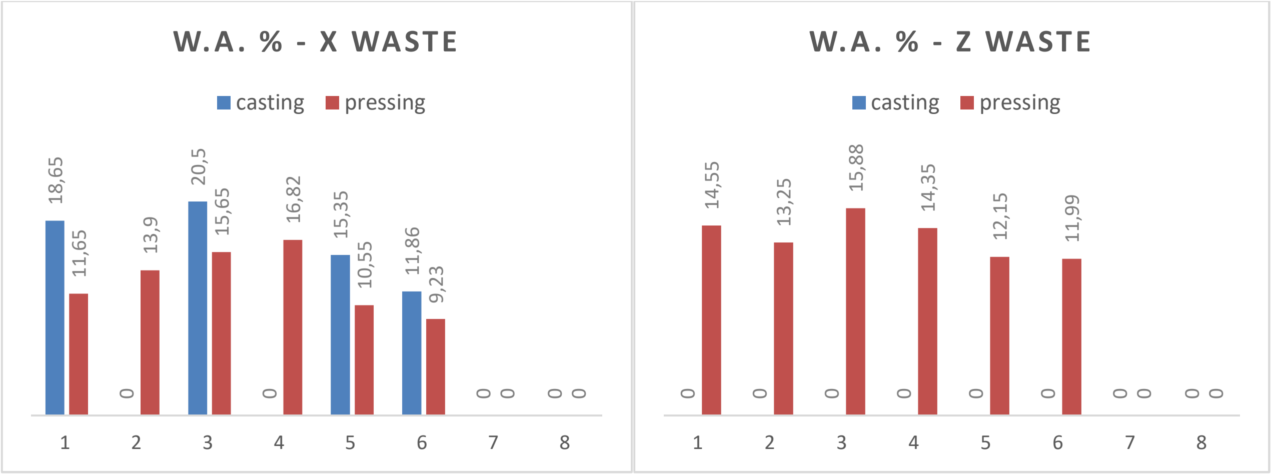


Figure 4.2 and 4.3 – Comparison of water absorption results for the different shaping method for the X (first figure 4.2) and Z wastes (second figure 4.3).

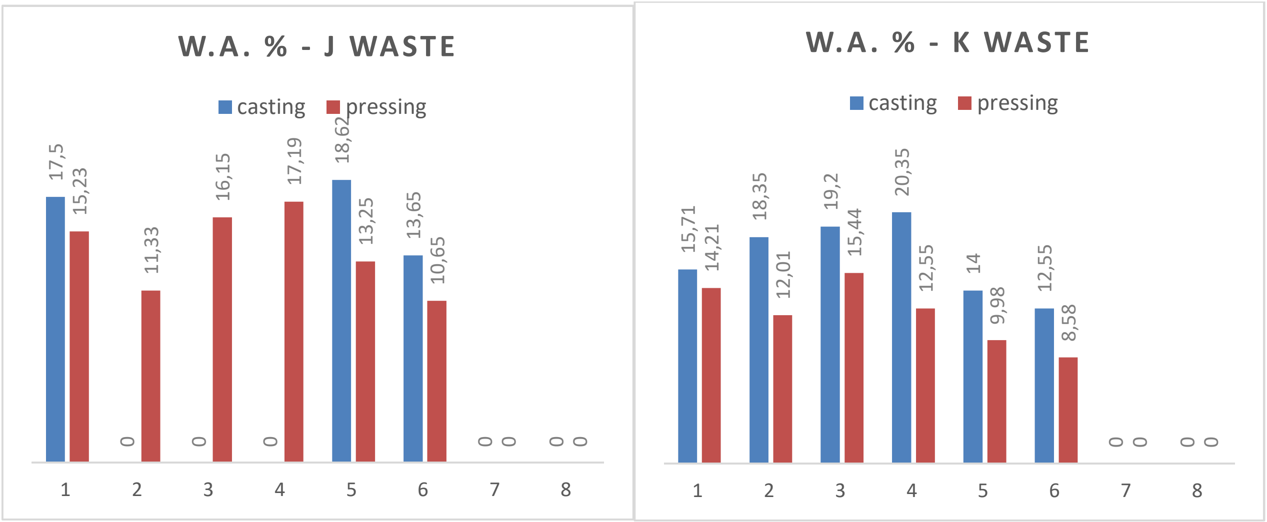


Figure 4.4 and 4.5 – Comparison of water absorption results for the different shaping method for the J (first figure 4.4) and K wastes (second figure 4.5).

It's possible to see from the figure 4.2, 4.3, 4.4 and 4.5 that the best water absorption results are obtained using the pressing method.

Comparing the results of water absorption, the best mix is the composition 6, and one other observation is that the best formulation has potassium hydroxide and potassium silicate in all the wastes. In figure 4.6, there is the test 6 for all the ceramic wastes, it's possible to see that the best geopolymerizing one (lowest water absorption) is the K.

Observing the preliminary tests, Y waste can't geopolymerize, the other wastes can geopolymerize, but they have a big problem, they are liquid, and the density of the sludge is very low, about 1200 g/l.

The sludges need to be dried and this process have an expensive thermal process. So, for this reason this research proceeds with the K waste. This waste is formed in the dry state and is the most abundant in the ceramic cycle (about 5 % in weight of all production), so the reuse of this waste is a great percentage of the total produced.

The comparison of the results obtained by geopolymers pressed and casted, suggest continuing with the pressing preparation method. The pressing process helps in compaction of the powder and reduce the pores.

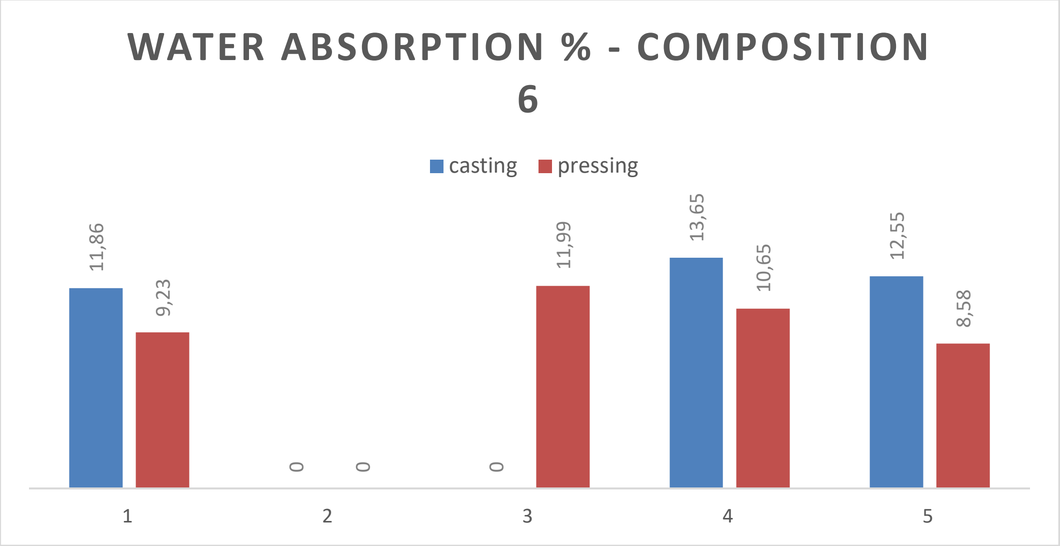


Figure 4.6 – comparison of the composition 6 for all the ceramic wastes.

WASTE POWDER CHARACTERIZATION

Was made a monthly campaign to check the constancy of the waste powder chemistry (Table 4.6). In terms of chemical composition, the alkali activation process can be applied to aluminosilicate sources with (SiO_2 + Al_2O_3) content > 80% (in this case the resultant products are known as geopolymers) or to precursors based on both aluminosilicate and Ca containing amorphous or crystalline phases (known as Inorganic Polymers (IP) and/or alkali activated materials (AAM)).

The waste powder contains always an amount of SiO_2 + Al_2O_3 higher than 80% and the content of CaO is very low, so the process of the research can be a geopolymerization process. The rate of dissolution of a precursor strongly depends on the chemical composition of the precursor. Tables 4.6 and 4.7 shows that the waste used in this study have very constant total silica and alumina contents, however not all silica and alumina are reactive. The reactive silica content and the reactive alumina content are from the vitreous ceramic phase, quartz and mullite are inert material.

Table 4.6 – Monthly chemical controls of the waste powder.

SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	ZnO	ZrO_2	BaO	PbO	LOI	C	S	TOTAL	TOTAL ALKALI
RPNOV16	70.27	18.30	0.74	0.64	1.10	0.20	1.98	4.67	0.00	0.10	0.10	0.00	0.60	0.08	0.02	98.80	6.65
RPDEC16	68.69	20.00	0.54	0.55	0.80	0.20	1.96	6.05	0.00	0.10	0.00	0.00	0.98	0.08	0.02	99.97	8.01
RPJAN17	70.55	18.77	0.46	0.59	0.97	0.30	1.64	5.95	0.00	0.10	0.00	0.00	0.46	0.05	0.01	99.86	7.60
RPFEB17	69.73	18.36	0.66	0.58	0.99	0.20	1.79	6.34	0.00	0.00	0.00	0.00	0.51	0.03	0.01	99.20	8.12
RPMAR17	69.17	20.65	0.74	0.73	0.65	0.30	1.65	4.53	0.00	0.00	0.00	0.00	0.52	0.08	0.01	99.03	6.18
RPAPR17	68.75	20.65	0.91	0.54	0.90	0.25	1.98	4.96	0.00	0.00	0.00	0.00	0.82	0.02	0.02	99.80	6.94
RPMAY17	68.07	19.97	0.87	0.52	0.83	0.32	1.99	6.43	0.00	0.00	0.00	0.00	0.83	0.04	0.03	99.91	8.43
RPJUN17	68.81	20.02	0.82	0.45	0.89	0.25	1.91	5.89	0.00	0.10	0.10	0.00	0.45	0.04	0.01	99.76	7.81
RPJUL17	69.09	19.95	0.52	0.87	0.74	0.31	1.98	4.91	0.00	0.00	0.10	0.00	0.63	0.06	0.01	99.16	6.89
RPAUG17	70.89	17.64	0.49	0.52	1.31	0.31	1.98	5.82	0.00	0.00	0.00	0.00	0.80	0.06	0.01	99.83	7.80
RPSEP17	70.02	19.73	0.64	0.52	1.17	0.24	1.93	4.51	0.00	0.00	0.00	0.00	0.74	0.05	0.01	99.56	6.44
RPOCT17	67.87	20.06	0.76	0.52	0.88	0.25	1.84	5.59	0.00	0.20	0.00	0.00	0.92	0.08	0.03	99.00	7.43
RPNOV17	68.28	20.78	0.78	0.78	1.16	0.27	2.00	4.91	0.00	0.00	0.00	0.00	0.55	0.06	0.01	99.58	6.91
RPDEC17	71.28	18.10	0.78	0.52	0.88	0.28	1.93	4.93	0.00	0.00	0.00	0.00	0.75	0.03	0.02	99.50	6.86
RPJAN18	67.91	20.69	0.73	0.53	0.99	0.31	1.94	5.63	0.00	0.00	0.00	0.00	0.55	0.05	0.02	99.34	7.57
RPFEB18	70.60	18.59	0.41	0.90	0.75	0.22	2.25	5.17	0.00	0.10	0.10	0.00	0.53	0.05	0.02	99.68	7.42
RPMAR18	68.42	20.67	0.62	0.41	0.74	0.20	2.01	5.92	0.00	0.20	0.10	0.00	0.65	0.01	0.02	99.97	7.94

RPAPR18	68.24	19.38	0.96	0.52	1.31	0.19	2.01	6.55	0.00	0.00	0.00	0.00	0.48	0.02	0.04	99.70	8.56
RPMAY18	70.15	18.48	0.80	0.52	1.29	0.25	1.60	5.99	0.00	0.00	0.00	0.00	0.58	0.05	0.01	99.72	7.59
RPJUN18	70.04	18.98	0.52	0.40	1.09	0.36	1.94	5.67	0.00	0.20	0.10	0.00	0.47	0.02	0.01	99.81	7.61
RPJUL18	68.96	19.82	0.63	0.59	1.09	0.32	2.17	5.77	0.00	0.10	0.10	0.00	0.39	0.01	0.01	99.96	7.94
RPAUG18	70.65	17.69	0.46	0.65	0.82	0.28	1.85	6.51	0.00	0.10	0.10	0.00	0.58	0.05	0.02	99.76	8.36
RPSEP18	69.70	19.30	0.97	0.35	0.87	0.21	1.94	5.76	0.00	0.10	0.10	0.00	0.48	0.06	0.01	99.86	7.70
RPOCT18	68.88	20.06	0.64	0.75	0.92	0.24	2.03	5.16	0.00	0.00	0.00	0.00	0.40	0.04	0.02	99.13	7.19
RPNOV18	69.89	18.59	0.59	0.51	0.65	0.25	2.22	5.41	0.00	0.00	0.00	0.00	0.85	0.04	0.02	99.03	7.63
RPDEC18	68.07	20.90	0.70	0.84	0.79	0.21	2.26	5.34	0.00	0.10	0.00	0.00	0.67	0.05	0.01	99.95	7.60
AVERAGE	69.35	19.47	0.68	0.59	0.95	0.26	1.95	5.55	0.00	0.06	0.03	0.00	0.62	0.05	0.02	99.57	7.51
MIN	67.87	17.64	0.41	0.35	0.65	0.19	1.60	4.51	0.00	0.00	0.00	0.00	0.39	0.01	0.01	98.80	6.18
MAX	71.28	20.90	0.97	0.90	1.31	0.36	2.26	6.55	0.00	0.20	0.10	0.00	0.98	0.08	0.04	99.97	8.56
DELTA	3.41	3.26	0.56	0.55	0.66	0.17	0.66	2.04	0.00	0.20	0.10	0.00	0.59	0.07	0.03	1.17	2.38

Table 4.7 - Monthly chemical controls of the waste powder.

SAMPLE	**SiO_2/Al_2O_3**	**SiO_2/K_2O**	**SiO_2/Na_2O**	**SiO_2/ALKALI**	**SiO_2/CaO**	**Na_2O/Al_2O_3**
RPNOV16	2.26	22.64	14.58	8.87	68.45	0.16
RPDEC16	2.02	22.36	11.00	7.37	92.00	0.18
RPJAN17	2.21	27.37	11.48	8.09	77.84	0.19
RPFEB17	2.24	24.88	10.66	7.46	75.50	0.21
RPMAR17	1.97	26.68	14.81	9.52	114.34	0.13
RPAPR17	1.96	22.14	13.44	8.36	82.23	0.15
RPMAY17	2.01	21.78	10.25	6.97	87.57	0.20
RPJUN17	2.03	22.93	11.32	7.58	82.53	0.18
RPJUL17	2.04	22.26	13.63	8.46	100.48	0.15
RPAUG17	2.37	22.82	11.80	7.78	57.93	0.20
RPSEP17	2.09	23.13	15.06	9.12	63.99	0.14
RPOCT17	1.99	23.51	11.76	7.84	82.54	0.17
RPNOV17	1.94	21.76	13.48	8.32	63.23	0.14
RPDEC17	2.32	23.55	14.02	8.79	86.52	0.17
RPJAN18	1.93	22.37	11.68	7.67	73.78	0.17
RPFEB18	2.24	20.05	13.23	7.97	100.67	0.17
RPMAR18	1.95	21.68	11.19	7.38	99.69	0.17
RPAPR18	2.08	21.65	10.10	6.89	55.77	0.21
RPMAY18	2.24	27.97	11.35	8.08	58.20	0.20
RPJUN18	2.18	22.98	11.97	7.87	68.82	0.18
RPJUL18	2.05	20.28	11.59	7.37	67.80	0.18
RPAUG18	2.35	24.30	10.52	7.34	92.67	0.22
RPSEP18	2.13	22.91	11.73	7.76	85.52	0.18
RPOCT18	2.02	21.65	12.93	8.10	79.84	0.16
RPNOV18	2.21	20.10	12.51	7.71	115.20	0.18
RPDEC18	1.92	19.22	12.35	7.52	91.79	0.16
AVERAGE	2.11	22.81	12.25	7.93	81.73	0.17
MIN	1.92	19.22	10.10	6.89	55.77	0.13
MAX	2.37	27.97	15.06	9.52	115.20	0.22
DELTA	0.45	8.75	4.96	2.63	59.43	0.09

GRANULOMETRY OF THE POWDER

The waste powder has high granulometry to be used in geopolymerization (Red line in figure 4.7). The powder has been fine milled to reduce the porosity of the final geopolymers and increasing the active surface of the precursor to be dissolved by the reactants.

Observing the diagram 4.7 it’s possible to see the progressive movement of the curves to low values of granulometry increasing the time of milling.

If we compare the data of Mean, Median and Moda reported in figure 4.8, it’s clear that the finest powder has also a large granulometric distribution at low values. The large granulometric distribution permit to have a best pores filling.

The Mean is the relationship between the sum of numerical data and the number of data, Median is the central value of extreme number data and Moda is the value that is presented with greater frequency.

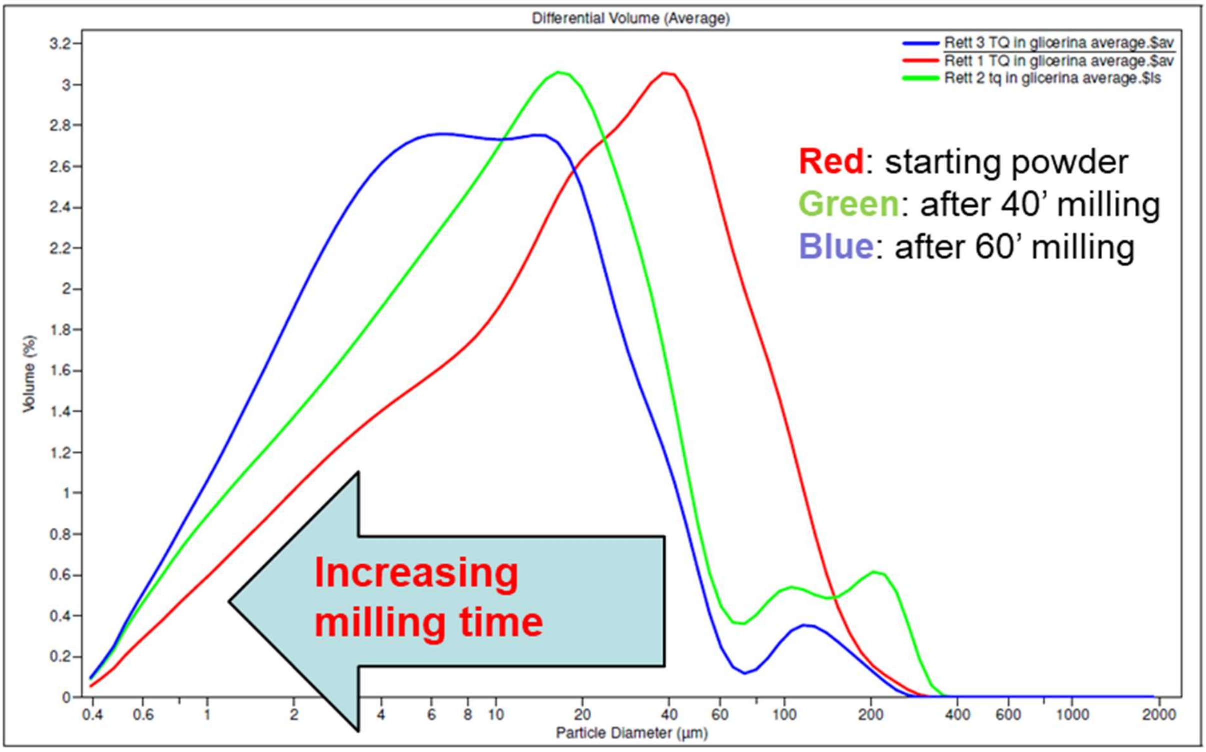
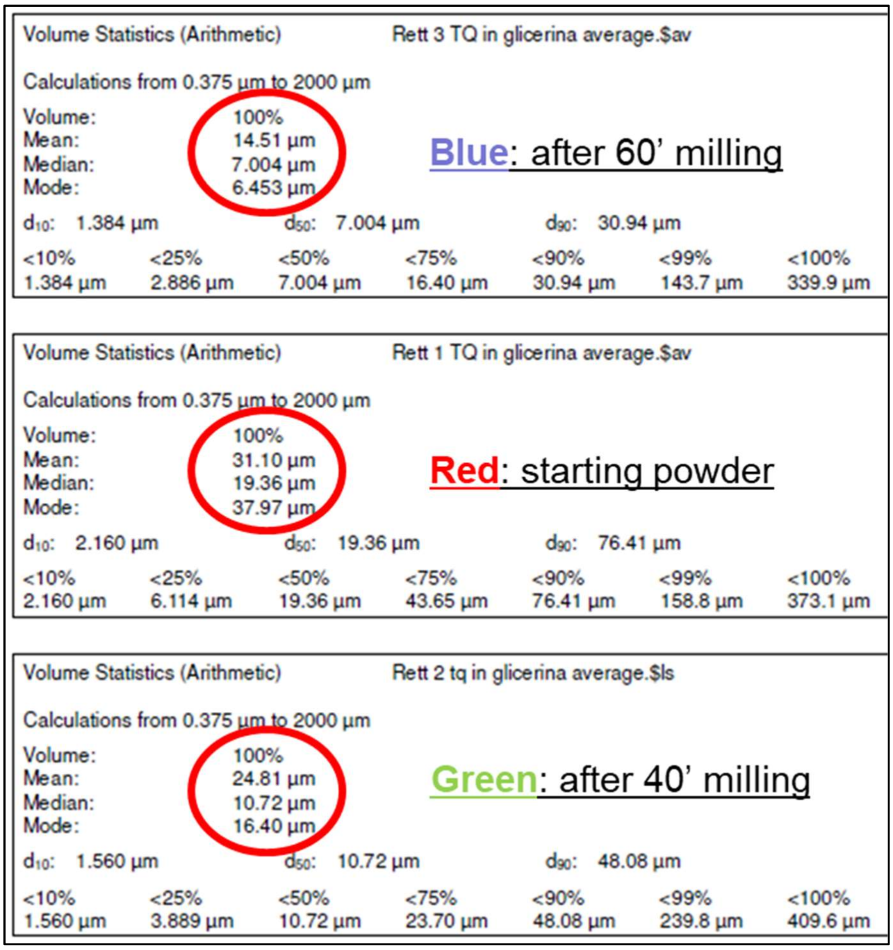


Figure 4.7 – Diagram of volume for each particle diameter.



```
Volume Statistics (Arithmetic)          Rett 3 TQ in glicerina average.$av

Calculations from 0.375 µm to 2000 µm
Volume:            100%
Mean:              14.51 µm
Median:            7.004 µm
Mode:              6.453 µm
d10:   1.384 µm             d50:   7.004 µm             d90:   30.94 µm
<10%        <25%        <50%        <75%        <90%        <99%        <100%
1.384 µm    2.886 µm    7.004 µm    16.40 µm    30.94 µm    143.7 µm    339.9 µm
```

Blue: after 60’ milling

```
Volume Statistics (Arithmetic)          Rett 1 TQ in glicerina average.$av

Calculations from 0.375 µm to 2000 µm
Volume:            100%
Mean:              31.10 µm
Median:            19.36 µm
Mode:              37.97 µm
d10:   2.160 µm             d50:   19.36 µm             d90:   76.41 µm
<10%        <25%        <50%        <75%        <90%        <99%        <100%
2.160 µm    6.114 µm    19.36 µm    43.65 µm    76.41 µm    158.8 µm    373.1 µm
```

Red: starting powder

```
Volume Statistics (Arithmetic)          Rett 2 tq in glicerina average.$ls

Calculations from 0.375 µm to 2000 µm
Volume:            100%
Mean:              24.81 µm
Median:            10.72 µm
Mode:              16.40 µm
d10:   1.560 µm             d50:   10.72 µm             d90:   48.08 µm
<10%        <25%        <50%        <75%        <90%        <99%        <100%
1.560 µm    3.889 µm    10.72 µm    23.70 µm    48.08 µm    239.8 µm    409.6 µm
```

Green: after 40’ milling

Figure 4.8 – Analysis of the granulometric distribution.

The instrument used for the granulometric analysis is a laser granulometer, a Beckman coulter LS 13 320 with dispersion of the powder in glycerin (Figure 4.9).

Figure 4.9 - Laser granulometer a Beckman coulter LS 13 320.

The particle shape and size (fineness) directly affect mechanical properties of geopolymers after activation. Smaller particles with higher surface area increase the level of both physical and chemical reactions of geopolymerization, such as dissolution rate, ions transportation, forming alumina-silicate species, which thereby control the initial setting time and geopolymeric gel phase (Chindaprasirt, *et al.*, 2010; Petermann, *et al.*, 2010). The flexural strength was also higher due to the change in morphology, allowing more dissolution rate of precursor particles in the alkaline environment (Kumar & Kumar, 2011). For fly ash geopolymers, the higher flexural strength was obtained using milled-fly ash (6.8 μm) compared to raw-fly ash (14.4 μm), including an ability to be cured at lower temperature (20 to 30°C) (Temuujin, *et al.*, 2009).

Milling of the powder

The ceramic waste was milled in a jar milling machine (Figure 4.10) for 40 minutes in the first case and for 60 minutes for the second step; after milling the material was sieved at 45 microns.

Figure 4.10 – Jar and jar milling machine.

MIX DESIGN

To develop this project, it is crucial the mix design. The dry waste powder is the more suitable waste than others ceramic wastes. All the tests made were in the direction to obtain geopolymers minimizing water absorption and maximizing mechanical strength. The samples in which -hydroxide (-OH), and - silicate were used, resulted to have lower water absorption, greater mechanical strength and lower efflorescence than samples with - introduction. In the table (4.8) below are present all the mixes tested following the explanation of table 4.9.

Table 4.8 - Evolution step by step of the geopolymer formulation mix design (the formulations are confidential, are available at the Marazzi laboratory).

SHAPING	**MIX DESIGN**								**PRESSING**	**CURING**						**CHARACHTERIZATION**		
	WASTE									**STEP 1**			**STEP 2**					
PRESSING	**RP**	**GRAN.**	**METAK.***	**KOH**	**NaOH**	**K silicate**	**Na silicate**	**H_2O**	**PRESSURE**	**TIME**	**TEMP.**	**R.H.**	**TIME**	**TEMP.**	**R.H.**	**SHRIINK.**	**MECH. STRENGHT**	**H_2O absorption**
	g	**TYPE**	**g**	**G**	**g**	**g**	**g**	**g**	**Kg/cm^2**	**h**	**T °C**	**%**	**h**	**T °C**	**%**	**%**	**N/mm^2**	**%**
RP1		1							300							1.2	4.2	14.21
RP2		1							300							2.1	5.4	12.01
RP3		1							300							0.9	3.8	15.44
RP4		1							300							2.3	5.6	12.55
RP5		1							300							2.5	11.1	9.98
RP6		1							300							3.1	13.2	8.58
RP7		1							300							0.2	N.M.	N.M.
RP8		1							300							0.3	N.M.	N.M.
RP9		1							300							0.9	4.8	16.85
RP10		1							300							1.1	5.3	15.22
RP11		1							300							1.7	5.9	13.47
RP12		-							300							0.6	2.3	22.15
RP13		1							350							2.2	8.4	12.55
RP14		1							350							2.7	10.5	10.48
RP15		1							350							0.9	7.9	14.69
RP16		1							350							1.9	10.1	11.32
RP17		1							350							3.3	14.3	7.52
RP18		1							350							3.4	14.2	7.02

RP19		1							350							0.2	N.M.	N.M.
RP20		1							350							0.4	N.M.	N.M.
RP21		1							350							1.1	6.9	14.33
RP22		1							350							1.4	7.5	13.58
RP23		1							350							2.0	8.6	12.34
RP24		-							350							0.4	2.7	21.25
RP25		1							400							3.1	10.9	9.88
RP26		1							400							3.5	12.3	8.56
RP27		1							400							2.8	9.8	11.25
RP28		1							400							3.1	10.4	9.85
RP29		1							400							4.4	15.8	6.67
RP30		1							400							4.6	16.2	6.02
RP31		1							400							0.4	N.M.	N.M.
RP32		1							400							0.5	N.M.	N.M.
RP33		1							400							2.3	10.3	11.25
RP34		1							400							2.1	11.5	10.56
RP35		1							400							3.1	12.9	8.98
RP36		-							400							0.8	3.5	18.64

* Metakaolin: Argical™ M1200S by Imerys, powder calcination in a flash calciner to obtain a hyper-reactive product with high specific surface.

N.M. - Not Measurable (not geopolymerized).

Table 4.9 – Mix design comments for the various formulations.

SAMPLE	COMMENTS
RP1	First samples were pressed at the pressure used for ceramic monoporosa at 300 Kg/cm^2 using the *tout-venant* precursor powder granulometry. All the activators have been tried with basic tests, the best tests have been identified those where - activators are used, to obtain the lowest water absorption and highest mechanical strength; the activators with - also give less efflorescence. The introduction of metakaolin has been tried to increase the polymerization and the reduction of water absorption without success. Curing was performed like in the following articles that tried to geopolymerize ceramic waste (Reig *et al.*, 2013; Sun *et al.*, 2013; Huseien, Ismail, *et al.*, 2018).
RP2	
RP3	
RP4	
RP5	
RP6	
RP7	
RP8	
RP9	
RP10	
RP11	
RP12	
RP13	The formulations of the previous tests were repeated by changing the pressing parameters. A higher pressure was tested, reaching 350 kg/cm^2. Increasing pressure, the results of water absorption and mechanical strength are better.
RP14	
RP15	
RP16	
RP17	
RP18	
RP19	
RP20	
RP21	
RP22	
RP23	
RP24	
RP25	Finally, was tested the pressure of 400 kg/cm^2, the maximum pressure reached by the laboratory press. It's possible to see that increasing the pressure the technological parameters improve. After these pressing tests, as the pressure increases, the general water absorption of all the geopolymer formulations decreases and the mechanical resistance increases. This behaviour show that the open porosity of the final samples decreases, thanks to a greater compaction of the powder. Increasing the contacts between the particles also increases the degree of dissolution, so geopolymerization, and densification increasing the mechanical resistance.
RP26	
RP27	
RP28	
RP29	
RP30	
RP31	
RP32	
RP33	
RP34	
RP35	
RP36	

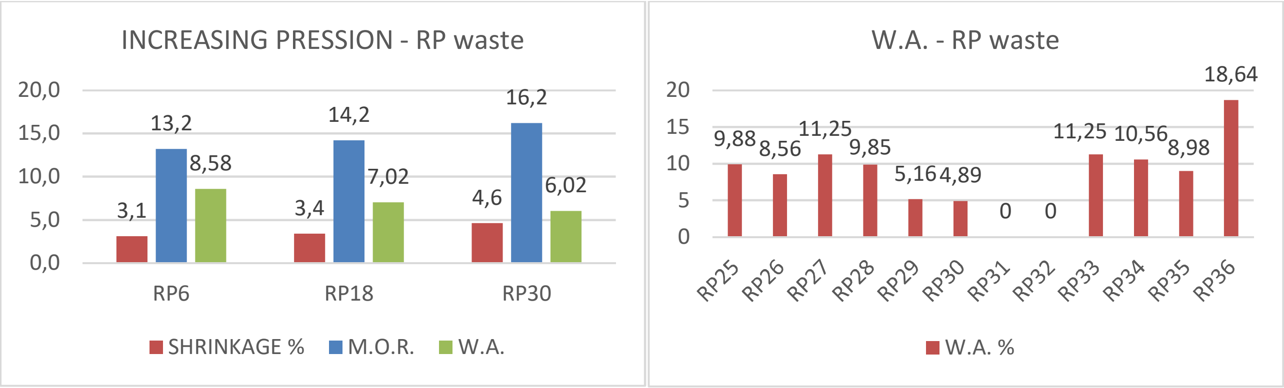


Figure 4.11 and 4.12 – The first figure shows increasing pressure results, RP6 pressed at 300 Kg/cm^2, RP18 pressed at 350 Kg/cm^2, RP30 pressed at 400 Kg/cm^2; Figure 4.12 show water absorption results of samples pressed at 400 Kg/cm^2.

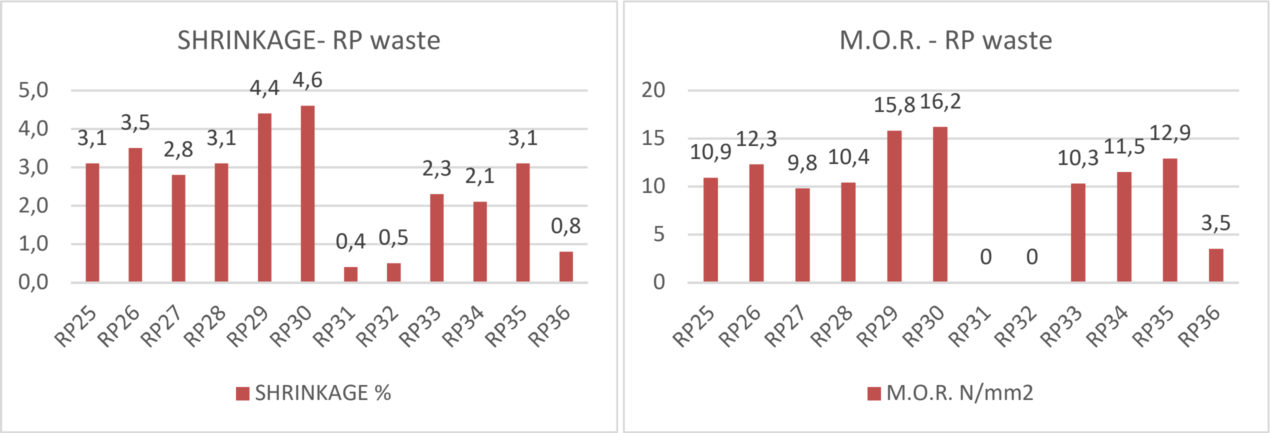


Figure 4.13 and 4.14 – The first figure show shrinkage results of samples pressed at high pressure 400 Kg/cm^2; the second figure show M.O.R. results of samples pressed at high pressure 400 Kg/cm^2.

Increasing pression of pressure (Figure 4.11) it's clear that the densification of the obtained geopolymer increase (shrinkage), so the water absorption decrease, and the mechanical strength go up. These three parameters are very strictly correlated and are very strictly correlated to the total grade of geopolymerization occurred. It's possible to see from the diagrams 4.12, 4.13, 4.14 the direct correlation between Modulus of rupture and the shrinkage, higher shrinkage values (more densification) correspond to higher strength. In the over parts the higher values of shrinkage correspond to the lower value of water absorption, obviously due to the more densification occurred in the matrix of the sample.

STUDIES ON CURING CONDITIONS

Research studies have revealed that heat curing is required to accelerate and improve the strength development in both early and later stages of geopolymerization. The applications applied to geopolymers production has the limitation of heat curing units (oven) and heat treatment technology. To widen its applications and being more convenient in practical works with reasonable strength, numerous researchers have attempted to develop geopolymers which suitable for curing varying the temperature. For the curing process is not only important the temperature, but other factors such as humidity, the activators present, and the characteristics of the precursor are equally important.

High humidity curing:

Khale and Chaudhary (2007) have reported the review of geopolymer by investigating the curing process with and without relative humidity control. Even though the curing temperature seems to be more dominant than relative humidity, curing samples in high humidity (in sealed bags) improved in strength compared to those cured without bags, the fast loss of interstitial water causes the cracking of the geopolymer matrix. So, is important to maintain the humidity during curing.

Concentration of alkaline activators:

As aforementioned, the increase in specific concentration of the alkaline activators could possibly produce geopolymers which can achieve reasonable strength at lower temperature and also give rise in compressive strength (Guo, *et al.*, 2010). Higher concentration increases stronger ion-pair formation than the lower one, providing more complete and quicker poly-condensation of particle interfaces (Xu & Van Deventer, 2000). The dissolution rate of the alumina-silicate materials could be observed in the rising up of reaction degree, indicating more beneficial for the geopolymerization (Mishra, *et al.*, 2008). The optimum concentration may vary due to many factors, like prime material composition or curing environment. Nevertheless, too low concentration could lead to inert binding activity, while too high concentration could lead to the forming coagulated structure and hinder the poly-condensation (Alonso & Palomo, 2001).

Fineness and shape of particles:

The particle shape and size directly affect mechanical properties of geopolymers after activation. Smaller particles with higher surface area increase the level of both physical and chemical reactions of geopolymerization, such as dissolution rate, ions transportation, forming alumina-silicate species, etc., which thereby control the initial setting time and geopolymeric gel phase (Chindaprasirt, *et al.*, 2010;

Petermann, *et al.*, 2010). The flexural strength was also higher due to the change in morphology, allowing more dissolution rate of precursor particles in the alkaline environment.

Mixing procedures:

In general, alumina-silicate prime materials and the combined alkaline solutions are incorporated and mixed together to form geopolymer material. It is, however, reported that other sequences of adopting alkaline solution could give shorter setting behaviour and higher strength than typical mixing process due to initial high leaching of Si and Al from hydroxide, followed by more binding activity from later added silicate (Chindaprasirt, *et al.*, 2007). Other examples of just adding with water were also studied to simplify working on-site or to achieve some curing criteria at low temperature e.g. crushing fully-activated final product into powder (Duxson & Provis, 2008) or using of pre-dry mixing process (working with solid activators instead of alkaline solutions).

Alternative heat curing sources:

As high curing temperature is able to improve mechanical strength of geopolymer material, many studies have attempted to gain benefit from this advantage. Previous studies have revealed that the strength improvement could be obtained by an extra heat curing from both external and internal heat sources. At early ages, the strength increases with the temperature since at higher temperatures the geopolymerization degree is higher, and therefore the amount of reaction products increases. On the other hand, at longer ages, when the geopolymerization degree is approximately the same, the quality of reaction products is the predominant parameter. The geopolymer developed at lower temperature grows slowly and then its quality is better in terms of lower porosity and higher toughness. The flexural strengths of specimens cured at different temperatures show the same trend as for compressive strengths (Rovnaník, 2010).

A lot of test were done modifying al the curing parameters and are showed in the table 4.10. All the approaches are listed in table 4.12.

All the tests were done taking into consideration the assumptions just made, mainly the fundamental thing is to have two curing steps, one at low temperature and one at higher temperature. With a combined approach, the components of high densification and increase in mechanical strength are tested.

Table 4.10 - Evolution step by step of the geopolymer formulation mix design modifying curing parameters (the formulations are confidential, are available at the Marazzi laboratory).

SHAPING	MIX DESIGN								PRESSING	CURING						CHARACHTERIZATION		
	WASTE									STEP 1			STEP 2					
PRESSING	RP	GRAN.	METAK.	KOH	NaOH	K silicate	Na silicate	H_2O	PRESS.	TIME	TEMP.	R.H.	TIME	TEMP.	R.H.	SHRIN.	MECH. STRENGHT	H_2O absorption
	g	TYPE	g	g	g	g	g	g	Kg/cm$_2$	h	T °C	%	h	T °C	%	%	N/mm^2	%
RP30		1							400							4.6	16.2	6.02
RP37		2							400							4.8	17.8	5.61
RP38		3							400							4.9	19.5	4.25
RP39		3							400							2.1	8.6	8.35
RP40		3							400							2.5	9.1	7.93
RP41		3							400							5.5	20.8	3.21
RP42		3							400							3.8	16.3	5.20
RP43		3							400							5.4	20.1	3.55
RP44		3							400							5.3	21.3	2.45
RP45		3							400							4.7	19.6	3.15
RP46		3							400							4.6	18.3	3.25
RP47		3							400							4.3	16.2	3.66
RP48		3							400							5.7	21.2	2.65
RP49		3							400							6.1	22.4	1.98
RP50		3							400							5.6	19.6	2.44
RP51		3							400							3.8	14.1	4.78

RP52		3							400							4.1	15.6	4.02
RP53		3							400							4.4	17.3	3.46
RP54		3							400							4.7	19.1	3.15
RP55		3							400							5.0	20.4	2.97
RP56		3							400							5.2	21.1	2.68
RP57		3							400							6.1	22.3	1.36
RP58		3							400							6.1	21.5	1.88
RP59		3							400							6.5	20.3	2.1
RP60		3							400							6.8	25.6	1.25
RP61		3							400							6.9	26.3	1.15
RP62		3							400							6.8	24.3	1.42
RP63		3							400							3.1	16.3	4.93
RP64		3							400							4.5	17.5	4.19
RP65		3							400							5.5	19.2	2.66
RP66		3							400							6.1	21.9	1.84
RP67		3							400							6.3	23.8	1.31

The best formulations were tested also with the casting method (table 4.11) but there is a big gap of results in water absorption and in mechanical strength, like the initial tests.

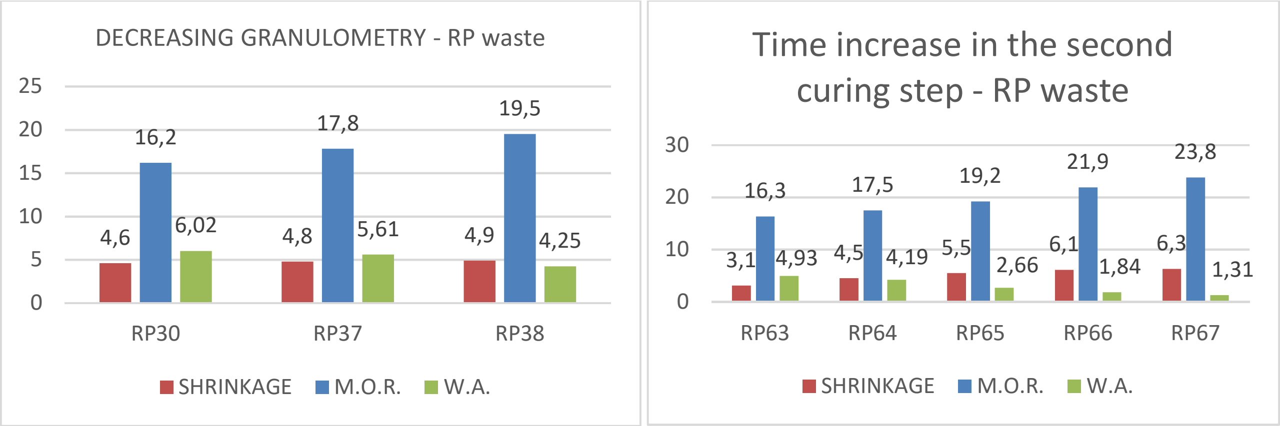
Table 4.11 - Evolution step by step of the geopolymer formulation mix design using casting method (the formulations are confidential, are available at the Marazzi laboratory).

SHAPING	**MIX DESIGN**								**PRESSING**	**CURING**						**CHARACHTERIZATION**		
	WASTE									**STEP 1**			**STEP 2**					
CASTING	**RP**	**GRAN.**	**METAK.**	**KOH**	**NaOH**	**K silicate**	**Na silicate**	**H_2O**	**PRESS.**	**TIME**	**TEMP.**	**R.H.**	**TIME**	**TEMP.**	**R.H.**	**SHRINK.**	**MECH. STRENGHT**	**H_2O absorption**
	g	**TYPE**	**g**	**g**	**g**	**g**	**g**	**%**	**Kg/cm^2**	**h**	**T °C**	**%**	**h**	**T °C**	**%**	**%**	**N/mm^2**	**%**
RP57		3							400							6.9	11.5	5.48
RP58		3							400							6.9	10.5	6.15
RP59		3							400							7.3	9.9	5.91
RP60		3							400							7.3	12.1	5.58
RP61		3							400							7.6	12.2	5.33
RP62		3							400							7.4	11.1	6.9

Table 4.12 – Comment on evolution step by step of the geopolymer formulation mix design modifying curing parameters.

PRESSING	**COMMENTS**
	After having identified a formulation that gave a good result, were tested the different technical parameters such as granulometry and temperatures, time and humidity of curing.
RP30	Tests to decrease the particle size until to reach the industrial milling limit (0.1% residual at 45 micron). It is observed that by decreasing the granulometry of the powder, the technological characteristics of the geopolymer are improving. There is more precursor surface that can react with the activators and there is greater compaction of the powders during pressing, the finer particles fill the smaller cavities.
RP37	
RP38	
RP39	Curing tests have been carried out in lower humidity environments but it can be observed from the tests that the samples with the best technological characteristics are obtained by curing in a high humidity environment. At low humidity the release of water creates cracks on the surface.
RP40	
RP41	Test of increasing temperature in the first 24 hours.
RP42	Test of reducing temperature in the second curing step.
RP43	Test of elimination of the first step of curing.
RP44	Test with curing methodology find in literature (Fernández-Jiménez *et al.*, 2008).
RP45	Tests to increase the curing temperature in the first step, using high temperatures at the start of curing. After 7 days the surface of the tile has steam expulsion cracks.
RP46	
RP47	
RP48	Temperature increase tests in the second step of curing using the methodology of (Fernández-Jiménez *et al.*, 2008).
RP49	Temperature increase tests in the first step of curing; second part of curing using the curing methodology of (Fernández-Jiménez *et al.*, 2008).
RP50	
RP51	Tests to reduce curing time at high temperatures with curing of (Fernández-Jiménez *et al.*, 2008).
RP52	
RP53	
RP54	
RP55	
RP56	
RP57	Starts the tests to improve the mix design, increasing the quantity of reagents up to saturation.
RP58	Tests to increase the quantity of reagents up to saturation.
RP59	Tests to increase the quantity of reagents up to saturation.

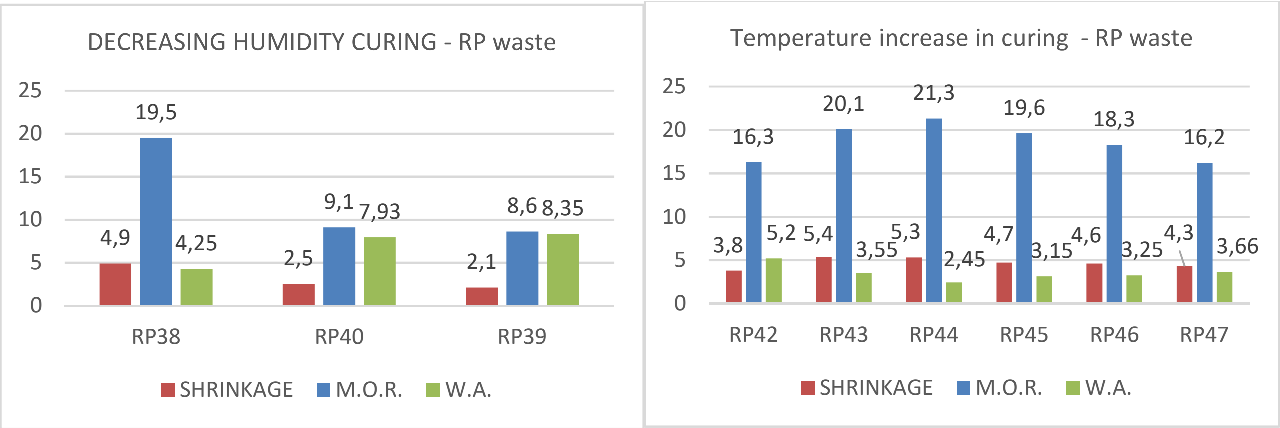
RP60	Saturation of -OH, was found unreacted - hydroxide.
RP61	Best formulation.
RP62	Saturation of -OH, was found unreacted - hydroxide.
RP63	Tests to decrease the curing times to optimize the geopolymer tile production process. After having tried to reduce the curing time was seen that the aging of the samples is fundamental to obtain good results. The geopolymerization process is not like the sintering process of the ceramic material, that gets stuck when the temperature drops, but continues over time with a slow structural reorganization of the matrix.
RP64	
RP65	
RP66	
RP67	
SHAPING **CASTING**	**COMMENTS**
	After identifying some formulation that gave a good result, we tested these formulations using the casting shaping method.
RP57	Tests to increase the quantity of reagents up to saturation.
RP58	Tests to increase the quantity of reagents up to saturation.
RP59	Tests to increase the quantity of reagents up to saturation.
RP60	Saturation of -OH, was found unreacted - hydroxide.
RP61	Best result for casting method.
RP62	Saturation of -, was found unreacted - hydroxide.



Figures 4.15 and 4.16 – The first image show the technological parameters decreasing the granulometry of the precursor; the second image show the technological parameters increasing the time of curing.

In the diagram 4.15 it's possible to see that the decreasing of the granulometric distribution help the geopolimerization. More the waste is milled and better are the technological features of the samples.

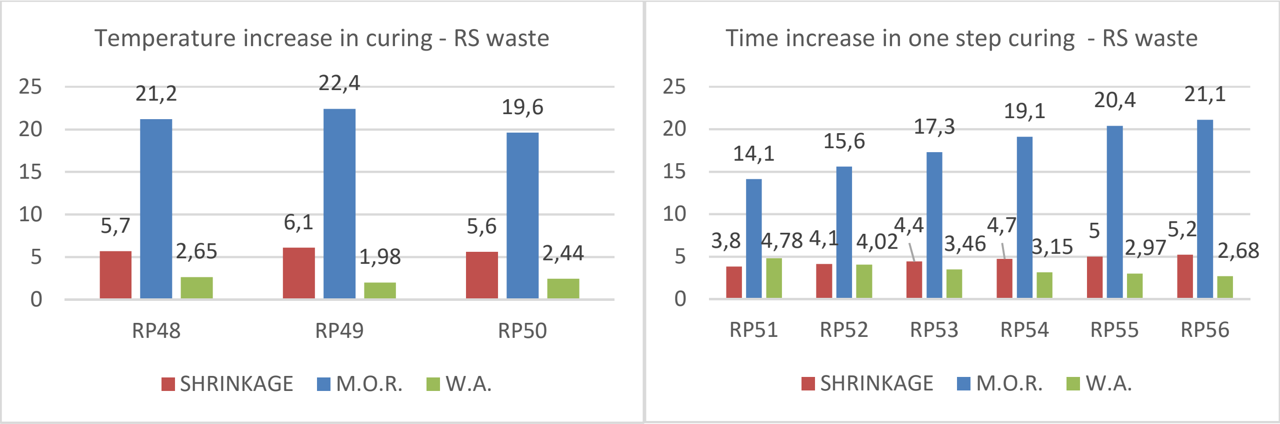
In the diagram 4.16 it's possible to see that increasing the time of curing in the second curing step help the geopolymerization process, all the technological parameters become better.



Figures 4.17 and 4.18 - The first image show the technological parameters decreasing the humidity of curing; the second image show the technological parameters increasing the temperature of curing.

Observing the diagram 4.17 is possible to see that is very important to maintain the highest humidity possible to reach a good curing condition, decreasing the curing humidity the geopolymerization is interrupted and the geopolymer matrix cracks for the water evaporation and contraction.

In the diagram 4.18 is shown that increasing the temperature in the second curing step from X to Y °C the technological features of the geopolymer become better, after the Y °C the improvement stop and the geopolymer start to get worse, probably because the water trapped inside the matrix evaporate and the condensation is interrupted.



Figures 4.19 and 4.20 - The first image show the technological parameters increasing the temperature of curing; the second image show the technological parameters increasing the time of curing.

In figure 4.19 is shown the results of trying to increase the temperature in the first curing step; from A °C, S °C to D °C; at S °C, the test RP49 reached the best results.

Trying to make only one curing step at the optimal temperature and decreasing time of curing, it's possible to see in the diagram 4.20 that time is already very important to develop the best technological feature and at 7 days the results are better, but the best tests have two curing step, and the first is at low temperature.

Regarding the last casted samples (Tab. 4.11), the addition of water, needed to reach acceptable workability, leads to a dramatic decrease in flexural strength, water addition decrease the precursor dissolution rate as the added water leads to a pH lowering (Bignozzi *et al.*, 2013).

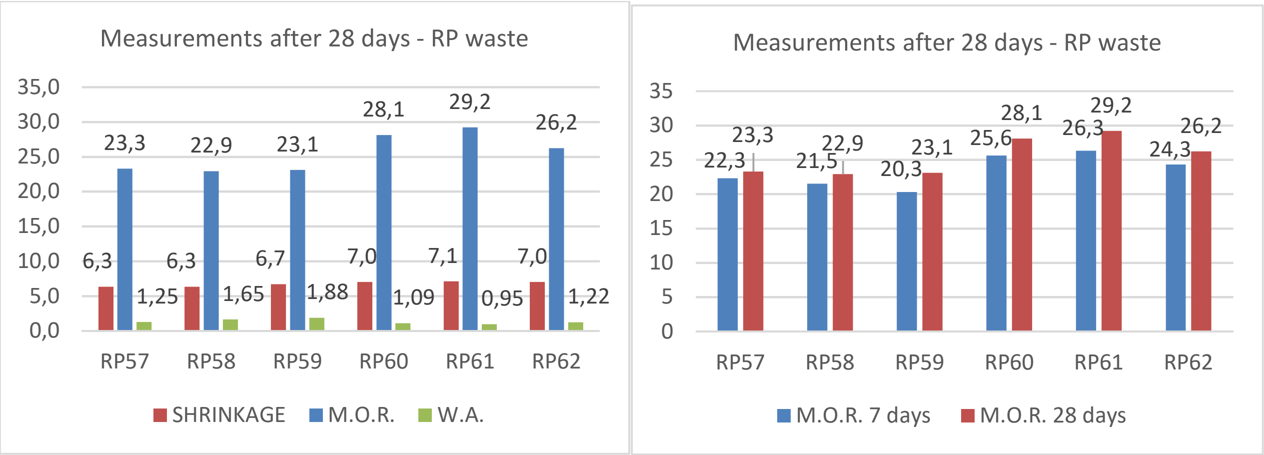
For the best pressed samples, the tests were repeated after 28 days to see if the process of geopolymerization was finished; but the results says us that the condensation process continue during the time and the geopolymer matrix continue in densification of the amorphous geopolymer material (Figures 4.21, 4.22, 4.23, 4.24).

Table 4.13 – Geopolymer samples characterization after 28 days.

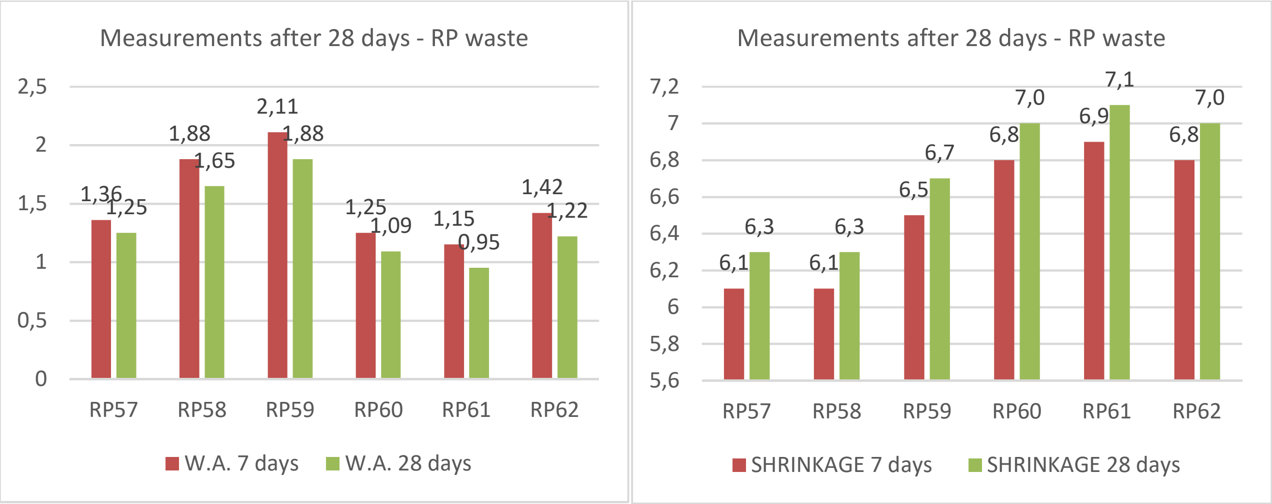
SHAPING	**CHARACHTERIZATION**		
PRESSING	**SHRINKAGE**	**MECH. STRENGHT**	**H_2O absorption**
	%	**N/mm^2**	**%**
RP57	6.3	23.3	1.25
RP58	6.3	22.9	1.65
RP59	6.7	23.1	1.88
RP60	7.0	28.1	1.09
RP61	7.1	29.2	0.95
RP62	7.0	26.2	1.22

Many previous studies confirmed that the strength of geopolymers can be improved at high curing temperature. At ambient temperature, the degree of geopolymerization underwent a very slow rate and the setting time cannot be measured within the first 3 days. The reaction kinetics depends on a series of intrinsic and extrinsic variables (particle size, chemical composition, pH of the medium, nature and concentration of the activator, curing time and temperature, etc.).

This behaviour was somehow expected since it is known that heat curing usually boosts the activation process, increasing the degree of reaction and therefore favouring the rapid development of a more resistant gel in terms of mechanical properties. But it's clear that also the time has a very important role in the geopolymer setting.



Figures 4.21 and 4.22 – The first image show the technological parameters after 28 days; the second image show the Modulus of rupture comparing the measurement after 7 days and 28 days.



Figures 4.23 and 4.24 - The first image show the water absorption comparing the measurement after 7 days and 28 days; the second image show the shrinkage comparing the measurement after 7 days and 28 days.

Curing considerations

The alkali activation produces the dissolution of the amorphous ceramic component (aluminosilicate material) and the formation, from dissolved precursor, of amorphous alkaline aluminosilicate gels. The amorphous compound formed displays the same characteristics of zeolites precursors reported during alkaline activation of metakaolin (Palomo *et al.*, 2008). In this process, an aluminium-rich phase was first formed and disappeared as the reaction progressed, to finally form a silicon-rich zeolite precursor. The study of mechanical properties as a function of time and temperature of activation shows the important role played by curing conditions. For a long curing time and high temperature, a continuous aluminosilicate matrix is formed that enhances mechanical behaviour of the formed product (Palomo *et al.*, 2008).

The slower the reaction that is produced (by decreasing the curing temperature), the higher the amount of aluminium is incorporated into the formed product. Moreover, different stages are produced during alkaline activation. An appropriate choice of reaction time and curing temperature can lead to the obtention of different products of reaction. The increase of the reaction time decreases the amount of aluminium incorporated in the final product, improving the mechanical properties. This improvement goes parallel to the formation of a homogeneous aluminosilicate matrix. When the time of reaction increases and curing temperature is kept at 85°C, a meta-stable intermediate aluminium-rich phase evolves to a more stable silicon-rich phase (Palomo *et al.*, 2008). The more stable silicon-rich phase increases the mechanical strength of the obtained geopolymer. The dissolution of the first formed aluminium rich phase and the formation of a new silicon-rich zeolite precursor indicates that stability of the second product is higher (Palomo *et al.*, 2008). An increase in curing temperature (85°C) gives an increase of chemical reaction, accelerating more geopolymeric gel formation in the matrices and enhancing the mechanical strength in early stage of geopolymerization (Rovnaník, 2010). However, many researchers have revealed that too high temperature of curing, or too long curing duration seemed to result in a decrease in strength (Demie, *et al.*, 2011; Reddy, *et al.*, 2012) but in this project seems that the time increase the strength.

Alkaline aluminosilicate gel is formed as the major reaction product regardless of the composition of the precursor. For short reaction times, formed gels are constituted by an Al-rich phase, in which Si tetrahedra are surrounded by four Al tetrahedra (Q^4(4Al) units). As the reaction progresses, this phase evolves into a more stable Si-rich phase, in which a higher amount of Si occupies Q^4(3Al) and Q^4(2Al) environments. In these materials, the increment of Si/Al ratios, improve considerably mechanical properties of aluminosilicate gels formed (Fernández-Jiménez *et al.*, 2006).

Combined effects of Na-KOH and Na-K_2SiO_3 in geopolymerization:

The mix of potassium hydroxide and potassium silicate solution is one of the most widely used alkaline activators for geopolymer production. From the previous testing, it is known that soluble hydroxide obviously dissolves Si and Al from source of materials while soluble silicate improves the poly-condensation of geopolymer and also controls the amount of silicate in mixtures as a binder. Typical geopolymers was not able to solidify, even left at ambient temperature for over 24 hours. The combination of silicate and hydroxide solutions with ceramic waste offers appropriate conditions for geopolymerization, leading to a larger increase of geopolymeric gel phase than that waste with either sodium silicate or sodium hydroxide alone. More dissolved Si and Al (from hydroxide solution) together with additional Si and more condensing activity (from silicate solution) led to the highest flexural strength.

The study of alkaline activators can be summarised as hydroxide solution played a very important role in dissolving prime materials and other compounds in ceramic waste. The soluble silicate, which is normally used as another source of silica, improves the binding activity or geopolymerization of samples. Therefore, the resulted products of the mixture synthesis with -OH and -SiO_3 obviously obtained better performances than those with hydroxides or silicates alone.

Increasing the proportion of potassium silicate solution in the formulations, generally encourages geopolymer gel formation. Use of higher amounts of -silicate resulted in flexural strengths for the geopolymer higher than those samples made with the lowest amounts of -silicate. These differences in strength can arise either from formation of more gel or more likely from a gel with optimal Si/Al.

Also, the contents of CaO in the precursor substance played a significant role to achieve the final hardening of geopolymers. An increasing CaO content caused the enhancement in the mechanical characteristics and subsequent reduction in setting time. There are two models to understand the binding characteristics of geopolymers with alkaline solution activation. First model concerns with the mild alkaline solution activation of silica (Si) plus Ca substances to produce C-A-S-H gels as main product (called alkali-activated). Second model deals with the alkaline solution activation of Si plus Al substances that needs a robust alkali solution to produce N-A-S-H gels as the major outcome (called geopolymer). N-A-S-H based geopolymers need of curing at higher temperature (Fernández-Jiménez *et al.*, 2008; Palomo *et al.*, 2008). The used precursor doesn't contain Ca so was increased the temperature in the second step of curing to obtain good mechanical behaviour of the samples.

5. TECHNOLOGICAL CHARACTERIZATION

There is a huge amount of literatures on the properties and applications of geopolymer material. Geopolymer material has been previously proven to have good physical and chemical properties, although depending on experimental conditions. The benefits from being a waste treatment process and a low carbon-dioxide material are also highly concerned together with benefits in cost reduction. Main properties of achieved geopolymer products can be summarised in this chapter.

For ceramic tiles, the reference standard is ISO 10545. The geopolymer tiles obtained were tested with the same procedures concerning ceramic tiles (Table 5.2).

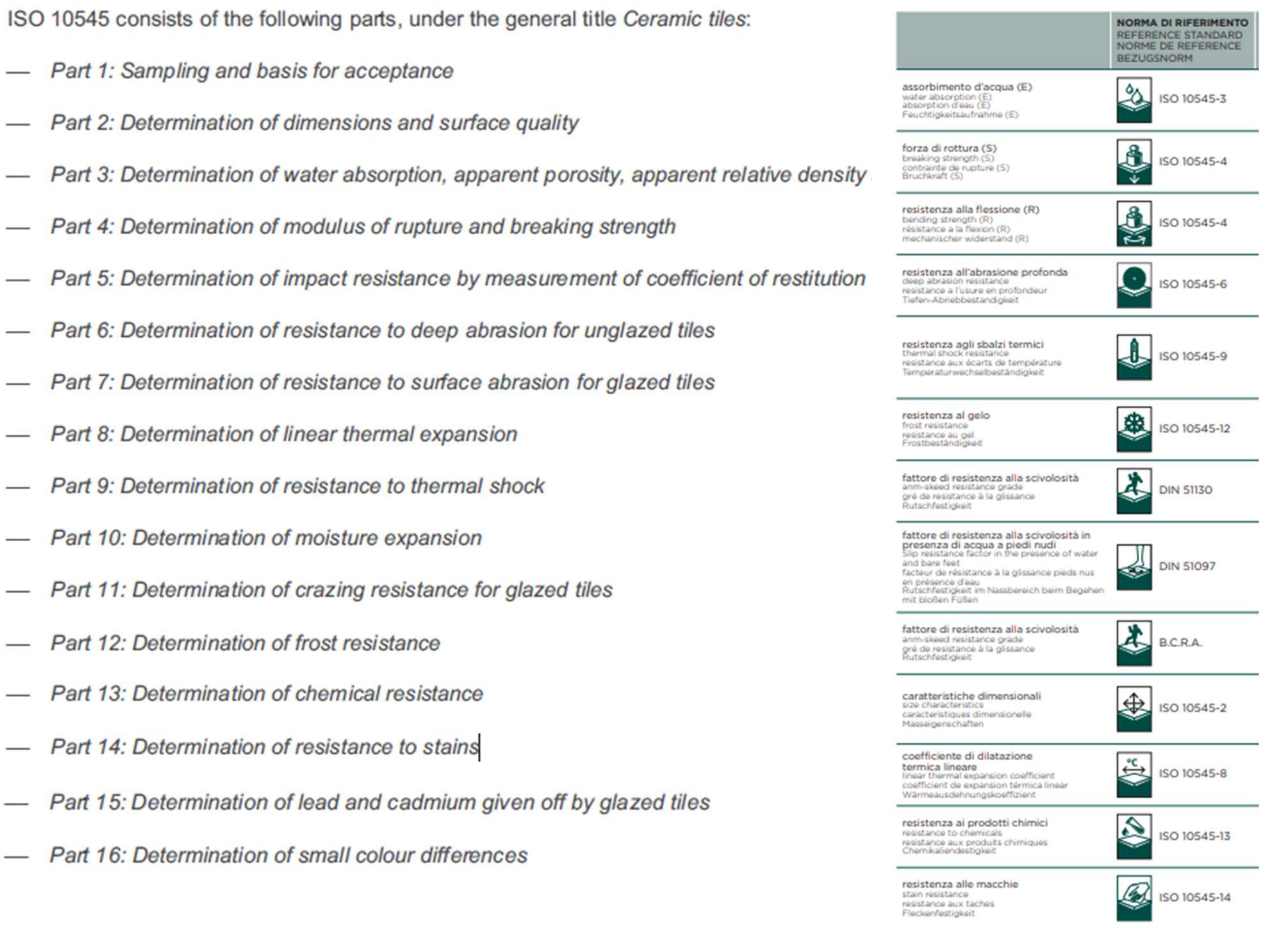
In the first part of the table 5.1 are indicated the norm tiles requirements of the ISO 10545, as the water absorption, the flexural strength and the modulus of rupture, these parameters classify the ceramic material. The quality of the ceramic material increases whit the decrease of the water absorption, the class BIa is the top of range.

In the second part of the table, it’s possible to see the technological parameters of the best geopolymers obtained with the two preparation methods. Observing these data, the pressing method resulted the most performing one because the geopolymer tiles can reach a greater class.

Table 5.1 – Requirement of the ISO 10545 standard and results of the best samples obtained.

CLASS	**Water Abs.**	**Flexural strength**	**Modulus of rupture**
BIa*	≤ 0.5 %	Thickness < 7.5 mm: ≥ 700 N Thickness ≥ 7.5 mm: ≥ 1300 N	≥ 35 N/mm^2
BIb*	0,5 %< X ≤ 3 %	Thickness < 7.5 mm: ≥ 700 N Thickness ≥ 7.5 mm: ≥ 1100 N	≥ 30 N/mm^2
BIIa*	3 %< X ≤ 6 %	Thickness < 7.5 mm: ≥ 600 N Thickness ≥ 7.5 mm: ≥ 1000 N	≥ 22 N/mm^2
BIIb*	6 %< X ≤ 10 %	Thickness < 7.5 mm: ≥ 500 N Thickness ≥ 7.5 mm: ≥ 800 N	≥ 18 N/mm^2
BIII*	> 10 %	Thickness < 7.5 mm: ≥ 500 N Thickness ≥ 7.5 mm: ≥ 800 N	≥ 12 N/mm^2
K-Geopolymer parameters: BEST SAMPLES			
PRESSING METHOD	**1.15 %**	**Sample thickness: 7.1 mm = 883 N**	**26.3 N/mm^2**
CASTING METHOD	**5.33 %**	**Sample thickness: 7.4 mm = 435 N**	**12.2 N/mm^2**

Table 5.2 - Tests required by the ISO 10545 standard.



ISO 10545 consists of the following parts, under the general title *Ceramic tiles*:

— *Part 1: Sampling and basis for acceptance*

— *Part 2: Determination of dimensions and surface quality*

— *Part 3: Determination of water absorption, apparent porosity, apparent relative density*

— *Part 4: Determination of modulus of rupture and breaking strength*

— *Part 5: Determination of impact resistance by measurement of coefficient of restitution*

— *Part 6: Determination of resistance to deep abrasion for unglazed tiles*

— *Part 7: Determination of resistance to surface abrasion for glazed tiles*

— *Part 8: Determination of linear thermal expansion*

— *Part 9: Determination of resistance to thermal shock*

— *Part 10: Determination of moisture expansion*

— *Part 11: Determination of crazing resistance for glazed tiles*

— *Part 12: Determination of frost resistance*

— *Part 13: Determination of chemical resistance*

— *Part 14: Determination of resistance to stains*

— *Part 15: Determination of lead and cadmium given off by glazed tiles*

— *Part 16: Determination of small colour differences*

	NORMA DI RIFERIMENTO REFERENCE STANDARD NORME DE REFERENCE BEZUGSNORM
assorbimento d'acqua (E) water absorption (E) absorption d'eau (E) Feuchtigkeitsaufnahme (E)	ISO 10545-3
forza di rottura (S) breaking strength (S) contrainte de rupture (S) Bruchkraft (S)	ISO 10545-4
resistenza alla flessione (R) bending strength (R) résistance a la flexion (R) mechanischer widerstand (R)	ISO 10545-4
resistenza all'abrasione profonda deep abrasion resistance resistance a l'usure en profondeur Tiefen-Abriebbestandigkeit	ISO 10545-6
resistenza agli sbalzi termici thermal shock resistance resistance aux écarts de température Temperaturwechselbeständigkeit	ISO 10545-9
resistenza al gelo frost resistance resistance au gel Frostbeständigkeit	ISO 10545-12
fattore di resistenza alla scivolosità anm-skeed resistance grade gré de resistance à la glissance Rutschfestigkeit	DIN 51130
fattore di resistenza alla scivolosità in presenza di acqua a piedi nudi Slip resistance factor in the presence of water and bare feet facteur de résistance à la glissance pieds nus en présence d'eau Rutschfestigkeit im Nassbereich beim Begehen mit bloßen Füßen	DIN 51097
fattore di resistenza alla scivolosità anm-skeed resistance grade gré de resistance à la glissance Rutschfestigkeit	B.C.R.A.
caratteristiche dimensionali size characteristics caracteristiques dimensionelle Masseigenschaften	ISO 10545-2
coefficiente di dilatazione termica lineare linear thermal expansion coefficient coefficient de expansion térmica linear Wärmeausdehnungskoeffizient	ISO 10545-8
resistenza ai prodotti chimici resistance to chemicals resistance aux produits chimiques Chemikaliendestigkeit	ISO 10545-13
resistenza alle macchie stain resistance resistance aux taches Fleckenfestigkeit	ISO 10545-14

WATER ABSORPTION PROPERTIES

For ceramic tiles, water absorption is used to classify ceramic tile products. The water absorption is in this case indicated like the open porosity of a tile. The impregnation of the open porosity is achieved by a vacuum method and a phase of suspension in water.

The ISO 13006 standard for tiles says that the correct methodology to measure the water absorption is the following one: the dry tile has to stay 30 minutes under vacuum (Figure 5.1) in a range of pressure 5-15 kPa. Then, maintaining the vacuum, slowly admit sufficient water, taking no longer than 10 minutes to cover the tiles by at least 5 cm. Then release the vacuum and allow the tiles to remain submerged for 15 minutes.

Water absorption test was carried out on geopolymer samples: Dried samples were weighted before (Mi) and after (Mw) the descripted vacuum test. Water absorption was calculated by the following equation: WA% = (Mw-Mi)/Mi*100.

Figure 5.1 – Vacuum machine.

Geopolymers has low water absorption due to its dense structure (Davidovits, 2002). Pores in structure partially depended on water content in mixing and affect the porosity of the final geopolymers. It was also found that overheating during curing leads to an increase of early strength with large pores while lower temperature of curing leads to a decrease of early strength but with smaller pores. By this, it means that the size of pores is directly related to aging, amount of water used and curing regimes in the processing, which dominate the final density of that geopolymers (Lizcano, *et al.*, 2012).

At early ages, the pores are slightly larger, but during aging the maximum volume shifts towards smaller pores and these changes in pore structure are practically finished in 7 days. This shifting of mean pore size can be explained by gradual filling of larger pores with reaction products as the geopolymerization proceeds (Rovnaník, 2010). Larger pores observed in heated geopolymer have their origin in rapid formation of hard structure. When the process of hardening proceeds too quickly, it results in less ordered structure of poorer quality with relatively larger pores left in the matrix, whereas in the geopolymer cured at lower temperatures the products of geopolymerization can gradually fill the voids in the basic structure and thus make it denser. This suggestion is supported by comparison of pore distribution in geopolymers cured at different temperatures. The pore volume slightly increases with rising temperature of curing. Therefore curing at higher temperatures results in increased pore volume and pore size, whereas low temperature curing increases the bulk density (Rovnaník, 2010). In this project was decided to make two different steps of curing, the first at low temperature to decrease the porosity of the final geopolymer, and the second at higher temperature to increase the mechanical strength.

MECHANICAL PROPERTIES

Flexural strength of tile sample (160mm x 80mm x 7mm) was determined by using the testing machine (Figure 5.2) in accordance with the ISO 10545. The samples were placed on the flexural test rig and are broken by applying a perpendicular force to the plane of the sample. Fragmented pieces were kept for other tests like XRD and SEM analysis.

The ISO 10545 standard for ceramic tiles comprises two magnitudes to assess mechanical strength:

Flexural strength or Breaking strength: is in direct relation to the load applied to the piece, with a correction coefficient that relates the distance between supports and the width of the specimen, expressed in newtons (N). The result of the test is a function of the thickness of the piece for the same type of material.

Modulus of rupture: Also known as bending strength, which is deduced from the breaking strength magnitude using a mathematical formula (breaking strength divided by the square of the minimum thickness in the break section). The result of the test, expressed in newtons per square millimetre (N/mm2; 1 N/mm2 = 1 MPa), provides us with an indication of the mechanical strength of the ceramic pieces, irrespective of their thickness. It is therefore understood that the modulus of rupture is an intrinsic characteristic of the material, in other words that two ceramic pieces manufactured according to the same process and which differ only in their thickness have the same modulus of rupture, although the force required to break them is much greater in the thicker piece.

Figure 5.2 – Flexural strength testing machine.

It was revealed that less setting time of geopolymers requires higher curing temperature at above room temperature as well as high concentration of alkaline solution, which eventually accelerates the hardening and rate of geopolymerization of geopolymer material (Hardjito, *et al.*, 2008; Rovnaník, 2010).

Mechanical strength is widely used to assess property of geopolymers, due to its representative, simplicity and low cost of testing. The compressive strength of fly ash based-geopolymer material could achieve up to 95 MPa at the age of 28 days (Fernández-Jiménez, *et al.*, 2007), which is equivalent to ultra-high strength concrete (MacGregor, 1997). In addition, other measurements on strength were also tested and proved to be equal to or even better than those of cement e.g. flexural strength (Fernández-Jiménez & Palomo, 2005), split tensile strength (Sofi, *et al.*, 2007) and bond strength (Hu, *et al.*, 2008). It can be drawn that the improvement in strength clearly refers to more completion of chemical dissolution and geopolymerization. But for this project it will be different from the literature because generally the comparison is between geopolymer and mortars, cement or concrete that have the same forming method; but in the case of the comparison with ceramic, the geopolymer has to be similar to a sintered product. The glassy products obtained by melting acquire a very high mechanical resistance.

The presence of a proper amount of soluble Si in the activation solution contributes the development of the flexural strength, thus geopolymers activated by silicate solutions exhibited much higher flexural strength than those activated by hydroxide solutions. For the case of geopolymer activated by the KOH and silicate solution containing K^+, they exhibit a higher flexural strength, the stronger basicity of K^+, allow higher rates of silicate dissolution (Sun *et al.*, 2013). Also, in another work all the minerals activated demonstrate higher compressive strength after geopolymerization in KOH than in NaOH, despite the higher extent of dissolution in NaOH than in KOH. When KOH was used, the mean compressive strength of all minerals was 42% higher than for NaOH (Xu and Van Deventer, 2000). Evidently, factors such as the % of CaO, % of K_2O and the molar Si/Al ratio in the original mineral, the type of alkali, the extent of dissolution of Si and the molar Si/Al ratio in solution during dissolution tests have a significant correlation with compressive strength. Of these factors, the % of CaO, the molar Si–Al in the original mineral, the use of KOH, the extent of dissolution of Si and the molar Si/Al ratio in solution show a positive correlation, while the % of K_2O and the use of NaOH correlate negatively with strength (Xu and Van Deventer, 2000). It is worth noting that the hardness of the original minerals, which gives an indication of the original strength, has a positive correlation with the ultimate strength, but it is not as significant as the other variables mentioned above (Xu and Van Deventer, 2000). This suggests that the geopolymeric matrices where are not merely the products of different mineral particles acting as fillers or aggregate in a stabilised gel formed from the dissolution in the presence of silicate solution. Instead, the significance of the molar Si/Al ratio during the alkaline dissolution of the individual minerals indicates that compressive strength is the result of complex reactions between the mineral surface and the concentrated alkaline silicate solution (Xu and Van Deventer, 2000). After geopolymerization, the undissolved particles remain bonded in the matrix, so that the hardness of the minerals correlates positively with final compressive strength, as expected. By "forward selection", the following three factors were identified as having a significant effect on strength: 1) the type of alkali, 2) %K_2O in the mineral, and 3) ppm Si in solution (Xu and Van Deventer, 2000). The larger K^+ favours the formation of larger silicate oligomers with which $Al(OH)_4^-$ prefers to bind. Therefore, in KOH solutions more geopolymer precursors exist which result in better setting and stronger compressive strength of the geopolymers than in the case of NaOH (Xu and Van Deventer, 2000).

It can be that the mechanical strength of the material increases during formation of the gel in first stage of the alkaline activation (coating of particles with an Al-rich aluminosilicate gel, Gel 1), but increases further as a result of the Si enrichment of the materialitious materials (formation of the Si enriched aluminosilicate gel, Gel 2). In the case of high "(Si/Al) Reactive" ratio, the lowest mechanical strength is obtained as a consequence of the smaller amount of Si incorporated into the aluminosilicate gel (low degree of reaction attained) (Fernández-Jiménez *et al.*, 2006).

The availability of dissolved Al and Si at a given moment highly influences the kinetics of the geopolymerization. Other variables, as concentration of the activator, curing temperature and curing time, play also a significant role in kinetics of gels formation. From a thermodynamic point of view the process of activation can be divided up to three main stages:

- Stage 1 (Dissolution stage): Most of the vitreous component is dissolved. No mechanical strength development is observed during the dissolution process.

- Stage 2 (Induction period): During the induction period a massive precipitation of a metastable Gel (named Gel 1) takes place, that produces the coating of unreacted particles. This gel displays the singular characteristic of incorporate (into the microstructural framework) a big part of the reactive aluminium existing in the precursor, but not all the silicon. The beginning of this stage is associated to the initial setting of the paste. In this case a real degree of reaction 2 around 70–80% (the apparent degree of reaction 3 has been estimated about 30–40%), is obtain but the mechanical strength development of the material is not important.

- Stage 3 (Silicon incorporation stage): Finally, stage 3 corresponds to a period in which Gel 1 is transformed into Gel 2. This new gel is a Si-rich material since it accommodates into the structural framework that silicon which is more slowly dissolved in the alkaline medium.

Naturally, during the time in which Stage 3 is running the reaction degree continues advancing till reaching values > 90%. At the same time, mechanical strength increases considerably. When the content of Gel 1 in the alkali activated materials is higher than the content of Gel 2, the mechanical strength development is low, however when the content of Gel 2 is higher than Gel 1, the mechanical strength gain notably increases (Fernández-Jiménez *et al.*, 2006).

Mechanical properties depend strongly on the characteristics of the continuous precipitate that interconnect unreacted particles. In particular, the absence of the continuity in particles connection between particles should reduce considerably mechanical performances. Differences on the amount of the deposited aluminosilicate explain different compressive strengths measured. The coverage of precursor particles with formed aluminosilicates produces also a substantial slowdown of the reaction, retarding the dissolution of silicon and aluminium required to the formation of gels. As the reaction progresses, further amounts of SiO_2 and Al_2O_3 are dissolved, favouring the evolution of the initial Gel 1 (Al-rich phase) into a new Gel 2 (Si-rich phase) (Fernández-Jiménez *et al.*, 2006).

An index of achievement of good mechanical resistance is also the drying shrinkage, that is the decrease in volume of geopolymer material with time and is independent of the external actions. But sometimes it leads to cracking or dropping in load-carrying capacity if it is not properly controlled. Alternatively, expansion can cause cracks when its parts fail to withstand the force or the repeated cycles of expansion. Previous research studies have indicated that geopolymers had superior shrinkage and expansion resistance (Fernández-Jiménez, *et al.,* 2007; Wallah, 2009), including thermal properties when exposed at elevated temperature (800 to 1000 °C).

Reinforcement of geopolymers with fibers

Fiber reinforced geopolymer composites may be considered a solution to improve flexural strength and fracture toughness. Woven fabrics, mats or unidirectional fibers, such as carbon, E-glass, Kevlar or basalt fibers have been so far the most widely used to cast continuous fiber-reinforced composites in civil engineering applications. More recently, structural composite materials obtained from inorganic matrix have been designed to deal with the major drawbacks deriving from the use of organic polymer resins. As a matter of fact, a significantly low resistance to UV radiation and high-temperatures is largely limiting organic matrix use in a wide field of applications (Natali, Manzi and Bignozzi, 2011).

With the aim to go on with the research on inorganic matrices, fiber reinforced composite materials based on geopolymers are currently widely investigated in literature. Different types of fiber reinforcements have already been employed in various geopolymer systems to improve their flexural strength, impact behaviour and failure mode. It has been reported that adding reinforcing fibers to a brittle matrix helps to control micro and macro-cracks diffusion through the material by generating a bridging effect, as well as to change the post-cracking behaviour of the material from a brittle fracture mode to a ductile one, thanks to its enhanced strain energy dissipation ability (Natali, Manzi and Bignozzi, 2011).

In literature there is a lot of research concerning the reinforcement of geopolymers with fibers of different materials (Natali *et al.*, 2011; Masi *et al.*, 2015; Carabba *et al.*, 2017). Obviously also in this case some possible usable materials have been provided, the important thing is that these fibers are not porous material because they would increase the absorption of water and worsen the general technological features of the geopolymeric tile.

Therefore the possible usable fibers are those with low porosity such as ceramic fibers, mineral fibers, basalt fibers, glass fibers or steel fibers (Lorenza Carabba *et al.*, 2017).

MICROSTRUCTURE INVESTIGATIONS

Microstructure investigation has been carried out by SEM (Scanning Electron Microscope) and EDS (Energy Dispersive X-ray Spectrometry) with the aim to find a relationship between physical-mechanical properties of geopolymer samples and reagents.

At first was made a preliminary SEM study on the samples prepared for the identification of the best geopolymerizing ceramic waste. The mixes were done considering the total amount of precursor like ceramic waste, for testing the capability to geopolymerize of these materials. The samples shaping was done in two different methods: Casting method and pressing method. The first by transferring the slurry in a mould, the second by pressing the powder whit a lab press. The figure 5.3 is a macro view of samples obtained with the casting method and pressing method. Is clearly shown that the casted samples (1) 1FCW CAST and (3) 1RP CAST have a macro-porosity with less dimension in relation of the pressed samples (2) 1FCW PRESS, (4) 1RP PRESS.

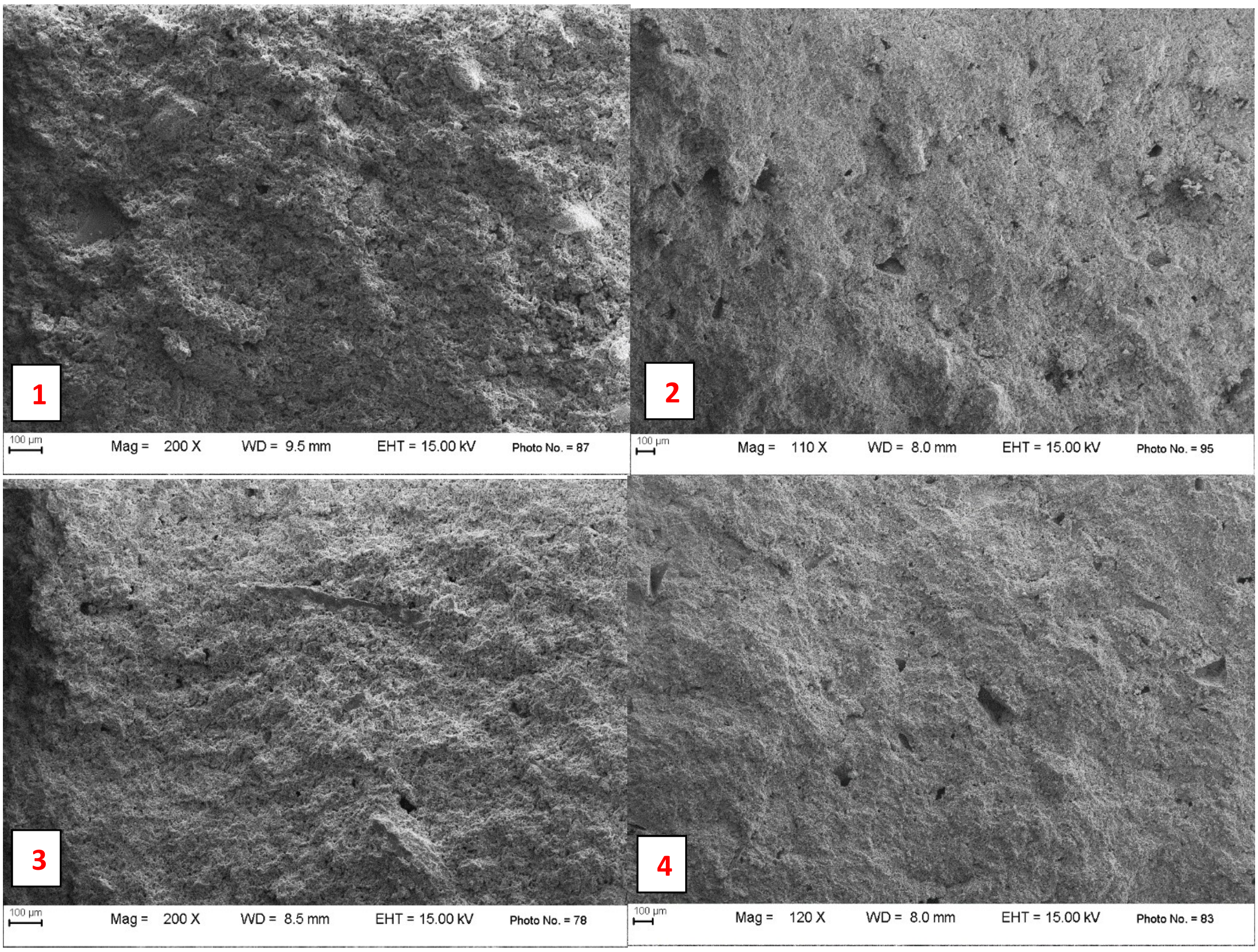


Figure 5.3 - SEM micrographs of (1) 1FCW CAST, (2) 1FCW PRESS, (3) 1RP CAST, (4) 1RP PRESS.

In Figure 5.4 are focused the pores and it's possible to see that with the cast method (1, 3) the morphology of the pores is probably caused by bubbles formed during the mixing of the sludge. The mechanically adjustment to remove by vibration the entrained air wasn't completed.

In the samples obtained by pressing (2, 4) the pores have polygonal dimension. This characteristic probably is due why they were formed after the dissolution of unreacted pieces of reagents. These unreacted pieces dissolves during curing time and leave polygonal pores in the final sample.

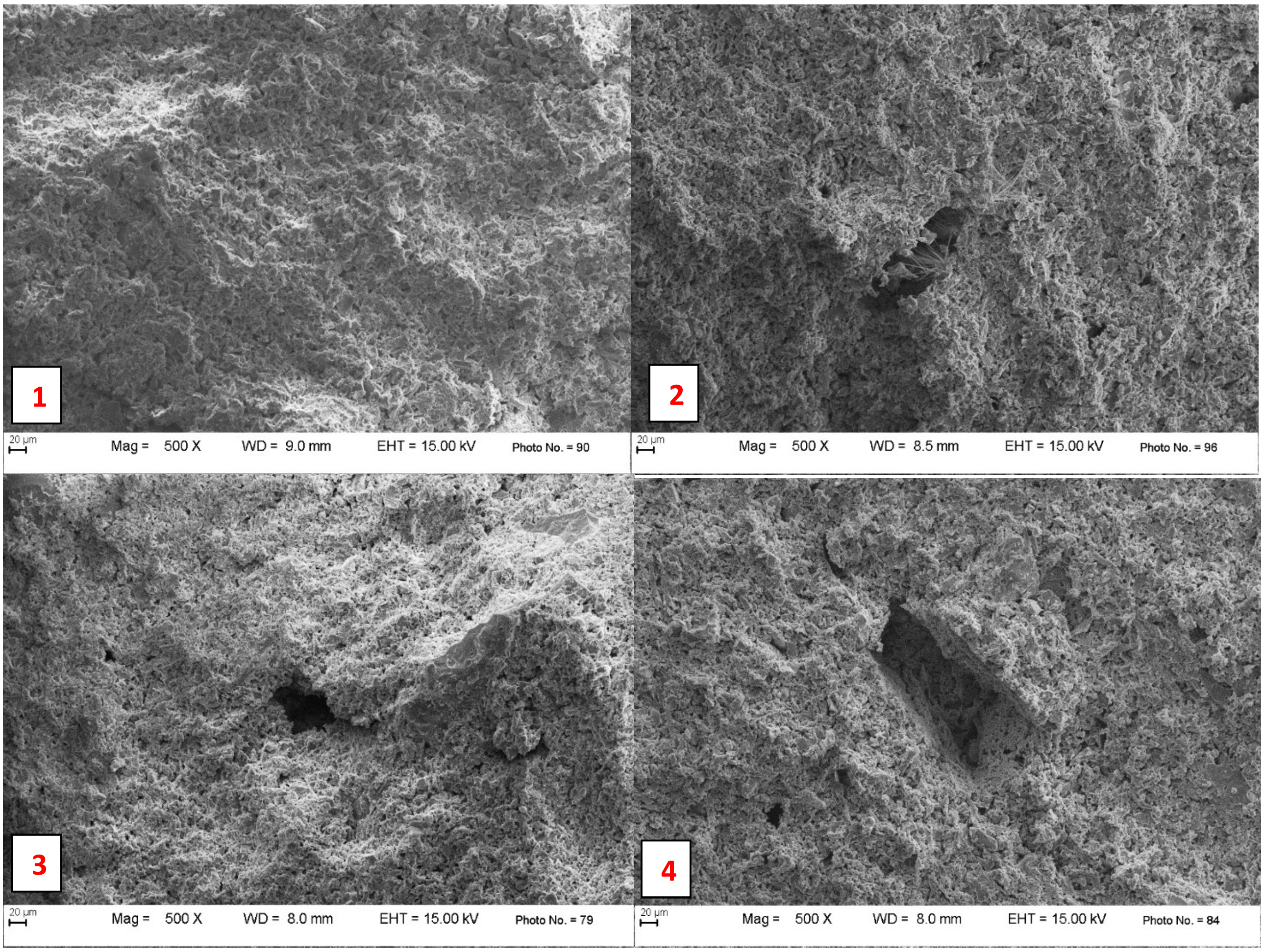


Figure 5.4 - SEM micrographs of (1) 1FCW CAST, (2) 1FCW PRESS, (3) 1RP CAST, (4) 1RP PRESS.

In Figure 5.5 it's possible to observe the micro-porosity of the samples (1) 1FCW CAST, (2) 1FCW PRESS, (3) 1RP CAST, (4) 1RP PRESS. In this case all the samples seem to have the same characteristics. The grains of ceramic wastes are connected by geopolymer matrix, but the reacted material isn't enough to fill the interstitial pores. The grains are too big to be dissolved and to fill the interstitial pores. And the degree of geopolymerization is too low to produce enough matrix to fill the pores.

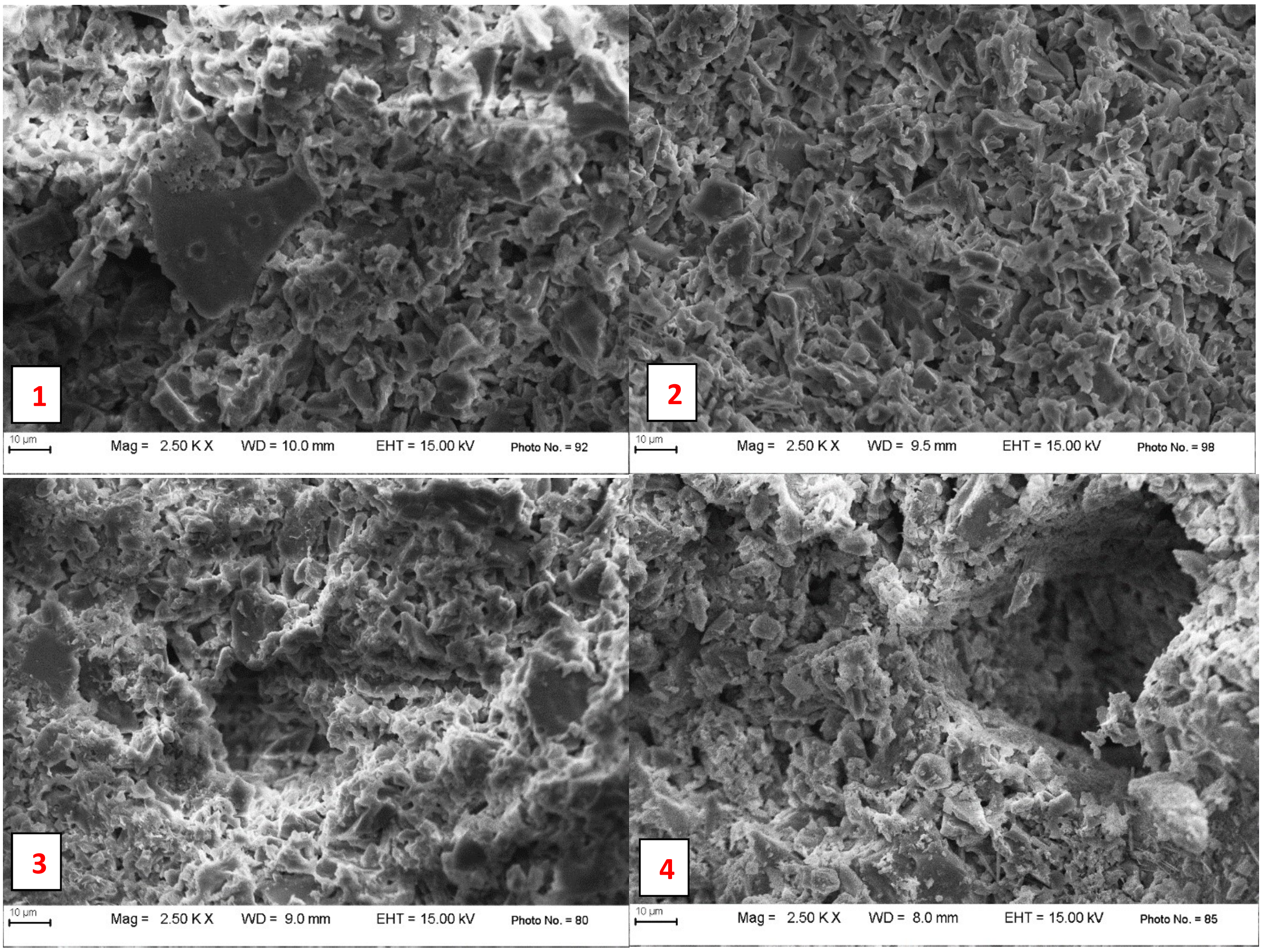


Figure 5.5 - SEM micrographs of (1) 1FCW CAST, (2) 1FCW PRESS, (3) 1RS CAST, (4) 1RS PRESS.

In Figure 5.6 were exposes acicular minerals funded in the samples. In Figure 5.6 (1,2) are related to the 1FCW PRESS sample, are evident needle crystals rich in Na, Si and Al from EDS analysis of figure 5.7. These are new phases formed during the casting period. These crystals are present inside macro-pores (1) and also in micro-pores (2), in this case we can see the particular thing that these fibers start by ceramic waste grains. The needle crystals are present in all the samples.

In figure 5.6 (3, 4) is shown the contact between waste ceramic grains and the geopolymer matrix of new formation. Is highlighted a high degree of corrosion at the contact point. In figure 5.8 is show a semiquantitative analysis of the geopolymeric matrix.

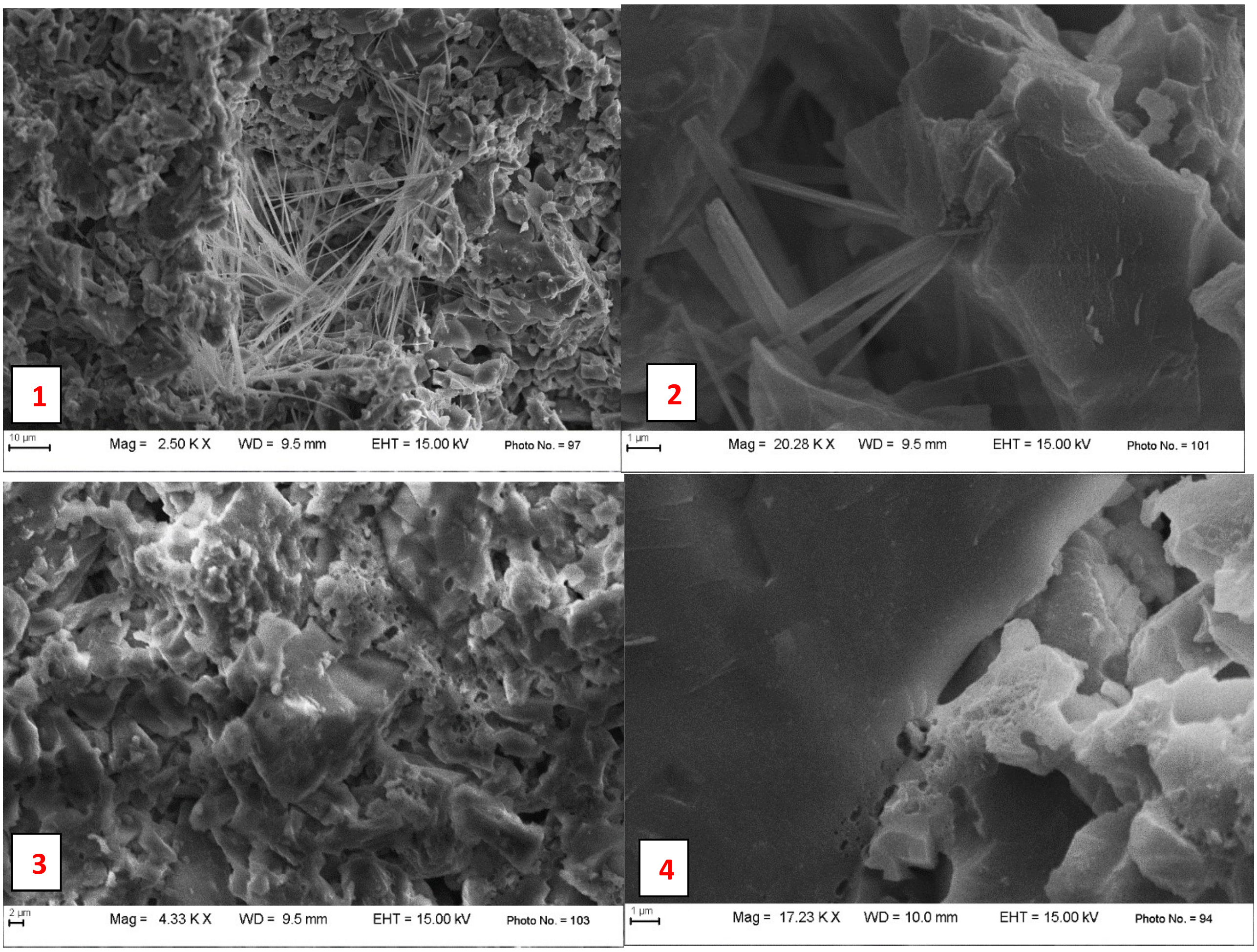


Figure 5.6 - SEM micrographs of (1), (2) 1FCW PRESS, (3), (4) 1FCW CAST.

Numerous needle crystals were found in both pressed and casted samples. These needle crystals have been identified as Natrolite using XRD analysis. Is the only neo-formed crystal of the detection analysis. Natrolite is a tectosilicate mineral species belonging to the zeolite group. It is a hydrated sodium and aluminium silicate with the formula $Na_2Al_2Si_3O_{10} \cdot 2H_2O$.

The crystals are frequently epitaxial overgrowths of natrolite, mesolite, and gonnardite in various orders. Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+}. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution.

EDS semi-quantitative analysis

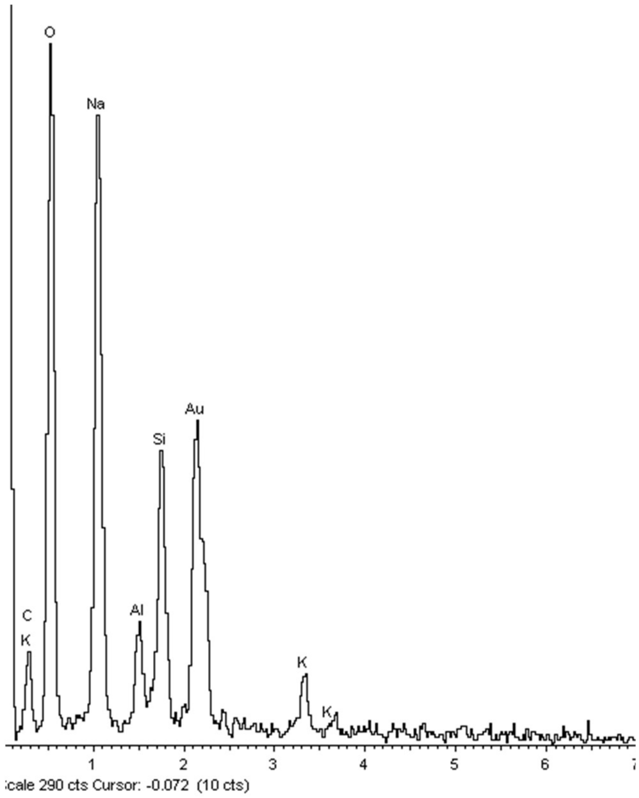


Figure 5.6 - EDS semi-quantitative analysis of needle crystals (Natrolite).

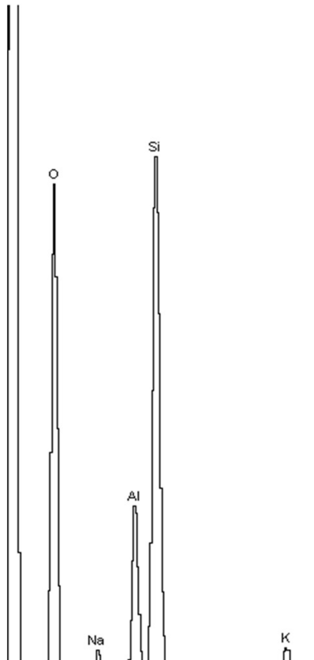


Figure 5.7 - EDS semi-quantitative analysis of geopolymer matrix.

Was performed a microstructural SEM study also on the final samples with low porosity and high mechanical strength and was observed that the internal structure has changed considerably after all the improvement reached modifying the mix design and curing parameters. In the images below (Figure 5.8) the porosity is considerably diminished and is evenly distributed from the underlying margin (1), to the center (3) and to the upper surface margin (2) of the sample. The microstructure is very compact, and the sample has conchoidal fractures typical of glassy materials.

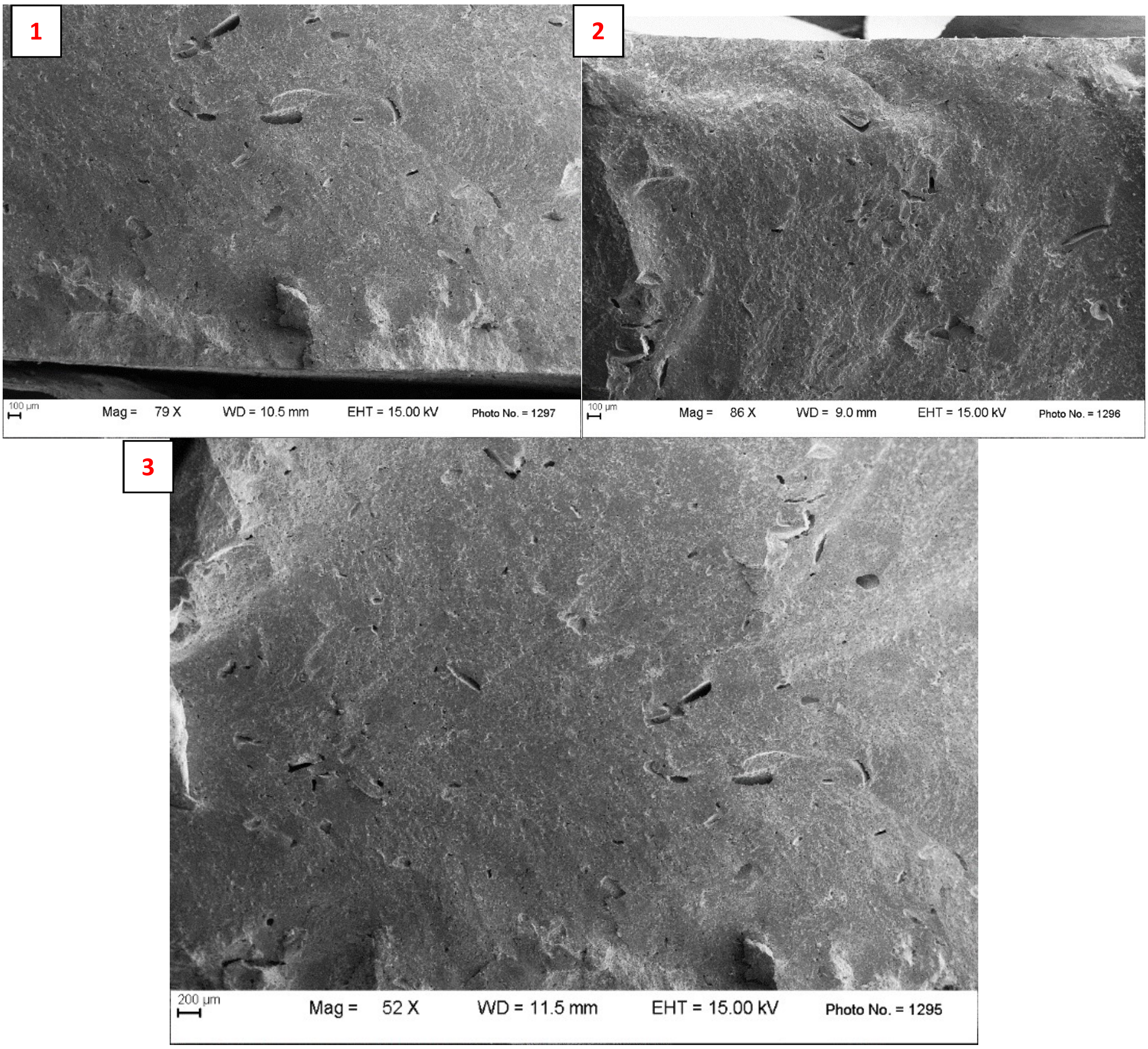


Figure 5.8 - SEM micrographs of a low porosity geopolymer.

In the photos below (Figure 5.9), it’s possible to observe the presence of micro-cracks that occur radially from the pores (2). Probably these pores contained trapped water and generated an expansion during the second step of curing, when the increase his volume at 85 °C. Water is mainly in the form of free water in the large pores and bound water in small pores. Therefore, the presence of large pores promotes higher mass loss values owing to evaporation of free water, whereas the contribution of mass loss owing to the dehydration of the bound water is more evident for heat-cured samples. Structure richer in small pores have a strong capillary pressure, and during dehydration is probably responsible for the cracking (Carabba *et al.*, 2017).

Heating process was normally accompanied by several transformations, moisture evaporation, internal vapour pressure, fine aggregate expansion, alkali activated paste contraction and chemical decompositions. During the early stage of heating these transformations may not have enough ability to cause crack. Except in situations where the rate of heating is quite high and the material is either dense or contains enough moisture content in which case spalling may occur within the first 30 min of exposure (Huseien, Sam, *et al.*, 2018).

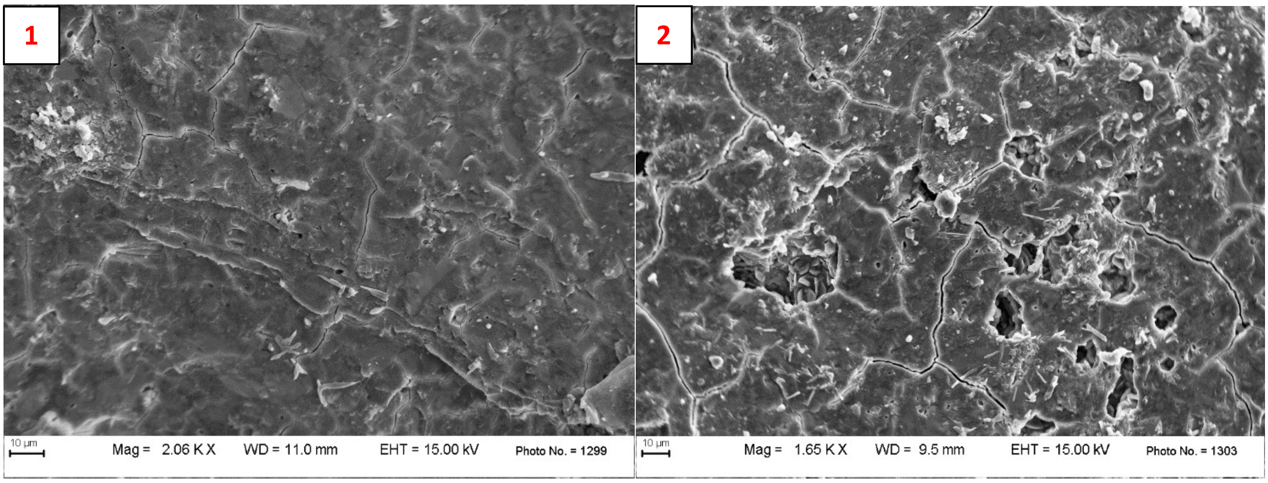


Figure 5.9 - SEM micrographs of a low porosity geopolymer, specific micro-cracks.

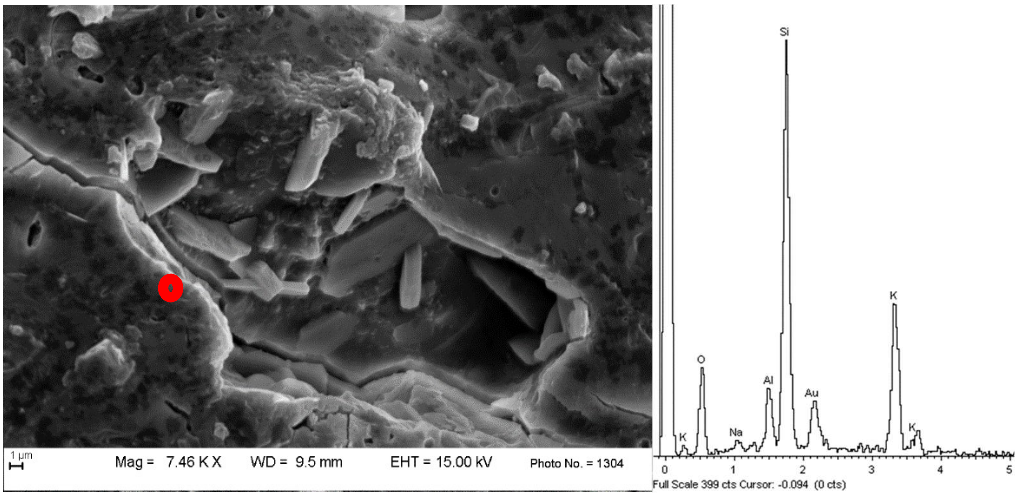


Figure 5.10 and 5.11 - SEM micrographs of a crystal in pore; EDS analysis of the crystal.

Inside the pores are present euhedral crystals (Figure 5.10), after making a punctual microanalysis EDS was seen that are potassium feldspar (Figure 5.11).

At high magnifications, structures that can be defined as dendritic or symplectitic have been identified in the geopolymer matrix (Figure 5.12, 5.13). They could be two non-miscible solid-state phases that are crystallized in a dendritic structure, or they can be two non-miscible solid-state phases separated by recrystallization.

In mineralogy they are known as structures occurring in case of changes in pressure, temperature or chemical stability. For example, in the case of potassium metasomatism (chemical instability), Mirmekites are formed.

The EDS analysis made on this geopolymeric material show two different phases, the first is a silicon oxide (Figure 5.14), the second is an alumina-silicate phases with sodium and potassium (Figure 5.15).

Sodium present in the EDS analyses of the geopolymeric matrix, is not introduced with activators but it is directly dissolved by the ceramic glass during the dissolution process at high pH. While the potassium is introduced with activators, until the creation of a balanced geopolymer with both cations.

In literature only one article describe a dendritic-shaped particles in a geopolymer, but of an iron mineral (Fernández-Jiménez, Palomo and Criado, 2005).

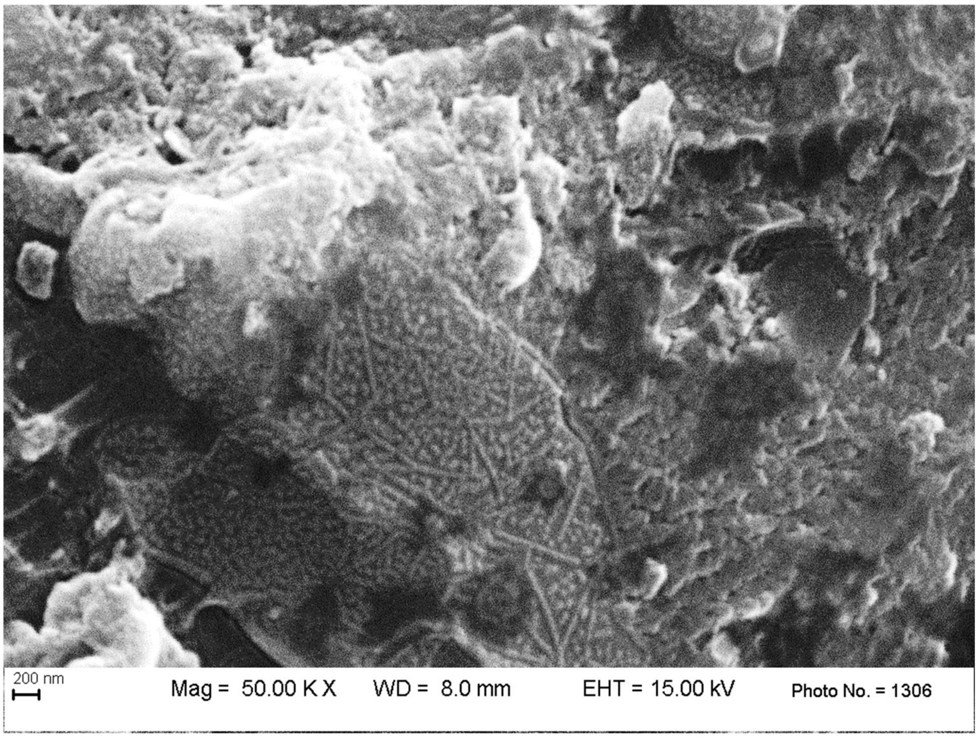


Figure 5.12 - SEM micrographs of symplectitic geopolymer material.

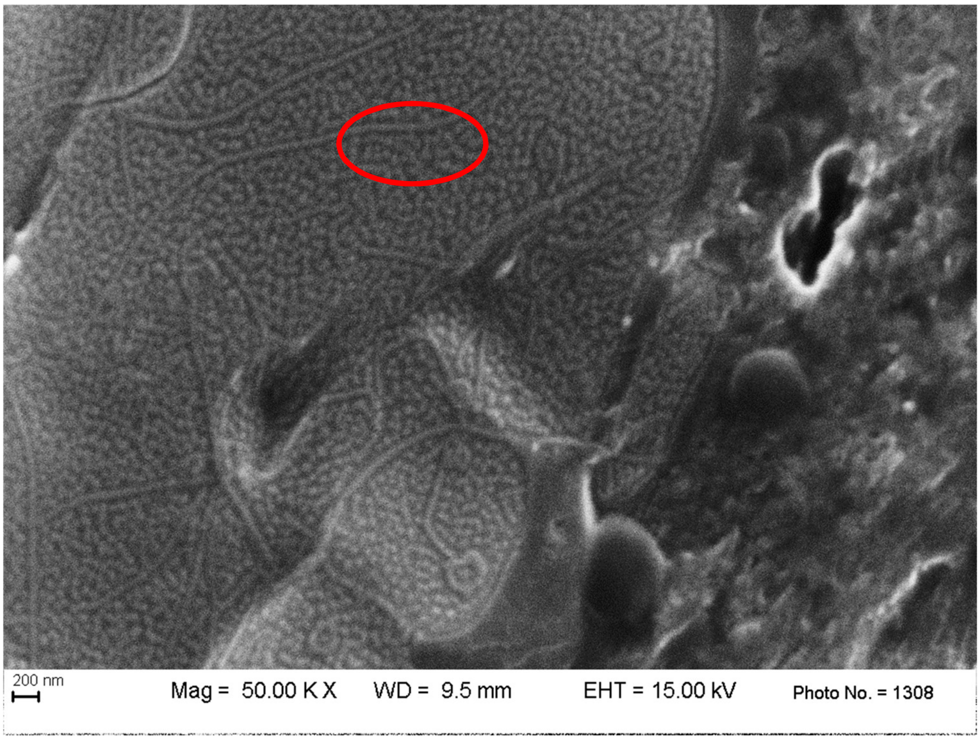


Figure 5.13 - SEM micrographs of symplectitic geopolymer material.

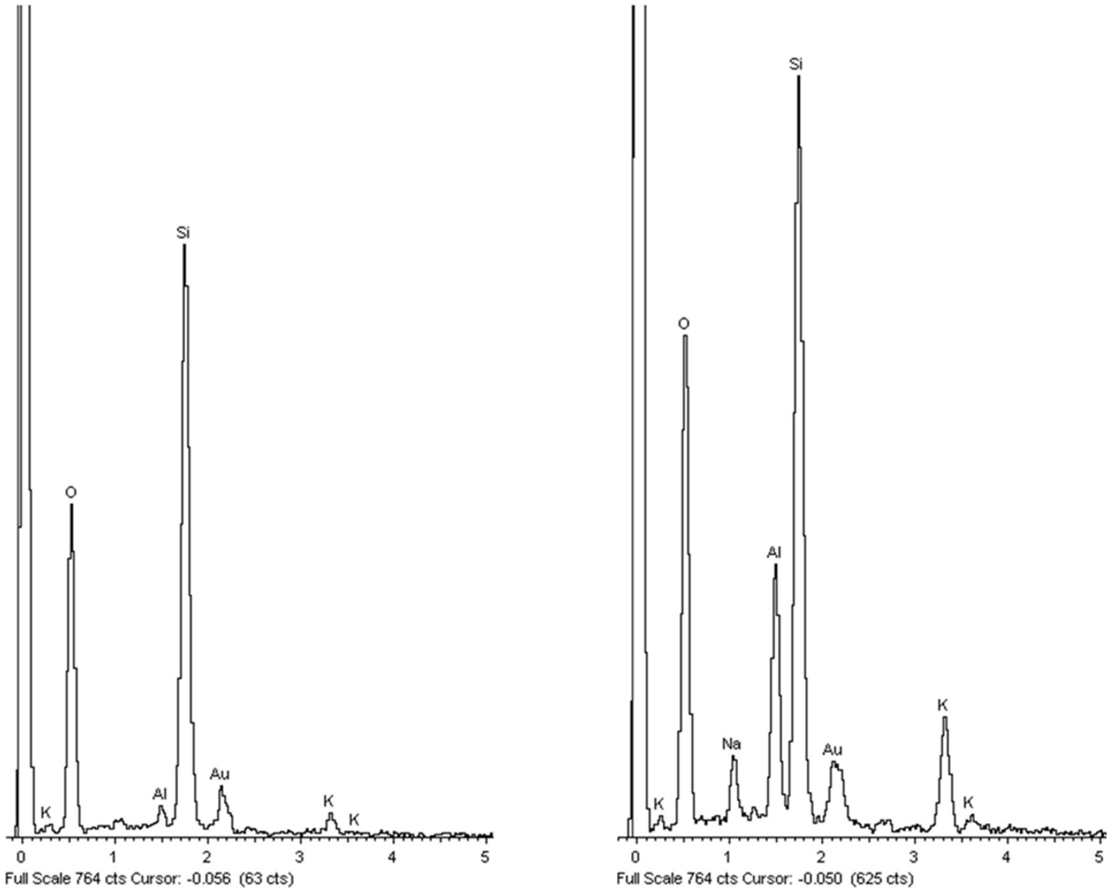


Figure 5.14 and 5.15 – EDS analysis of the two phases in the symplectitic geopolymer material.

The geopolymerization process evolves through different stages, the first stage can be divided into two substages respectively named: Destruction–Coagulation and Coagulation–Condensation (Fernández-Jiménez and Palomo, 2005). The main differences between zeolitic systems and alkaline activated binding systems come from the distinct experimental conditions employed in each synthesis process. In the case of the activation at low "liquid/solid" ratios and very high OH^- concentrations are employed. These particular conditions lead to a situation in which the crystal growth from the zeolitic nuclei formed (second stage) is extremely slow and therefore, an amorphous cementitious matrix (alumina-silicate gel or "zeolite precursor") is initially stabilized. In any case small amounts of zeolite crystals are detected to form part of our cementitious material. Its presence is probably indicating that crystalline zeolites are the thermodynamically stable phases towards which the system should evolve with time. The mechanism controlling the chemical reaction giving place to the pre-zeolite gel is initially associated to a dissolution process (the high concentration of OH^- ions in the system is responsible of the breakdown of the Si–O–Si, Si–O–Al and Al–O–Al bonds forming part of the vitreous phase of the ash and therefore of the formation of Si–OH and Al–OH groups). Later, on these chemical species condense giving place to the precipitation of zeolitic precursor. This gel possesses a 3-dimensional structure with a zeolitic order at short range (Fernández-Jiménez, Palomo and Criado, 2005; Fernández-Jiménez *et al.*, 2006, 2008). During this chemical process, the role played by the alkaline metals being incorporated to the system should be remarked. This role is essential since monovalent metals compensate the electrical load of the microstructure when Al^{3+} atoms replace Si^{4+} (Fernández-Jiménez and Palomo, 2005).

In summary, the main reaction product formed in all the cases faced in this investigation is that alkaline aluminosilicate gel. However, the presence, in the alkaline system, of different types of anions, can induce relevant differences in the final chemical composition of the gel. When the activating solution includes Na^+, K^+ and also soluble Si^{4+}, both elements are incorporated in the reaction products. In summary, the addition of soluble silicate to the activating solution enhances the polymerization process of the ionic species present in the system. Nevertheless, it should be emphasized that an activating solution made of KOH and potassium silicate must be optimized in terms of defining not only the SiO_2/K_2O ratio but also the total amount of K_2O and SiO_2 in the solution. In other words, equilibrium between KOH and silicate in the solution should be reached in order to maintain the system with a high pH and a high level of soluble Si^{4+} (Fernández-Jiménez, Palomo and Criado, 2005).

With respect to nucleation part (substage denominated polymerization) is considered, it is important to emphasize the following: it seems accepted that the 'zeolitic precursor' (the already mentioned as the main reaction product of the alkali activation) contains tetrahedra of Si and Al randomly distributed along the polymeric chains that are cross-linked so as to provide big enough cavities as to accommodate the charge balancing sodium ions (Fernández-Jiménez, Palomo and Criado, 2005). When the time of reaction increases a first formed meta-stable/intermediate Al-rich phase evolves to a more stable Si-rich phase (Palomo *et al.*, 2008). This latter phase presents a three-dimensional structure in which Si is present in a variety of environments. This arrangement leads to Si environments such as Q^4(1Al), Q^4(2Al) and Q^4(3Al). The predominance of the Q^4(nAl) depends on the polymerization degree, which depends on the curing conditions and the alkali activators used. Finally, the second stage, known as growth, begins when the nuclei reach a critical size and the crystals begin to grow, this stage is extraordinarily slow. The amount of liquid in the system affects to the saturation rate of ionic species but not to the rate of dissolution of those ionic species (Fernández-Jiménez, Palomo and Criado, 2005).

On the other hand, the quick precipitation of the material affects its crystallinity. It is well known that zeolites usually need some time for crystallization and a minimum amount of liquid. When the precursor powder is mixed with a small volume of alkaline solution, a paste is formed which quickly transforms into a harden solid. In such a situation, there is not enough time and space for the gel (product of reactions) to grow into a well-crystallized structure such as in the case of zeolites formation. The hypothetical evolution of this gel (zeolitic precursor) to form an orderly zeolitic crystal would entail depolymerization of the gel structure (Fernández-Jiménez and Palomo, 2005).

MINERALOGICAL INVESTIGATION

Mineralogical investigation has been carried out by XRD (X Ray Diffraction) analysis with the aim to determine the new phases formed whit the geopolymerization and for observing if the geopolymerization process formed the typical curve shift.

XRD was used to characterise phase compositions, including crystallinity.

A common qualitative analysis of the degree of geopolymer reaction is to measure how far the amorphous hump shifts to higher 2 theta values (Williams, Hart and Van Riessen, 2011).

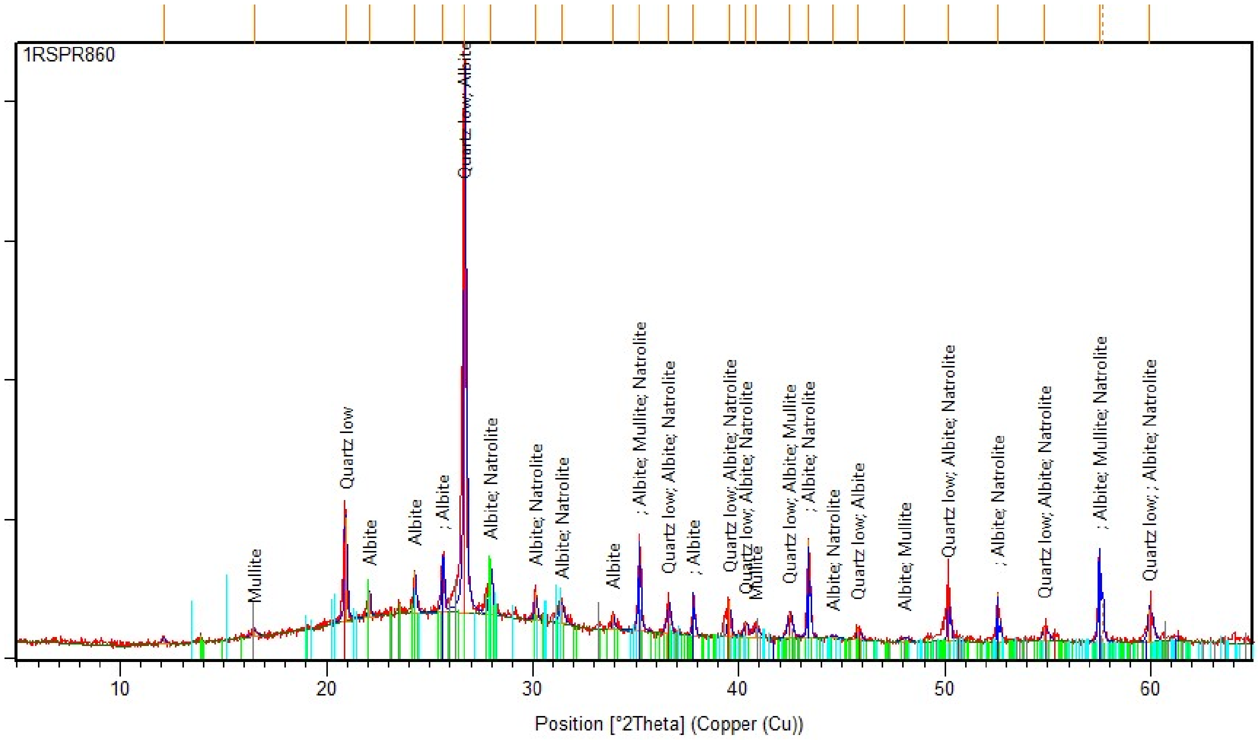


Figure 5.16 – XRD spectrum of the geopolymer material.

Observing the XRD spectrum (Figure 5.16) it's possible to make some consideration on the neo formed geopolymer. The neo formation needle crystals have been identified as a Zeolite, probably Natrolite. All other phases have been confirmed the same to the initial ceramic waste.

Figure 5.17 shows the X-ray diffractograms of the starting materials and the diffractograms of the products resulting from the alkaline activation of these materials. The starting raw material exhibit a hump at 2 Theta = 20° – 30°, which is characteristic of structurally disordered ceramic compounds, and a set of peaks corresponding to minor crystalline phases: quartz, mullite and albite.

After geopolymerization the previously described hump shifts to the right, towards 2 Theta angle positions between 25° and 35°. This shift is related to the formation of a reaction compound of an amorphous nature: a sodium-potassium aluminosilicate gel (a zeolitic precursor) which is the main origin of the material's binding properties (Fernández-Jiménez *et al.*, 2008). The minor crystalline phases detected were quartz and mullite. They were originally present in the starting materials; consequently, it indicates that these phases are apparently not attacked during the alkaline activation process.

Finally, the reaction process leads to the formation of some crystalline phases of a zeolitic nature (see Figure 5.17). Zeolites have a three-dimensional framework structure made by joining together $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ in polyhedral coordination. The isomorphous substitution of Al^{3+} for Si^{4+} into the component polyhedral causes a residual negative charge on the oxygen framework. This negative charge is compensated by the cations within the zeolite structure. Observing the curves comparison of the starting powder spectrum and the geopolymer spectrum we can see that:

- there is a shift to higher angles of the amorphous phase convexity due to geopolymerization;
- disappears two peaks corresponding to albite (by dissolution);
- appear two peaks corresponding to potassium hydroxide residues;
- appear a zeolitic neoformation phase (zeolite).

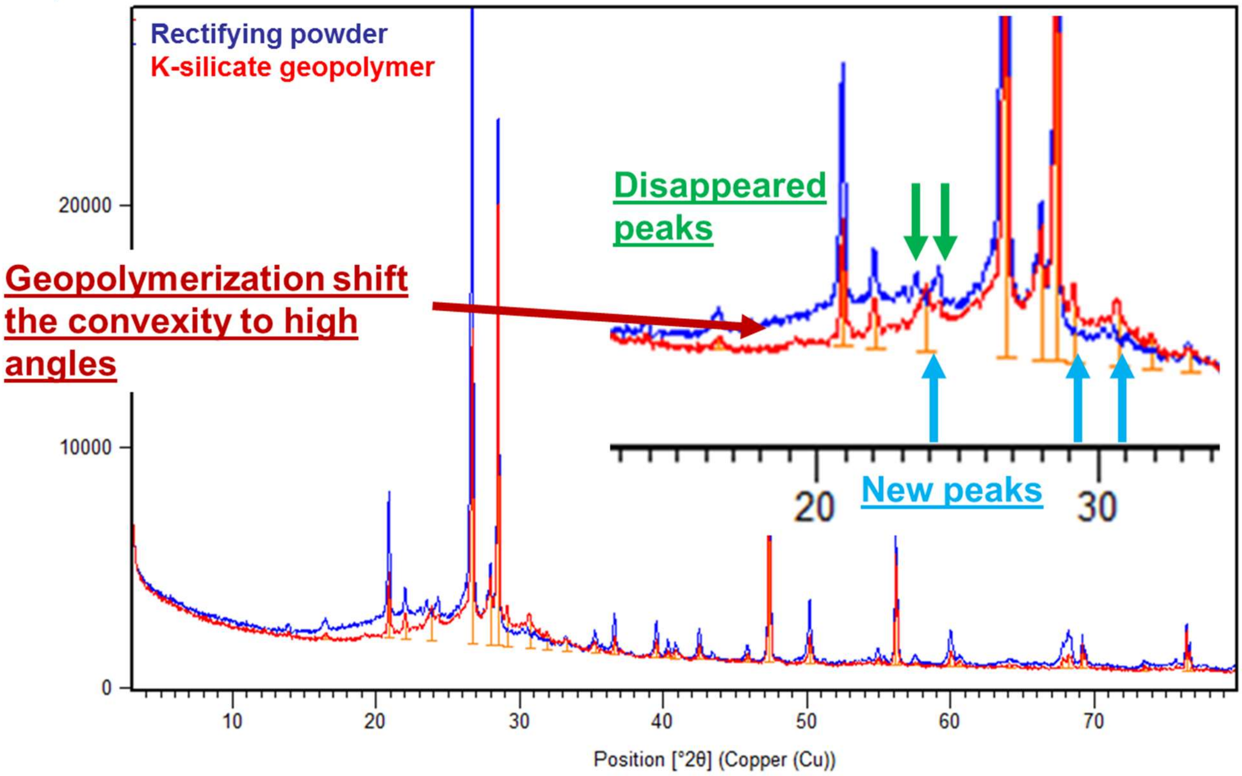


Figure 5.17 – XRD spectrum comparison of the ceramic precursor and geopolymer material.

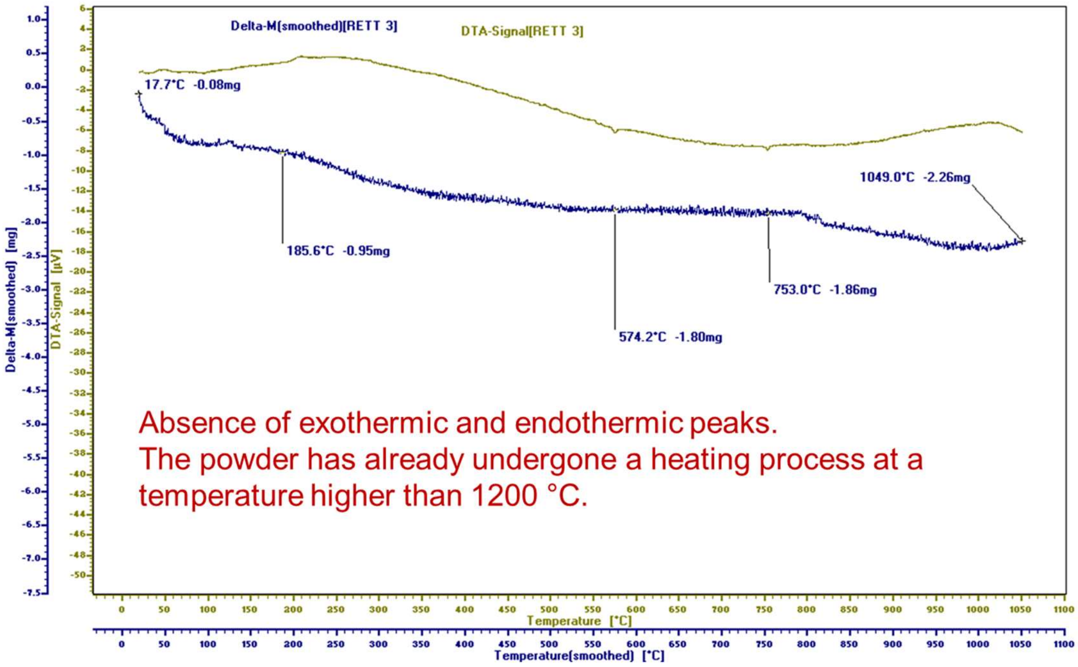
THERMAL PROPERTIES

DIFFERENTIAL THERMAL ANALYSIS (DTA) AND THERMO GRAVIMETRY (TG)

The thermal study starts with the differential thermal analysis (DTA) and the thermo gravimetry (TG) (Figure 5.18).

Figure 5.18 – DTA-TG instrument, Linseis STA PT 1600.

The DTA analysis is very important to understand the geopolymer thermal behaviors during an heating process (Heating rate: 5° c/min) because we know the DTA behavior of the starting ceramic powder (Figure 5.19) and we can compare all the difference to understand the new phases formed during geopolymerization.



Absence of exothermic and endothermic peaks.
The powder has already undergone a heating process at a temperature higher than 1200 °C.

Figure 5.19 - DTA curve of the starting ceramic powder.

The starting Waste powder DTA-TG (figure 5.19) show a complete absence of exothermic and endothermic peaks, the powder has already undergone a heating process at high temperature.

Observing and interpreting the DTA-TG analysis of the final geopolymer in figure 5.20, it’s possible to see that:

- Before 100 degrees there is an endothermic peak due to the loss of residual water.
- At 185 degree there is an endothermic peak due to the dehydration of the structural water.
- At 324 degrees there is an exothermic peak due to the structural collapse.
- After 800 degrees, there is a light endothermal peak due to a probable structural reorganization of the material in a feldspathoid phase.

Is reported in literature that K-geopolymer is more resilient to crystallization than Na-geopolymer, the neoformation phase evolution after 800 °C is always less that the sodium geopolymer. In K-geopolymer is reported in literature that starting from 650 °C the structure reorganization form Kaliophilite and Leucite (Duxson, Lukey and van Deventer, 2006, 2007)

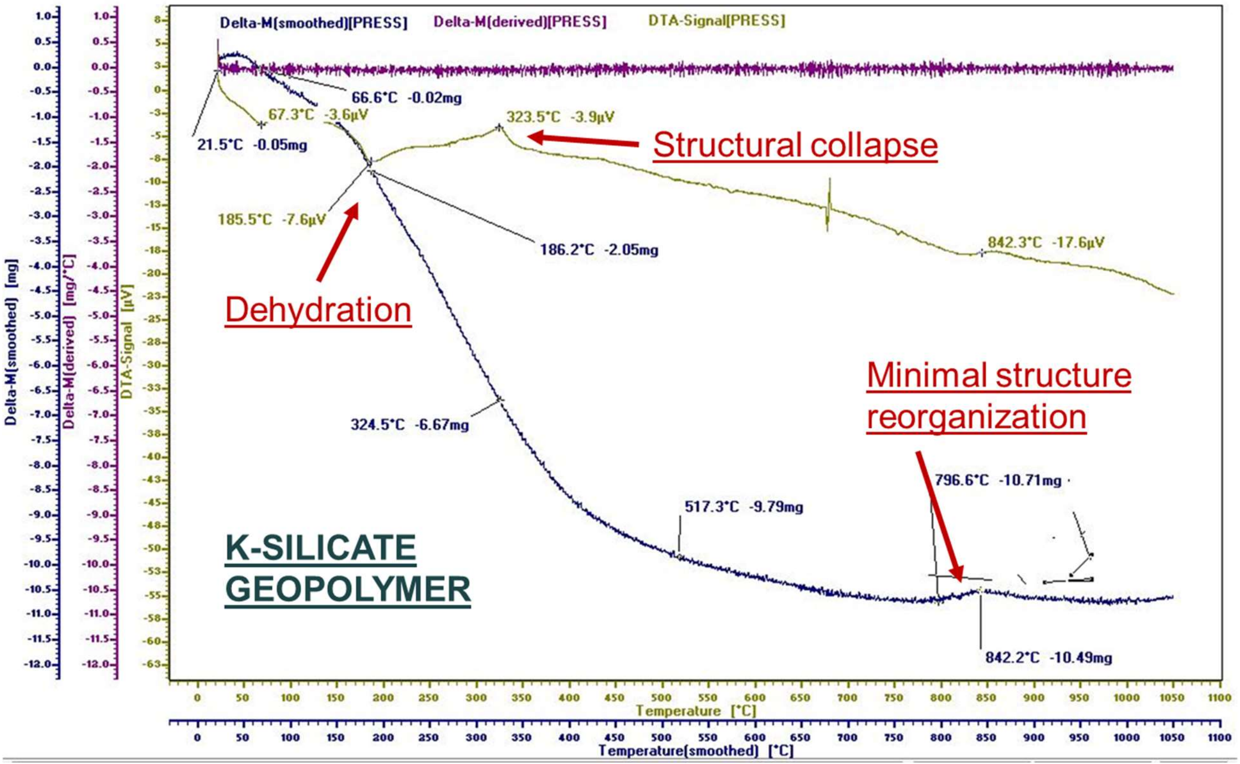


Figure 5.20 – DTA curve of the geopolymeric tile.

The structural evolution and crystallization of potassium-based geopolymer ($K_2O \cdot Al2O_3 \cdot 4SiO_2 \cdot 11H_2O$) on heating was studied in detail (Bell, Driemeyer and Kriven, 2009). On heating from 850 – 1100 °C, potassium-geopolymer underwent significant shrinkage and surface area reduction due to viscous sintering. In literature are described small 15–20 nm sized precipitates present in the unheated geopolymer coarsened substantially in samples heated between 900 and 1000 °C. However, the microstructural surface texture was dependent on the calcination conditions. Leucite crystallized as the major phase after being heated to > 1000 °C, although a minor amount of Kalsilite was also formed. Prolonged heating for 24 h at 1000 °C led to the formation of 80 wt% of leucite, along with 20 wt% of remnant glassy phase. The surface of geopolymers heated to 1000 °C attained a smooth, glassy texture, although closed porosity persisted until 1100 °C. Thermal shrinkage was completed by 1100 °C, and the material reached 99.7% of the theoretical density of tetragonal leucite (Bell, Driemeyer and Kriven, 2009).

OPTICAL DILATOMETER

The optical horizontal dilatometer (Figure 5.21) was used to investigate more precisely the thermal dimensional stability of the developed composites.

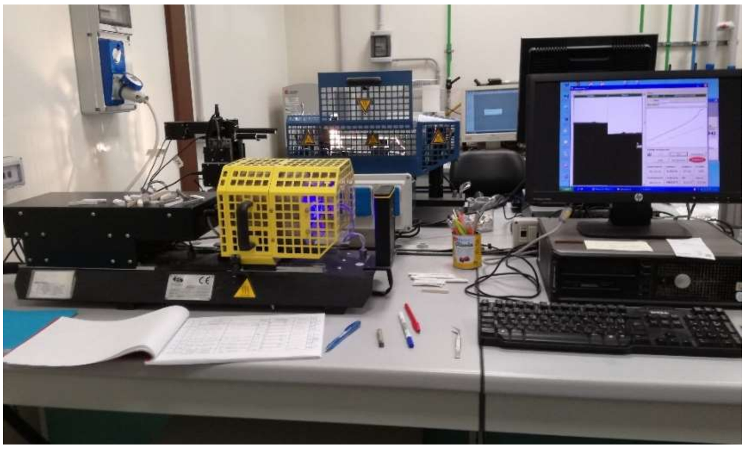
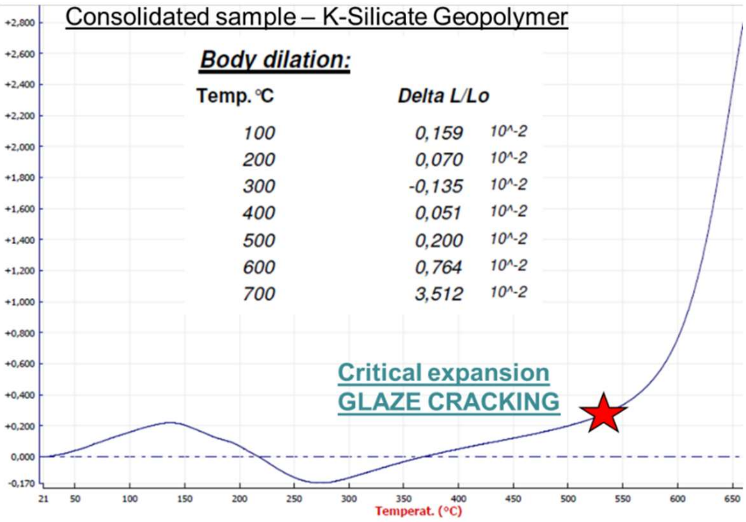


Figure 5.21 – Optical horizontal dilatometer instrument.



Body dilation:

Temp. °C	Delta L/Lo	
100	0,159	10^-2
200	0,070	10^-2
300	-0,135	10^-2
400	0,051	10^-2
500	0,200	10^-2
600	0,764	10^-2
700	3,512	10^-2

Figure 5.22 – Optical dilatometer measurement of a geopolymeric tile.

The sample shows a critical expansion after 500 °C. This expansion prevents firing of the material at higher temperatures otherwise it would cause drastic damages to the integrity of the decoration and of the geopolymer material.

HEATING MICROSCOPE

One of the most interesting features of geopolymers is their remarkable thermal stability owing to the intrinsic thermal resistance of their inorganic structure. Most of the research on thermal behavior of geopolymers focuses on metakaolin (MK)-based systems because of the relatively pure oxide composition of this precursor. Results obtained so far show that the thermal behavior of geopolymers is sensitive to the Al/Si ratio and to the alkali activator chosen for the process and have revealed that, when properly designed and cured, MK-geopolymers withstand up to 1300 °C without significant changes in their structure (Carabba *et al.*, 2017).

Was performed a thermal study of the final geopolymer, made using ceramic waste, using a heating microscope. This study began observing the dimensional and shape changes of the sample during heating. The analysis has been performed with an optical heating microscope (Figure 5.23) and the thermal cycle was 20° c/min till the melting of the sample.

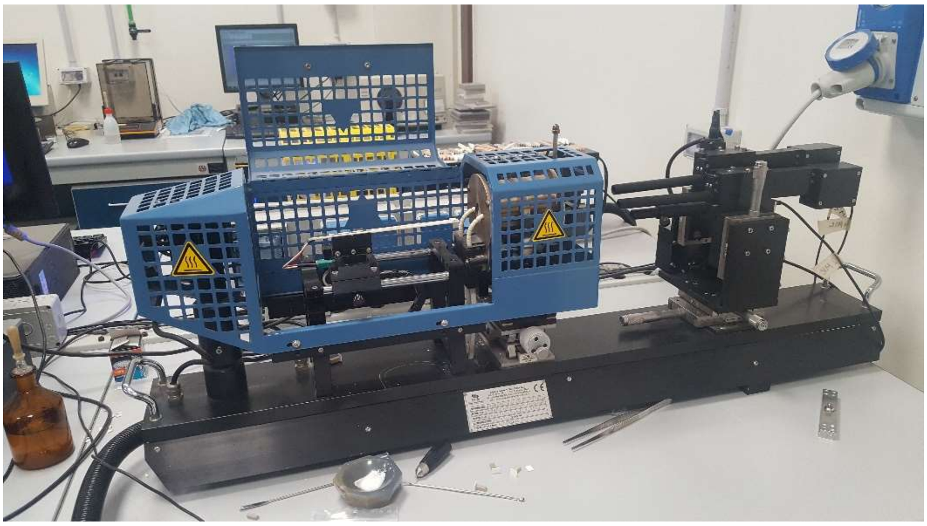


Figure 5.23 - Optical heating microscope.

The heating microscope analysis allows the observation of the geometrical modification of the samples during heating at a constant rate of 5 °C/min up to the complete melting of the material (Figure 5.24). In this way, it is possible to identify the temperature above which the material undergoes significant geometrical modification, which is therefore considered the maximum temperature of its thermal dimensional stability. For the sake of brevity, only some of the images obtained with the heating microscope are shown in figure 5.24. Generally, geometrical thermal stability up to 1000 °C is determined and it is not significantly influenced by the curing conditions. All samples show no movements up to 530 °C. The dehydration identified based on mass loss measurements, which occurs for temperatures below 105 °C, does not seem to cause shrinkage. Between 530 and 640 °C, shrinkage is observed, mainly linked to a densification. The most evident shrinkage among the investigated samples is found in the region of 660 to 850 °C. In this range of temperature, the literature does not report a clear trend in linear dimensional changes, which vary according to the material's composition.

Then there is a little thermal expansion until the structure collapse (at 1205 °C) due to the sample melting. So, the geopolymers tiles are very resistant to heating because the first sign of shape changing occur at 1205 °C.

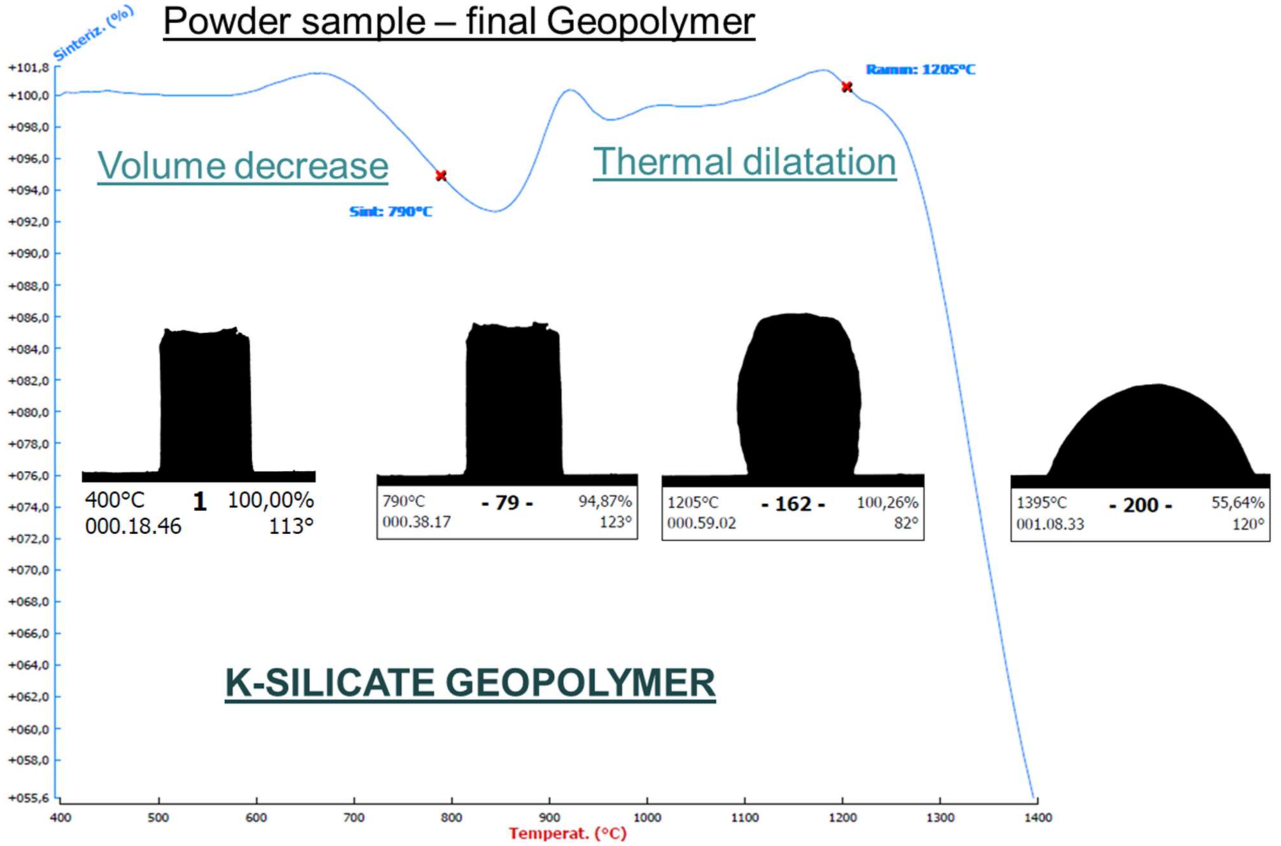


Figure 5.24 – Thermal analysis of a final sample.

Comparing the dimensional behavior during heating of the geopolymers with a ceramic mixture it is clear that the ceramic material has a great stability during heating up to the collapse due to the melting.

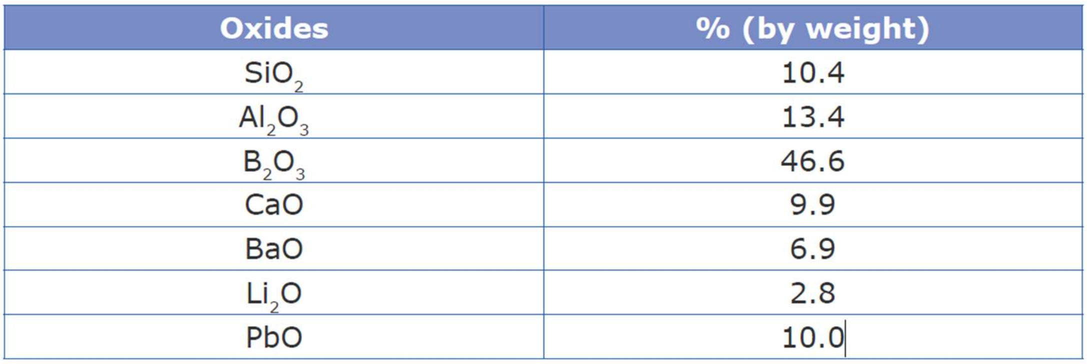
This stability in firing allows to obtain ceramic materials without structural defects such as dilatation cracks and allows the decoration using a thermal treatment.

6. GEOPOLYMER SURFACE DECORATION

In literature only two references were found about that show the intention of decorate a geopolymer surface.

In the patent of Kumar *et al.* filed in the 2007, is identified a process of self-decoration. The invention is that geopolymerization is more intensive at the bottom surface of a geopolymeric material due to accumulation of more alkalis. A different reaction mechanism occurs at the bottom surface leading to formation of more and closely packed alumina-silicate gel. As a result, glaze surface occurs at the bottom. Novelty of the present invention is that the glazed surface occurs on the geopolymer tile automatically, without any secondary processing. Another characteristic is that the tiles uses two major industrial waste, fly ash and granulated blast furnace slag, as the major raw material (up to 95% of total composition).

Vincent *et al.* in the 2012 speaks about decoration of a geopolymer surface using a glazing process. They developed the possibility of glazing the geopolymer obtained using a firing heating process. Based on the research results, they tested three different composition systems: 'BaO-B_2O_3-SiO_2', 'ZnO-B_2O_3-Na_2O-SiO_2', and 'Li_2O-B_2O_3-SiO_2'. With a view to avoiding cracks and achieving good bonding between the substrate and the glaze, the coefficient of expansion of the substrate needed to be very similar to that of glaze. The foregoing compositions were therefore reformulated and a more appropriate frit for the needs of the product was prepared by the researchers (Tables 6.1 and 6.2).



Oxides	% (by weight)
SiO_2	10.4
Al_2O_3	13.4
B_2O_3	46.6
CaO	9.9
BaO	6.9
Li_2O	2.8
PbO	10.0

Table 6.1 – Chemical analysis of the frit studied by Vincent *et al.*, 2012.

Raw materials	% (by weight)
Alumina	9.5
Boric acid	58.9
Barium carbonate	6.3
Lithium carbonate	3.3
Lead oxide	7.1
Calcium oxide	0.7
Wollastonite	14.2

Table 6.2 – Composition in raw materials of the frit studied by Vincent *et al.*, 2012.

The greatest problem posed by using a low-temperature frit that is applied by the wet method is the overlapping of organic matter decomposition with the glaze sealing phase at the same temperature. In order to avoid the presence of organic matter in the glaze composition, a series of actions were undertaken by the authors: First, the carboxymethyl cellulose (CMC) additive, which is usually added to the glaze composition, was suppressed. Owing to the elimination of CMC from the composition, it was considered convenient to use a vehicle (one of those that are typically used in glass decoration, since they exhibit the singularity of having a high vapor pressure and therefore evaporate at low temperatures) that could partly perform the functions of the CMC. This solution turned out to be inappropriate and the fired glaze continued to display a dark color.

It was then thought by the authors that the organic matter existing in the kaolin (a raw material that is also added to the frit in preparing the glaze composition) might be having an impact. It was therefore attempted to prepare a suspension solely with frit; however, the result was not satisfactory either.

Finally, it was decided by Vincent *et al.* to replace kaolin with metakaolin (in preparing the glaze composition) in order to provide the composition with a certain plasticity without introducing any organic matter. Since all the actions undertaken to suppress the dark/greyish color of the glaze composition, which was applied by the wet method, did not work, dry glaze application was studied. The frit involved was therefore dry milled until a grit of $d < 120$ μm was obtained. The grit was applied with an applicator rod that was 15 μm thick. The resulting piece (substrate obtained by alkaline activation + dry grit application) was then fired at 600 ºC. Results are not declared.

DECORATION USING AN HIGH TEMPERATURE THERMAL TREATMENT

The main characteristics of a ceramic tile are the technological performances and the decoration. The decoration for ceramic is carried out before firing using a digital printer and one or more application of glazes, but to reach the technological performance typical of a ceramic material the semi product needs a thermal treatment at temperature higher of 1100 - 1200 °C.

The activity started testing the classical methodologies of decoration for ceramic tiles, that need a temperature thermal treatment, for the decoration of geopolymers obtained in this research.

The different types of surface decoration tested are:

- Digital printing;
- Glazing.

The part of digital decoration has been faithfully done like the ceramic process, using the same printer and the same inks; was seen that the process has worked correctly, and the digital decoration was performed. The only problem was that digital decoration applied without glaze didn't guarantee the correct resistance of the surface and therefore needed a protective layer as in the case of their use in the ceramic process where a protective glaze is applied.

For this reason, it was recreated in laboratory the low temperature melting glaze used in the work of Vincent *et al.* in the 2012. With this glaze want to reach the final result using a firing cycle of 600 °C like in the research of Vincent and his collaborators. With a view to avoiding cracks and achieving good bonding between the substrate and the glaze, the coefficient of expansion of the substrate needed to be very similar to that of glaze.

The greatest problem posed by using a low-temperature glaze that is applied by the wet method is the overlapping of organic matter decomposition with the glaze sealing phase at the same temperature. Was decided to replace kaolin with metakaolin (in preparing the glaze composition) in order to provide the composition with a certain plasticity without introducing any organic matter like the cited work.

The formulation of the glaze has the chemical components showed in the table 6.3. From the original formulation showed on the article (table 6.1) In this research was eliminated the PbO because is declared very dangerous for human health.

Before the application of the studied glaze it's also applied the decoration using a ceramic digital printer.

Table 6.3 – Chemical analysis of the studied frit.

Oxides	% (by weight)
SiO_2	10.9
Al_2O_3	14.1
B_2O_3	47.3
CaO	5.5
BaO	6.9
Li_2O	15.3
PbO	0

The application of the digital inks is made using a lab digital printer IN.TE.SA (Figure 6.1), and the application of glaze is made by liquid airless application (Figure 6.2).

Figure 6.1 - IN.TE.SA digital printer.

Figure 6.2 - Glaze liquid airless applicator.

In the images below (Figure 6.3) it's possible to see the geopolymeric samples with the application of the digital inks. And in figure 6.4 It's show the geopolymeric samples covered by the glaze after decoration.

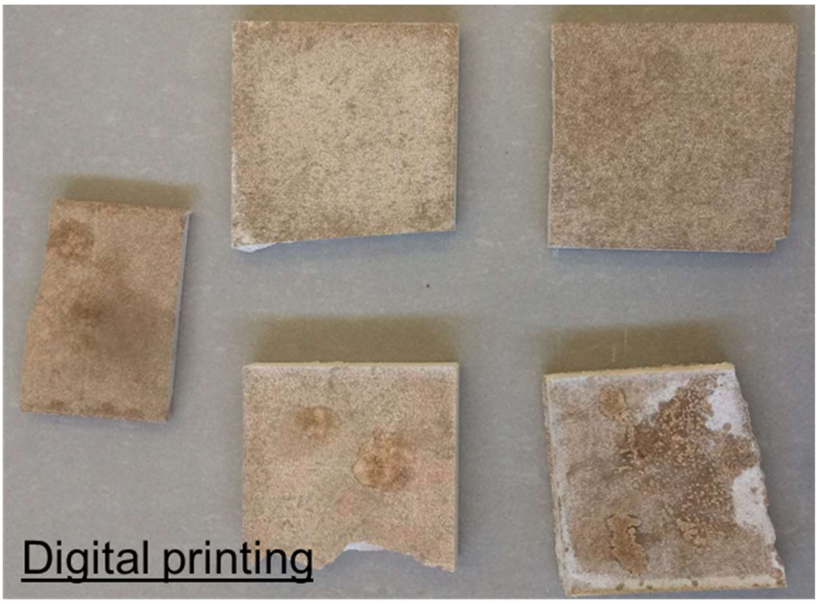


Figure 6.3 – Digital printed samples.

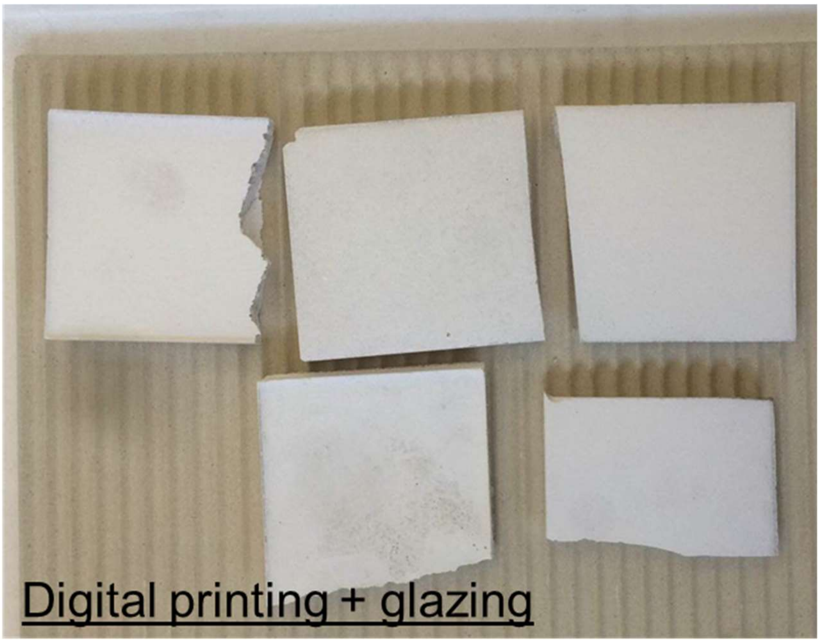


Figure 6.4 – Digital printed samples covered with glaze.

After the firing treatment at 600 °C, the samples show lot of cracks (Figure 6.5). These decoration methodologies need a firing process at high temperature, more than 600 °C, with the optical dilatometer (in the previous chapter) it's possible to see that up to 500 °C, geopolymers have a drastic expansion and for this reason the glaze cracks.

The fired samples show a bad dilatometric coupling with the glaze and a bad firing behavior.

The glaze is well fired, has the correct grade of sintering, but have a lot of cracks. Due to the excessive expansion of the geopolymeric support.

Figure 6.5 – Final fired samples.

COLD DECORATION TECHNOLOGY

Mohawk Group, owner of Marazzi Group, has patented a type of tiles decoration process that don’t need a thermal treatment. The activity of decoration was continued in the US in Dallas, to try to decorate the geopolymers obtained with this new method for ceramic decoration to the R&D lab of Dal-Tile using UV decoration system.

Ceramic Cold decoration with UV printing patent: UNITED STATES PATENT No. US 10,024,058 B2 (2018). Applicant: Mohawk Carpet Corporation. Title: Tile edge systems and methods.

In the previous part of this chapter it’s shown that is impossible to obtain a geopolymer decorated surface using technologies that need a thermal treatment; the result is the achievement of a totally cracked surface.

In this patent the process is presented for a third firing decoration for printing the edges of ceramic tiles, but in this project is shown that there is a good behaviour also in decoration of geopolymer material.

Following are descripted the strengths point of this technology:

- Rapid and consistent results using digital printing with fast UV curing;
- No glaze firing cycle or spray painting;
- Design and colors reach the design of the tile;
- The UV cured protective coating provides high durability and scratch resistance.
- Process optimization, no need firing cycle;
- Fast digital production with instantaneous UV curing;
- Rapid color and process changes, see end results in seconds;
- Significantly improved appearance with consistently repeatable print quality;
- Excellent durability;
- Reduced paint wastage, digital inkjet application is highly accurate;
- Reduced production line footprint;
- Low VOC emissions compared with paint.

Patent description:

Some aspects of the patent relate to a method of manufacturing a bullnose tile, comprising printing a decorative coat comprising print media on a bullnose edge of the bullnose tile, and curing the print media. The print media comprises UV radiation curable ink. In some embodiments, the method of manufacturing a bullnose tile further comprises coating at least one of a tie coats or a base coat on the bullnose edge of the bullnose tile and curing at least one of the tie coats or the base coat. In some embodiments, the method of manufacturing a bullnose tile further comprises coating a protective coat on the bullnose edge of the bullnose tile and curing the protective coat. In some embodiments, the curing process comprises exposing the print media to a radiation lamp. In some embodiments the method further comprises wet cutting a tile to form the bullnose tile, profiling the tile to provide a smooth rounded edge to the bullnose tile, drying the bullnose tile after wet cutting, and sorting and packaging the tile after the curing process.

Some aspects of the patent relate to a system for manufacturing a bullnose tile comprising a first printing station configured to print a decorative coat, onto a bullnose edge of a bullnose tile, and a first curing station for curing the decorative coat. In some embodiments, the system can further comprise a first coating station configured to coat at least one of a tie coat or a base coat onto the bullnose edge of the bullnose tile, and a second curing station for curing the at least one of the tie coat or the base coat. In some embodiments, the system can further include a second coating station configured to coat a protective coat onto the bullnose edge of the bullnose tile, and a third curing station to cure the protective coat (Figure 6.6). In some embodiments, the first printing station comprises one or more inkjet printers. In some embodiments, the inkjet printers printing print media comprise radiation curable ink. In some embodiments, the curing station comprises one or more radiation lamps. In some embodiments, the system further comprises a second printing station. In some embodiments, the system is configured to transport the tile from the first curing station to the second printing station. In some embodiments, the system is configured to transport the tile from the second printing station to a second curing station.

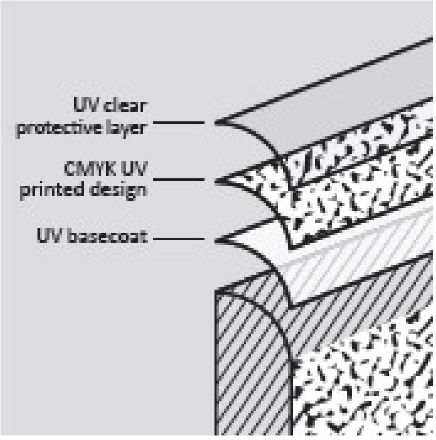


Figure 6.6 – Complete UV applications.

In some embodiments, the decorative edge is one of a bullnose edges, a straight edge, a bevelled edge and a lower perimeter portion. The tile further comprises a second coat printed onto the decorative edge and cured. In some embodiments, the second coat is a decorative coat. In some embodiments, the tile further comprises a third coat printed onto the decorative edge and cured.

In some embodiments, the print media, or decorative inks, can include one or more radiation curable inks applied in one or more layers. More specifically, the print media can include a radiation curable base coat, radiation curable decorative coat, and, optionally, a radiation curable protective coat. The print media and inks can be cured after each layer is applied, after some layers are applied, or after all layers are applied. These radiation curable inks provide several advantages. For example, they dry quickly when exposed to radiation lamps, they enable more accurate color and design matching than conventional paints, and they are simple to apply with the right equipment. In addition, there are zero VOC and solvent emissions associated with 100% solids radiation curable print media. In some embodiments, the base coat and/or the protective coat can be applied by techniques other than printing, such as, for example, by roller coating and/or spray coating, while the decorative coat is applied by printing as described herein. Decorative inks can be acrylate monomer and oligomer based, UV curable, and can be available in multiple colors, for example, cyan, magenta, yellow and black.

A tie coat can be a coating used to improve the adhesion of a base coat to the surface of the tile. A tie coat can have a low viscosity and/or be water-based. For example, a tie coat can be a UV curable, water based polyurethane dispersion. According to some embodiments, a tie coat can penetrate the pores of the tile, thereby adding durability to the coatings applied to the surface of the tile. A base coat or tie coat can be applied by first coating station using a coating element. As will be understood by those of skill in the art, a coating element may take many forms, such as, for example but not limited to, rollers that roll the coat onto the surface of the tile, sprayers that can spray a coat onto the surface of the tile, or dispensers that can pour the coating onto the surface of the tile. According to some embodiments, if a tie coat is used in addition to a base coat, there can be an additional step of flashing off water in a dryer chamber before coating the base coat on top of it. In some embodiments, the tie coat does not need to be UV cured separately before coating the base coat and they can be cured together at the same time.

The first coat can be cured by exposing the coat to radiation lamps at one or more first curing stations. After curing the first coat, the conveyor system can transport the tiles through a printing station. The print station can comprise printers that can print a decorative coat on the surface of the bullnose edge on top of the base coat (optionally including the tie coat). The decorative coat may comprise one or more layers of print media, which can include radiation curable ink(s), on the bullnose edge of the tile at step. Similar to what was previously described, after printing, the radiation curable inks can be cured by exposing the inks to radiation lamps at one or more second curing stations. Likewise, if one or more additional layers of print media are desired to be applied on top of the tiles, multiple printing stations and second curing stations can be placed in series. Alternatively, the conveyor system can have an optional rerouting pathway, or loop, to redirect the tiles through the print station and second curing station as many times as desired or necessary.

After being cured at second curing station, the tiles can then be transported by the conveyor system through one or more second coating stations. Coating station can be configured to apply a second coating to the bullnose edge of the tile in a manner similar to that described above with respect to the first coating station. A second coating can be a protective coating. A protective coating can be a clear coating that adds protection to the surface of the tile and prevents the decorative tile from scraping or wearing off. A protective coat can be water resistant and/or provide a desirable finish to the surface of the tile. According to some embodiments, a protective coat is a UV curable, clear coat based on polyurethane or polyester chemistries. After a second coating is applied to the bullnose edge, the second coating can be cured by exposing the coating to radiation lamps at one or more third curing stations. The third curing station can cure the second coating in a manner similar to that previously described with respect to the curing of the first coating and the decorative coating.

Moreover, the print media, including the inks, can be applied in one or more layers. For example, in some embodiments, a radiation curable base coat can be applied first, a radiation curable decorative coat can be applied next, and a radiation curable protective coat can be applied last. In some embodiments, an optional tie coat may be applied before the base coat. Each of these layers, and other additional layers, can be optionally applied or applied multiple times. In some embodiments, a base coat can be applied to the bullnose edge first. The base coat can be white to provide a desirable surface upon which to print subsequent layers. After the base coat, a decorative coat can then be applied, which can include or apply the design or graphic on the tile. A wear resistant clear coat may then be applied on top of the decorative coat to provide a desirable finish. In addition, a clear coat can be desirable to protect the other printed layers of the tiles as these layers may not be as durable as the layers on the top of the tile, depending on a number of factors, including the types of print media and/or inks used.

In some embodiments, the radiation curable inks can be 100% solid, solvent-borne or water-based, or solid powders (such as in powder coatings). The inks can comprise binders/monomers based on acrylate, unsaturated polyester, polyester-acrylate, epoxide-acrylate, urethane-acrylate, polyurethane or polyurethane-acrylate dispersions (PUD), or blends of the above. The inks can be tinted with organic or in-organic pigments, dyes or colorants. In some embodiments, the inks or protective clear coat are not tinted or colored to maintain clarity. The inks and coatings can further comprise carefully selected combinations of photo-initiators that may include hydroxy-ketones and/or acyl phosphine oxides. The inks can be ultraviolet (UV) curable inks.

In some embodiments, the inks can be electron beam (EB) curable inks. The main difference in EB curable inks, as compared to UV curable inks, is the energy or wavelength of radiation and the need for photo initiator chemicals used in the inks. EB inks are more energetic with a shorter wavelength range, typically less than 1 nanometer, that generally does not require a photo-initiator being added to the ink. On the other hand, UV inks are less energetic with longer wavelength range, generally between 200 and 400 nanometers, that requires a photo-initiator.

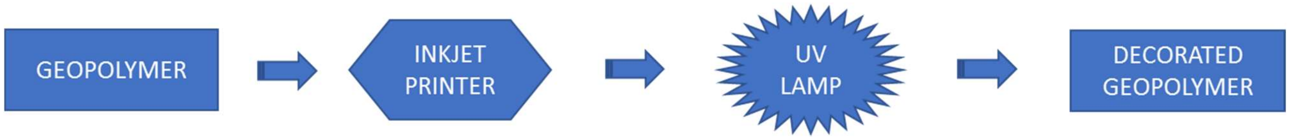
In some embodiments, curing stations can include one or more radiation lamps. The radiation lamps can be UV radiation lamps or EB radiation lamps, or both, depending on the type of ink used. The curing stations can therefore expose the tile, including the radiation curable inks, to the radiation lamps, which can be disposed above the tile. The radiation lamps can thus cure the radiation curable inks on the tile. In some embodiments, curing of the inks is carried out by properly selecting radiation lamps with output spectra that match the absorption range of photo-initiators in the inks. Thus, when the inks are exposed to the output spectra from the lamps, the inks can cure on the tile.

As referenced above, the radiation lamps can cure the inks after each layer of ink is applied, or after two or more of the layers of ink are applied. Thus, the lamps can cure the inks between each printing step, or after all printing steps, are completed. Advantageously, the radiation lamps can cure the radiation curable inks very quickly. This can be extremely advantageous over known paint drying techniques, which can routinely take twenty minutes or longer. In addition, the radiation lamps can cure the inks at room temperature. Thus, the tiles emerge cool, and ready for subsequent processing. There is also no need to maintain a large dryer at a high temperature, or to wheel carts into or out of the dryer. Thus, curing under radiation lamps can increase manufacturing speed and can also reduce overhead costs. In some embodiments, the tiles can be cured on the conveyor system.

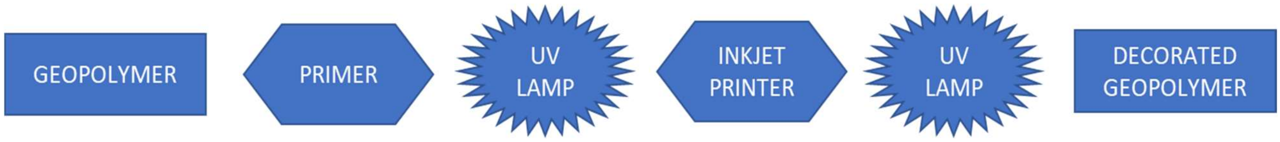
As explained above, a plurality of printing stations and curing stations can be configured in series. This can enable the printing and curing of multiple layers of ink on the tiles.

During this PhD research were tried two ways for printing with UV radiation curable inks:

- Printing directly using a UV digital printer (Figure 6.7) on the geopolymer tile, and then curing with Lab Curing station with Gallium and Mercury lamps (Figure 6.8).

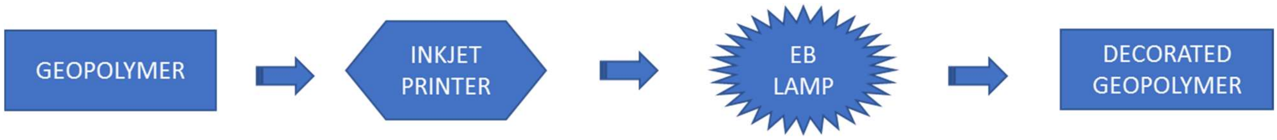


- Two steps of decoration on the geopolymer tile, the first is the application of the base coat and the second is the printing of the image of decoration and then curing with UV lamp.



Printing with electron beam (EB) radiation curable inks, two ways (possibility not yet experimented):

- Printing directly on the geopolymer tile, and then curing with electron beam lamp.



The decorated samples obtained are very similar to a decorated ceramic tile using a high thermal treatment (Figure 6.9).

The surface characterization is explained in the next chapter.

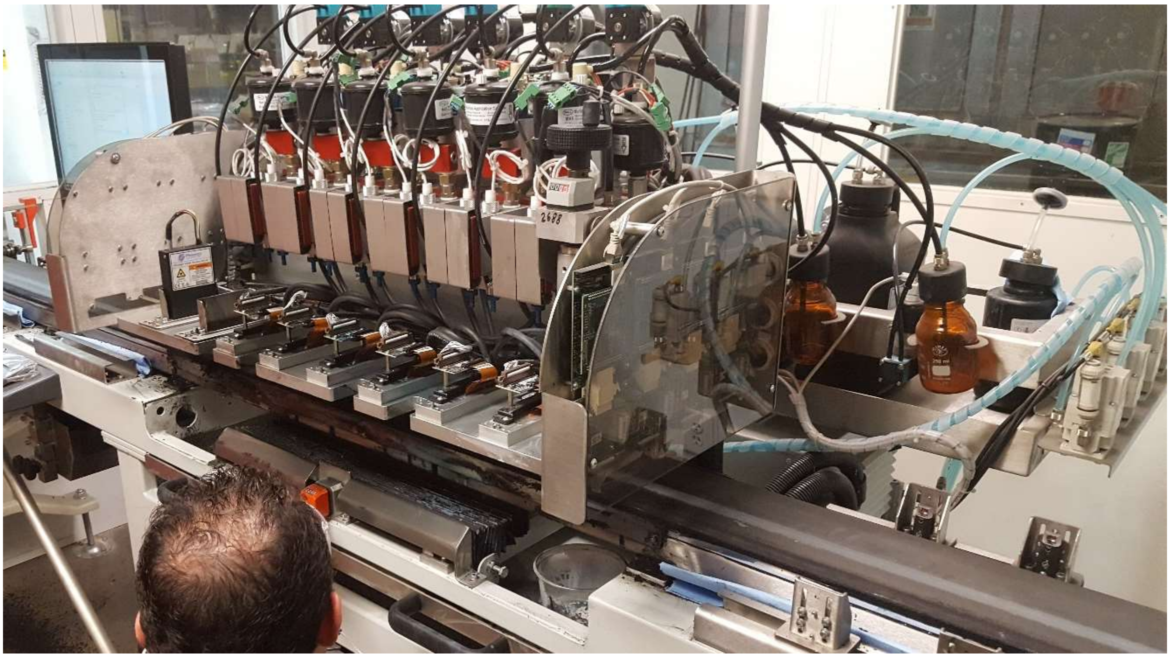


Figure 6.7 – Ceramic Digital printer equipped with UV lamp.

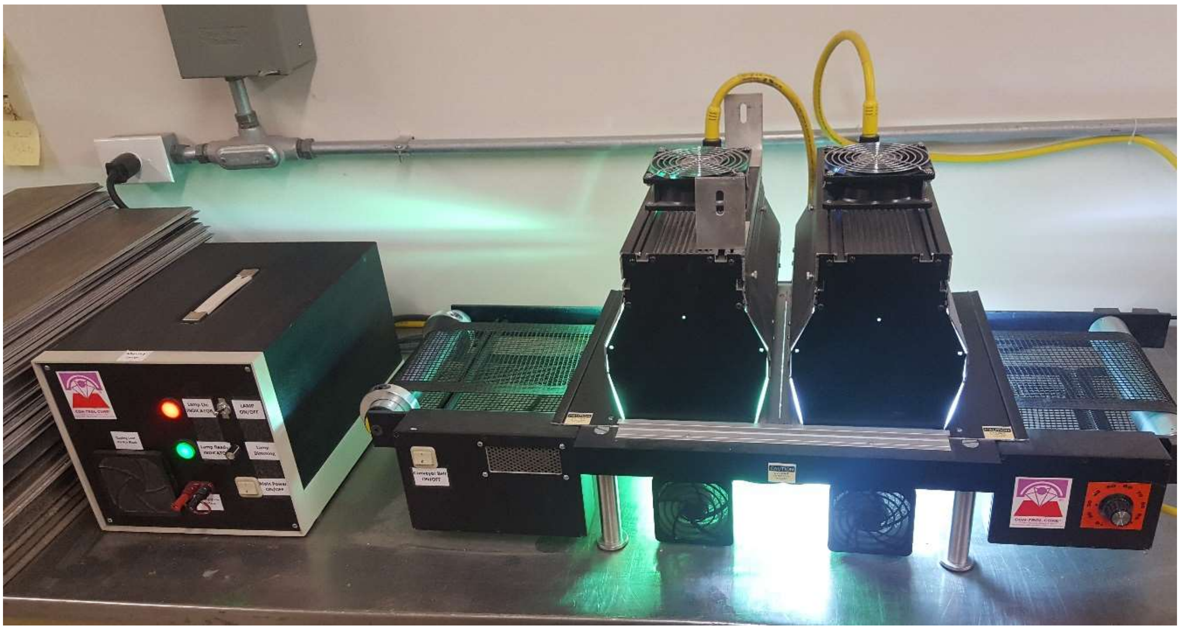


Figure 6.8 – Lab Curing station with Gallium and Mercury lamps.

Figure 6.9 – Final decorated geopolymers.

COLORING OF THE GEOPOLYMER BODY

In the decoration goals there is another part regarding coloring the geopolymer body.

Were tested some colors, added during the preparation of the mixing, to obtain some colored geopolymer tiles. The colors are metal oxides added during the mixing of the waste powder with reactant and water.

The color tested are black, brown, grey and orange (Figure 6.10). All the color are used at a percentage of 0,9 % on weight of the dry materials.

All the technological parameters as water absorption and mechanical strength are confirmed after the curing time in comparison to the non-colored geopolymer.

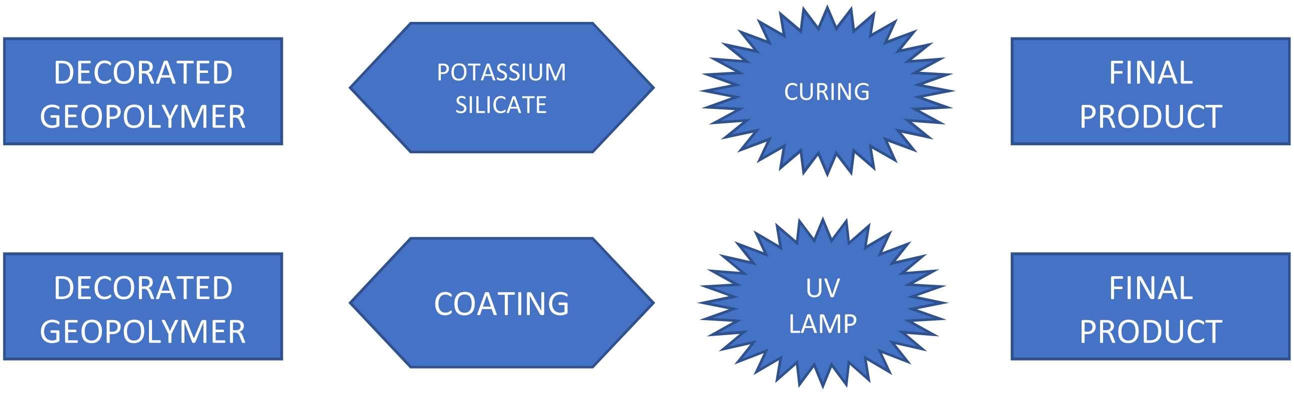
Figure 6.10 – Final colored geopolymer samples.

SURFACE TREATMENTS

The decorated surface using UV inks isn't very resistant to chemical and mechanical agents, so it was necessary to identify a cold surface treatment in order to protect the surface decoration.

The surface treatments that were tested are the following:

- Deposition of a thin layer of liquid potassium silicate on the surface using an airless spray gun (60 g/m^2);
- Deposition of a thin layer of UV curing coating on the surface using a roller coating or a digital printer (40 g/m^2) (Figure 6.11).



All the results deriving from the characterization of the decorated geopolymers with the addition application of a protective surface treatments are described in the following chapter.

Figure 6.11 – Deposition of a thin layer of the UV curing coating.

SURFACE RESISTANCE

Performing the scratch test with a special tool to engrave with stainless steel tips gave a positive result using the UV coating. There is no trace of incision after scratching by applying pressure and pulling the instrument (Figure 6.12).

Figure 6.12 – Scratch test.

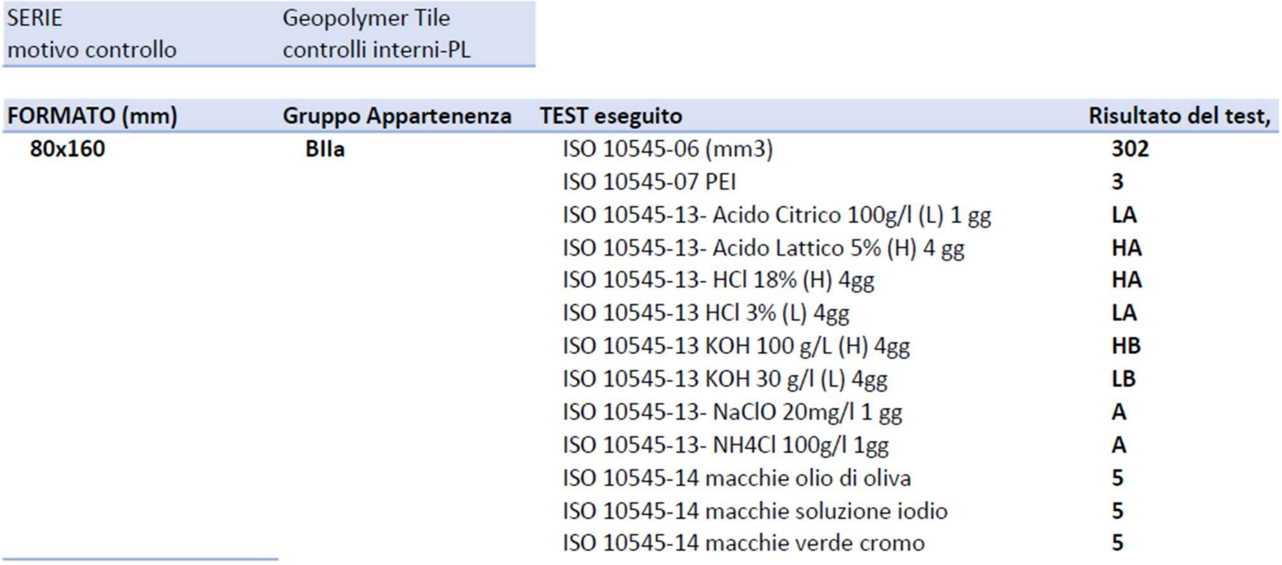
Using the potassium silicate surface treatment, the surface doesn't reach the same hardness of the geopolymer treated with UV curing coating. Using this potassium silicate application, the scratch test is not passed.

7. GEOPOLYMER SURFACE CHARACHTERIZATION

ISO STANDARDS - SURFACE CHARACTERIZATION

A complete characterization of the geopolymer decorated surface was carried out at the Marazzi quality lab, respecting the procedure provided from the tile standards. The results are shown in the following table (Table 7.1), this characterization indicates that the product can be classified as BIIa according to the reference standard. The class of classification is attributed following the categories provided of water absorption, flexural strength and modulus of rupture, previously determined.

This characterization has the scope to investigate the quality of the surface.



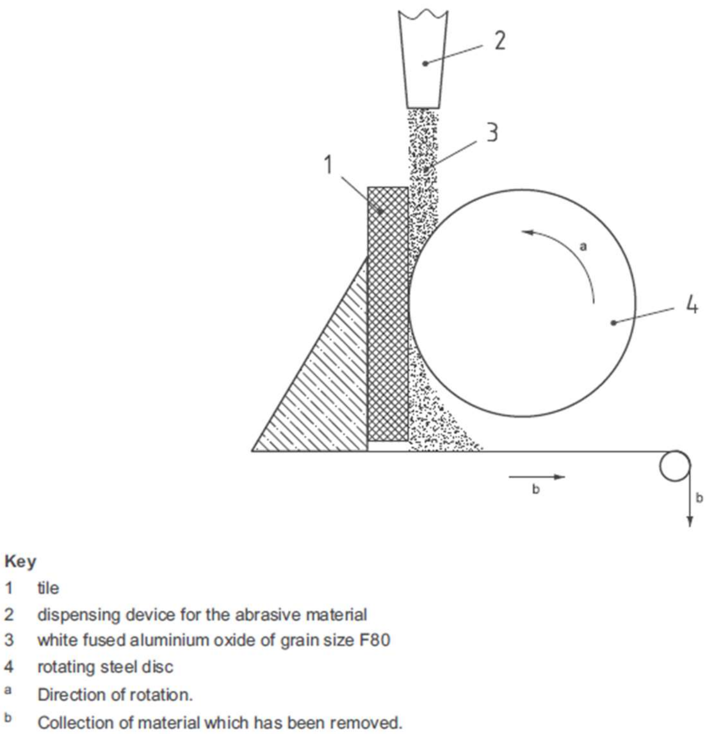
SERIE	Geopolymer Tile
motivo controllo	controlli interni-PL

FORMATO (mm)	Gruppo Appartenenza	TEST eseguito	Risultato del test,
80x160	**BIIa**	ISO 10545-06 (mm3)	**302**
		ISO 10545-07 PEI	**3**
		ISO 10545-13- Acido Citrico 100g/l (L) 1 gg	**LA**
		ISO 10545-13- Acido Lattico 5% (H) 4 gg	**HA**
		ISO 10545-13- HCl 18% (H) 4gg	**HA**
		ISO 10545-13 HCl 3% (L) 4gg	**LA**
		ISO 10545-13 KOH 100 g/L (H) 4gg	**HB**
		ISO 10545-13 KOH 30 g/l (L) 4gg	**LB**
		ISO 10545-13- NaClO 20mg/l 1 gg	**A**
		ISO 10545-13- NH4Cl 100g/l 1gg	**A**
		ISO 10545-14 macchie olio di oliva	**5**
		ISO 10545-14 macchie soluzione iodio	**5**
		ISO 10545-14 macchie verde cromo	**5**

Table 7.1 – Results of the surface characterization.

Description of all the tests:

ISO 10545-06: Determination of the abrasion resistance of the tiles by measuring the length of the groove produced in the proper surface by means of a rotating steel disc (Figure 7.1), under given conditions and with the use of abrasive material. Result of the test: 302 mm^3.



Key
1 tile
2 dispensing device for the abrasive material
3 white fused aluminium oxide of grain size F80
4 rotating steel disc
a Direction of rotation.
b Collection of material which has been removed.

Figure 7.1 - Schematic diagram of deep abrasion equipment and method (ISO 10545).

ISO 10545-07: Determination of the abrasion resistance of the glaze by rotating an abrasive charge on the surface and evaluating the wear based on the visual comparison of abraded and non-abraded test samples; the classification is made using the values listed below. Result of the test: Class 3.

Abrasion visible after a number of revolutions equal to:	Class
100	0
150	1
600	2
750, 1500	3
2100, 6000, 12000	4
>12000	5

ISO 10545-13: determination of the resistance to chemical attack of the samples by direct contact with the substances required by the standard (Citric acid, Lactic acid, HCl, KOH, NaClO, NH_4Cl). Results of the tests: Citric acid (LA) no visible effect, Lactic acid (HA) no visible effect, HCl 18% (HA) no visible effect, HCl 3% (LA) no visible effect, KOH 100 g/l (HB) discernible change in appearance, KOH 30 g/l (LB) discernible change in appearance, NaClO (A) no visible effect, NH_4Cl (A) no visible effect.

ISO 10545-14: Determination of the resistance to stains by maintaining test solutions and materials in contact with the proper surface of the tiles for a suitable length of time (olive oil, iodine solution, chrome green); the surfaces are then subjected to defined cleaning method, and finally inspected for visual changes. Result of the test: Class 5.

The decorated and treated surface was also observed and characterized with the SEM microscope.

Using the Scanning Electron Microscope, it's possible to see the micro defect of the samples. The surface of the geopolymeric tile is homogeneous without cracks but the surface roughness is high (Figure 7.2, 7.3), probably the roughness can be improved using a different laying of the surface coating. The thickness of the UV coating was measured in 4.5 microns (Figure 7.4, 7.5), it is possible to proceed with the increase in thickness to improve surface roughness and porosity.

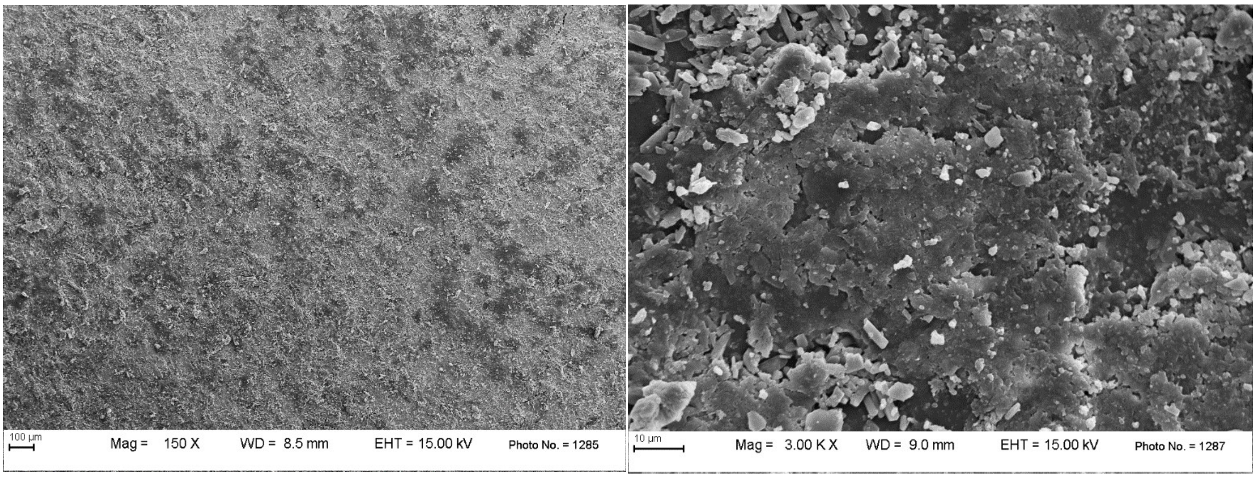


Figure 7.2 and 7.3 – Geopolymeric tile surface images at different magnifications.

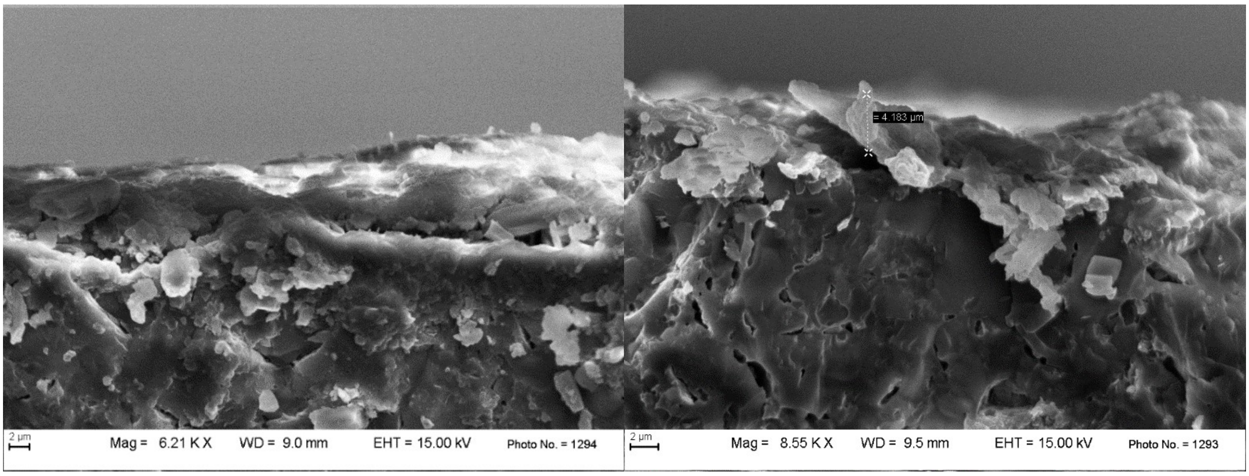


Figure 7.4 and 7.5 – Geopolymeric tile section images at different magnifications.

SURFACE EFFLORESCENCES

Efflorescences are usually observed in geopolymers synthesized by sodium hydroxide and sodium silicate solutions (Bignozzi, Fusco, *et al.*, 2014). On the investigated geopolymers, efflorescences were visible at different grades during the curing process and, in general, their amount increases with curing time in the samples containing sodium reactants. In the samples synthesized by potassium hydroxide and potassium silicate solution the efflorescences are very low. Analysis of efflorescences in geopolymer showed that they are mainly constituted by sodium carbonate (Bignozzi, Fusco, *et al.*, 2014). But in the samples made by ceramic waste the calcium content is very low. Increasing the content of potassium silicate solution in the mix till the saturation, efflorescences become less evident probably according to a higher degree of geopolymerization.

To prevent the problem of surface efflorescence, two test methods have been studied (previous chapter); the first was to treat the sample with a layer of liquid potassium silicate; the second is the deposition of the surface UV coating. The second option gave satisfactory results.

Comparison of the surface treatments after 90 days:

- Deposition of a thin layer of liquid potassium silicate on the surface using an airless spray gun → there is the presence of efflorescence in small points even if much less present than the untreated geopolymer;
- Deposition of a thin layer of UV curing coating on the surface using a roller coting or a digital printer → the efflorescences are not present.

8. STUDY FOR INDUSTRIALIZATION OF THE GEOPOLYMER TILE

PRODUCTIVE TECHNOLOGIES

Industrial steps identification, corresponding to the lab geopolymers production steps (Figure 8.1):

1. **Milling of the waste powder** → Industrial dry milling process using a vertical mill.
2. **Powder humidification with the activator solution** → Industrial granulation process.
3. **Pressing** → Industrial hydraulic press, the pressing phase will also be possible with another method, vacuum pressing method during a vibration phase. In literature is already validated the extruding process and the casting process.
4. **Curing process** → Industrial oven with controlled atmosphere (temperature and humidity).
5. **UV printing decoration** → Industrial decoration line with UV curing station.
6. **Finishing** → UV coating application and sorting.
7. **Packaging** → Packaging line.

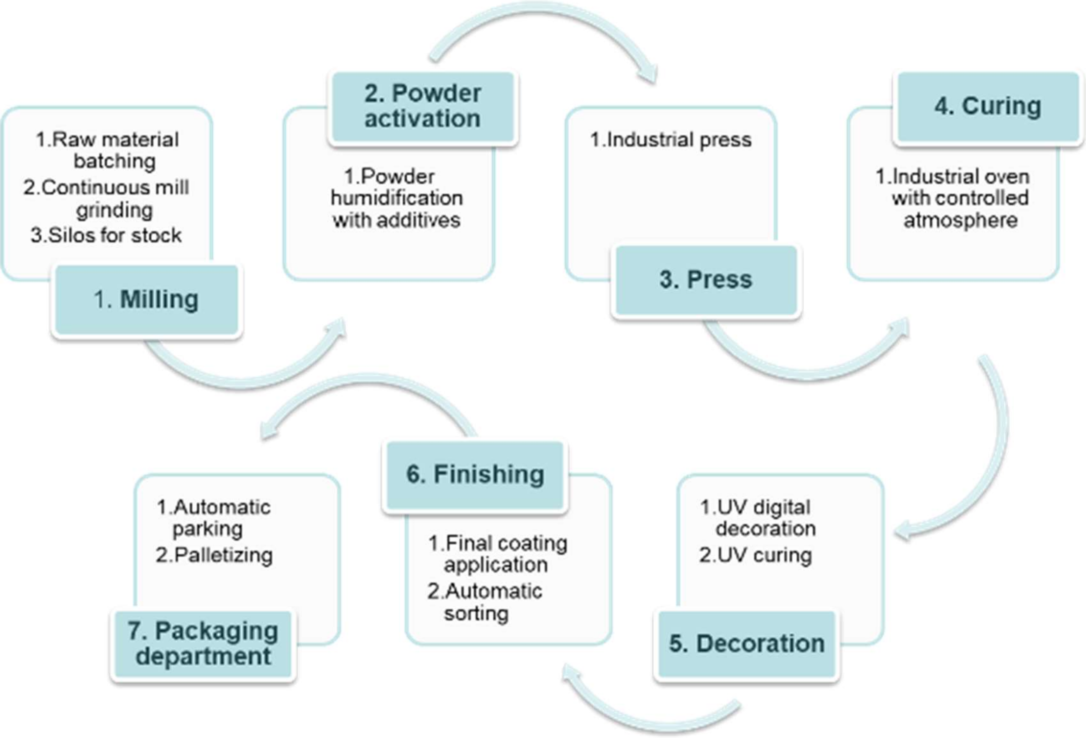


Figure 8.1 – Geopolymeric tile production process.

MILLING AND ACTIVATION OF THE POWDER

The waste powder deriving from the dry grinding process is already granulometrically fine but, to improve the technological characteristics of the geopolymeric tile, it needs to be milled even more finely. Since it is already dry it was decided to use a mill for dry milling, to save energy and emissions due to the spray dry phase used during the wet milling process for drying the slip.

The vertical roller mill (Figures 8.2 and 8.5) is the main component of the dry milling process for ceramic mixtures. It is an efficient machine, its construction allows optimal milling of different materials, such as clay, carbonate and feldspar, with a low and high hardness. The grain size range obtained is variable and can reach extremely low values. Materials with different physical characteristics and particle sizes can be milled together to provide a perfectly even compound.

After the powder milling phase there is the humidification phase with the addition of additives such as liquid potassium silicate and potassium hydroxide. The technology identified to perform this process is the granulation. The continuous granulator (Figure 8.3 and 8.4) ensures optimal powder agglomeration thanks to its construction and operating principle. In the ceramic industry, this technology includes the granulator for the micro-granulation of dry milled bodies to have a better feature during the pressing process. Granulator is made up of a rotating movable body installed on a static solid base. The rotating body is divided into two separate parts. The first section of the machine, where material is loaded, consists of a cylindrical barrel complete with a special intensifying bar. The binding liquid is inserted in this first section by means of spraying nozzles. The second part of the machine has a peculiar sinusoidal shape; at the end of this section it is located the unloading mouth. The rotating body of the granulator is made of internally polished stainless steel, and the supporting base is in carbon steel.

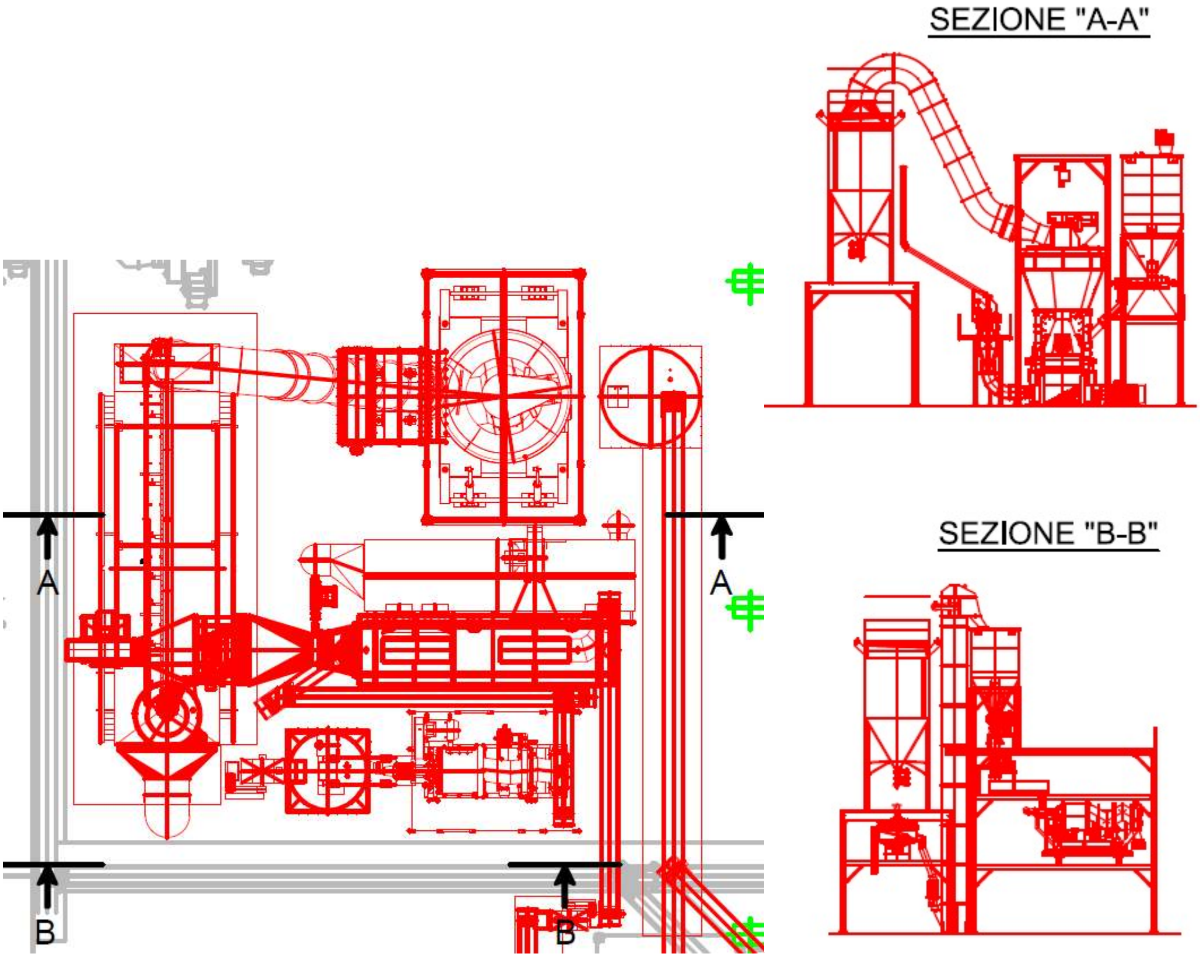


Figure 8.2 – Schematic layout of the milling and activation line, plan view and section view.

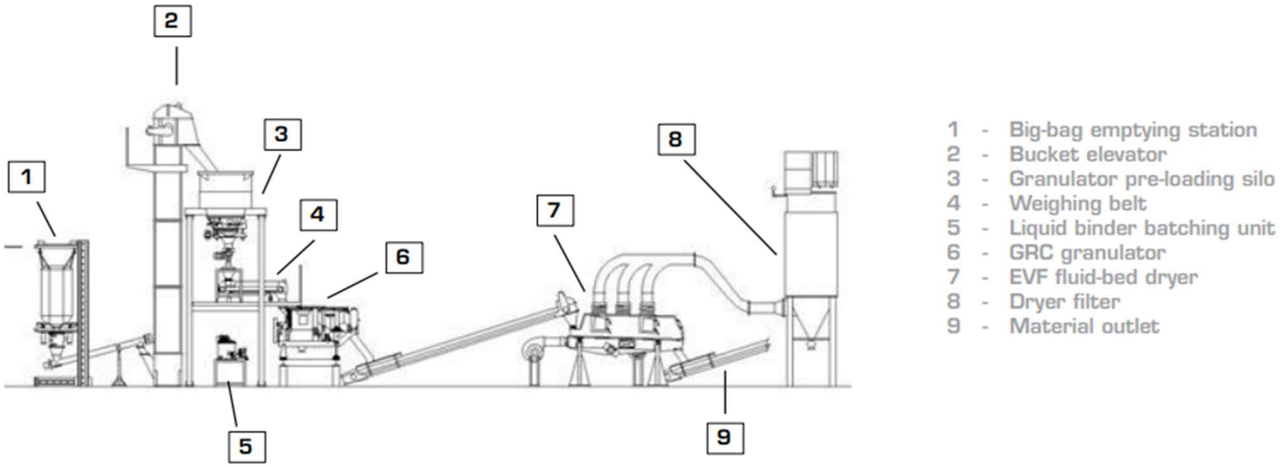


Figure 8.3 – Schematic granulation line.

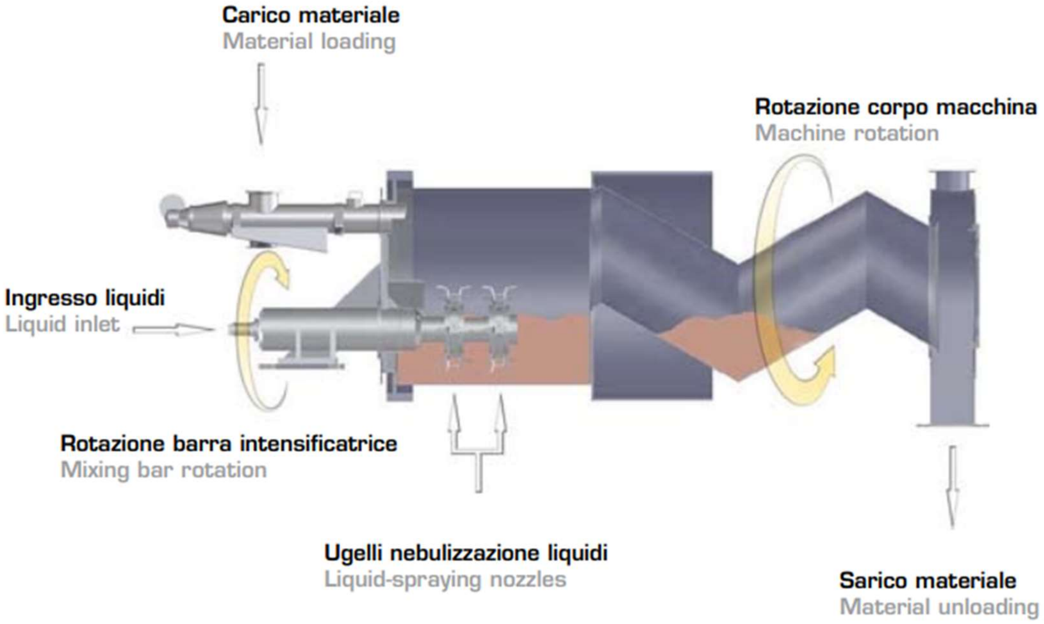
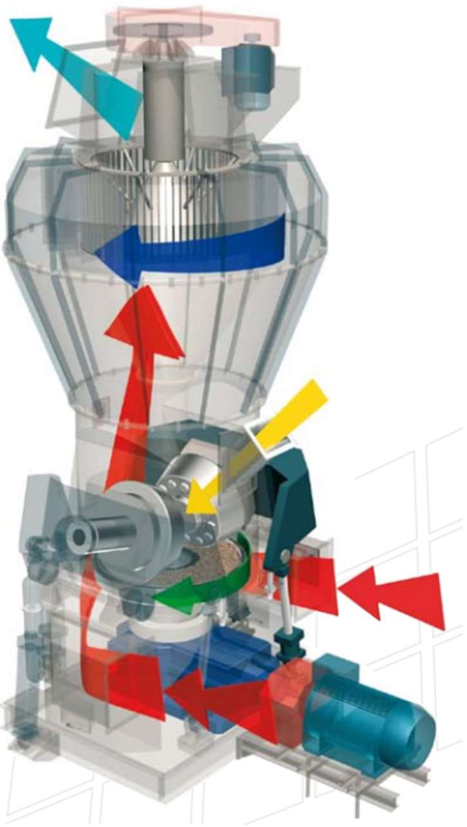


Figure 8.4 – Granulation machine.



🟨 The material, batched by feeder, enters the mill through a hopper and drops onto the track.

🟩 The grinding rollers exert a crushing and grinding action on the material running on the track. Crushing force is exerted through an automatically-adjusted hydraulic circuit.

🟥 An air flux - that is heated if the material is particularly moist - conveys the crushed material to the dynamic separator.

🟦 The dynamic separator classifies the ground material on the basis of its particle size.

🟦 Outgoing material is conveyed to a special bag filter that separates the air from the dust.

Figure 8.5 – Vertical mill.

PRESSING → INDUSTRIAL HYDRAULIC PRESS

The step of pressing of the activated powder will be done with an industrial hydraulic press for dry pressing (Figure 8.6). The free-flowing powder containing a low percentage of moisture, flows from a hopper into the forming die. The material is compressed in a steel cavity by steel plungers and is then ejected by the bottom plunger. Automated presses are used with high operating pressures (up to 500 Kg/cm^2).

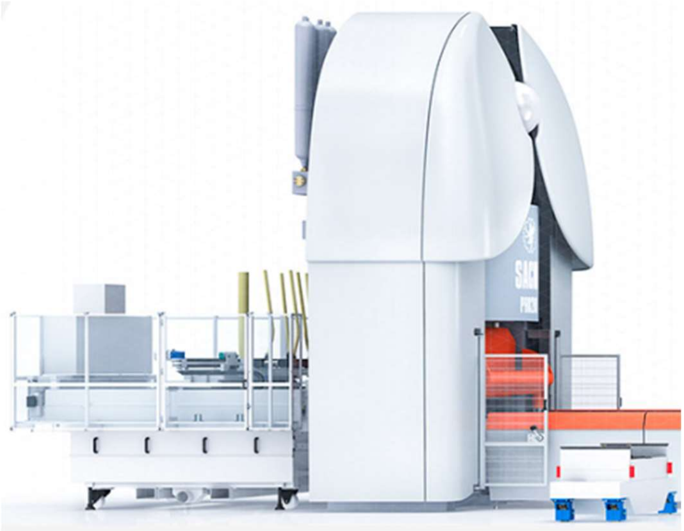


Figure 8.6 - Industrial hydraulic press for dry pressing.

CURING PROCESS → INDUSTRIAL OVEN WITH CONTROLLED ATMOSPHERE AND HUMIDITY

The curing process as to be done with a fixed temperature and a fixed humidity, so there is the need to have a flat conveyor belt in a humidity-controlled industrial oven for the time needed for the hardening of the geopolymer tiles. We have to create a machine that can perform the curing of the material; in the following image (Fig 8.7) there is a ceramic industrial dryer that can make this work adjusting the control of the humidity of the air.

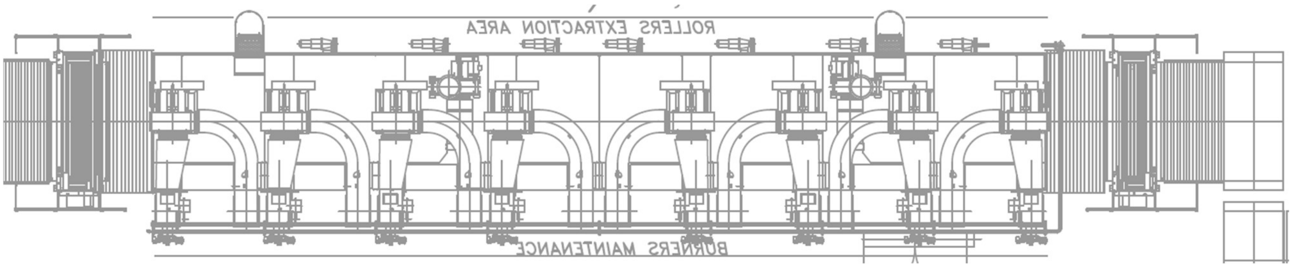


Figure 8.7 – Industrial ceramic dryer.

UV PRINTING AND COATING APPLICATION → INDUSTRIAL DECORATION LINE WITH UV CURING STATION

The decoration line for geopolymer tiles (Figure 8.9) includes a first station where the UV hardening primer is applied, which will be the basis for the digital decoration, the primer can be applied both digitally and through a screen printing roller for direct contact with the surface to be decorated, with the presence of a subsequent curing station with UV lamp.

The second station foresees the presence of a digital printer with hardening UV inks for printing surface decorations and a following curing station with UV lamp (Figure 8.8).

The third station on the line is represented by the application of UV curing coating, this coating is applied by means of a machine that distributes by direct contact a light film of liquid on the decorated surface and a subsequent presence of a UV curing lamp.

Figure 8.8 – Industrial digital printer with UV radiation lamp.

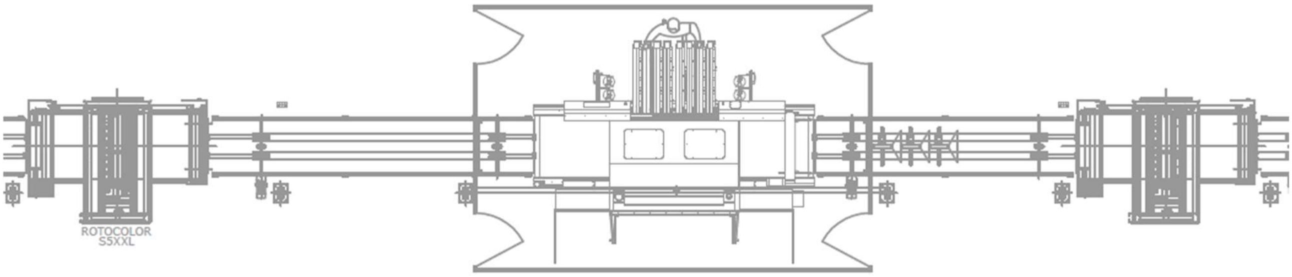


Figure 8.9 – Industrial decoration line with all the application that a geopolymeric tile need; primer application, digital printer with UV radiation lamp and coating application.

9. CONCLUSIONS AND RECOMMENDATIONS

The geopolymerization approach can be used to obtain tiles according to the requirements reported in ISO 13006. The obtained geopolymer tiles can be considered potentially appealing for floor and wall covering applications, but an improvement is necessary if technological features comparable to porcelain tiles (BIa) are desired.

This work has achieved a successful geopolymerization grade of ceramic waste obtaining a material with high flexural strength, low water absorption and good temperature properties. The flexural strength of waste ceramic-based geopolymers depends on the initial reacting system, and the alkaline activating solution plays an important role in geopolymerization process. The ceramic waste based geopolymer exhibits also a favorable thermal stability after thermal exposures.

These technological features are reached thanks to an amorphous geopolymeric matrix which simulates the behavior of the amorphous ceramic glass.

In the activation process of aluminosilicates, immediately after the alkali solution comes into contact with the raw materials, the high OH^- concentration of the alkaline medium favors the break of covalent Si–O–Si, Si–O–Al, and Al–O–Al bonds present in the original precursor, releasing the silicon and aluminum ions into the solution, where they form species with a high number of Si–OH and Al–OH groups (dissolution stage). During the gelation stage, the ionic species in the solution (mono-silicate and mono-aluminate units) condense to form Si–O–Al and Si–O–Si bonds, giving rise to a three-dimensional alumina-silicate gel with alkaline cations which compensate the deficit charges associated with Al for Si substitution. The extent of the precursor dissolution, aluminum release rate, pH of the system, soluble silicon concentration, water content, are critical variables controlling this geopolymerization process. Thus, since Al–O–Si bonds are more likely to form in aluminosilicate gels than Si–O–Si bonds, the aluminum release rate during starting material dissolution initially controls the aluminosilicate formation rate, as well as the stoichiometry and extent of the reaction. The different mechanical behavior observed depend not only from the microstructure but also on the nature and chemical composition of the arising reaction products (aluminosilicate gel). Al-rich gels develops low strength matrix then Si-rich gels, this is in relation with the degree of reaction for the precursor (Fernández-Jiménez *et al.*, 2008). The Si content in the geopolymeric matrix increases with the reaction time, it seems that the addition of - silicate to the activating solution enhances the condensation process of the ionic species at the system as a media is produced with a high concentration of OH^- and a large amount of soluble silicates are produced (Fernández-Jiménez *et al.*, 2006).

Respect to the first stage of geopolymerization reaction, that is controlled by the aptitude of the alkaline compound to dissolve the solid ceramic network and to produce small reactive species of silicates and aluminates, it would be reasonable to think that in the case of sodium and potassium hydroxides, it should be -OH the compound showing greater dissolvent activity due to its higher level of alkalinity (Fernández-Jiménez, Palomo and Criado, 2005). The ion size difference is a determinant factor that intervenes in the kinetics of the reactions and the sodium cations have better 'zeolitization' capabilities because they are smaller than potassium cations (Fernández-Jiménez, Palomo and Criado, 2005), so the structure with the potassium cations became more disordered with a lower geopolymer recrystallization associated with it, helping to obtain an amorphous geopolymer matrix.

Finally, with respect to the curing conditions, it should be remarked that temperature is observed to play an important role in determining the structure and properties of the reaction products. Time and temperature are key factors in the development of mechanical performance of these types of materials. Thus, flexural strength increases with the curing temperature. However, flexural strength is observed to reach the maximum value for a certain temperature, beyond which it starts to decrease. In the present case, strength peaks at temperatures between X and Y °C. This is because when the temperature is raised excessively, the microstructure is weakened, probably owing to partial loss of part of the combined water. This suggests that it is necessary to keep small amounts of structural water in order to reduce crack formation and maintain the microstructural integrity of the material. Also, the time is very important during the curing process, results showed that the degree of reaction increased with curing time. In the results is possible to see that during the time of curing the mechanical strength increase and consequently the water absorption decrease.

The last important factor in formation of high mechanical strength geopolymer matrix is the water-solid ratio evolvement during the reaction, with less water the concentrations of activators are greater in the mix, increasing the dissolution rate, this is the advantage of the pressing method compared to the casting method.

PRODUCTION COSTS

Comparing the ceramic and geopolymeric processes to produce tiles, it’s possible to establish that there is a reduction in production costs associated with geopolymer, mainly due to two factors:

1) Shorter industrial process.

2) Energy consumption.

Complete replacement of natural clay, feldspar and natural sands with industrial waste will allow a significant reduction in production costs, but the reagents are expensive. In the following table is presented an indicative cost analysis using one of the best formulations (Table 9.1). Costs of reagents are considered using an indicative offer of a supplier and the waste is considered like negative value because is the usual disposal cost.

MATERIAL COST ANALYSIS FOR GEOPOLYMERIC TILE			
	€/ton	%	€/ton
-SILICATE	1000	17	170
-OH	500	13	65
WASTE	-45	70	-31,5
TOTAL		100	203,5
	Kg/m^2	m^2/ton	€/m^2
7 mm THICK GEOPOLYMER TILE	16	62,5	3,26

Table 9.1 – Cost analysis for a geopolymeric tile.

In the following table is reported a comparison between an indicative cost of production for a ceramic tile and a geopolymeric tile (Table 9.2), the comparison show that the order of cost is very similar.

COST COMPARISON	CERAMIC	GEOPOLYMER
	€/m^2	€/m^2
MIXTURE	1,95	3,26
GLAZE - INKS	0,70	0,70
ENERGY	1,17	1,17
METHANE	1,62	0,30
TOTAL	5,44	5,43

Table 9.2 – Cost analysis comparison between a ceramic tile and a geopolymeric tile.

The complete elimination of the firing process, geopolymerization do not require a sintering process, and the elimination of the spray drying process, because there is a dry milling phase, results in a reduction in energy consumption and a consequent reduction in CO_2 emissions in the atmosphere. Methane consumption for spray drying and firing will decrease by 100% (methane consumption for these phases is about 90% of total ceramic cycle consumption), the methane cost per 1 m^2 of production will decrease by 90%. Remains only the consumption of methane for the curing process, but it's possible to study an electric curing oven to eliminate completely the methane consumption of using the recovery heat from ceramic kilns.

Concerning the body mix, the industrial dry milling process will require less energy consumption (about 20%) due to the fully substitution of natural sands and feldspars with ceramic powder, that is already well milled but for this comparison we maintain the same cost.

These considerations can give us an important cost indication, the two materials have the same order of cost and the geopolymerization can be considered as a competitive alternative solution to make tiles.

The fact that the CO_2 emissions were almost totally eliminated imply that is not necessary to purchase greenhouse gas emission allowances bringing big savings on costs.

Actually, in the ceramic production cycle, part of the waste is recycled within the process and part is disposed to landfills. Disposal takes place because excessive use of waste in ceramic can give instability problems during firing and defect called point black due to the residual grinding wheels present in the waste.

The recycling of the powder in the ceramic mixture involves intermediate processing; initially it requires a point of accumulation of the powders and dissolution in water, then it must be sieved to remove the coarser pieces and then there is a liquid storage before being introduced in the cycle. The depreciation of the plants, the energy used, and the cost of employees and maintenance is to be distributed over the waste.

SUSTAINABILITY

Ceramic replacement with unconventional constituents deriving from recycling waste is an attractive route to produce sustainable tiles. However, it is very important that the selected waste has an almost constant composition and is available in large amount. Limits to the development of innovative materials are imposed by the necessity to start a complete standardization process of all the properties and to ensure the total absence of undesired chemical reactions. Moreover, the national and European legislation must approve the use of the new materials and processes. Geopolymers are receiving particular attention in these recent years, although they have been developed in the first part of 1900. In Europe geopolymers are only commercialized in small-scale plants for special applications.

The proposed solutions for Geopolymeric tile manufacturing have the potential to be substantially more sustainable, from a life cycle perspective, than current ceramic tiles. They are more sustainable both in the process and in the material produced.

The main forecast environmental benefits include:

(a) Reduction of Greenhouse gas emissions: the geopolymerization process eliminate the sintering process, the lower methane consumption during firing and spray drying implies a significant CO_2 emission reduction.

(b) Reduction of energy consumption in the milling process due to the thinness of the ceramic waste powder than the substituted sands and feldspars from domestic and foreign mines and quarries.

(c) Contribution to sustainable waste management in terms of the recovery of the amount of ceramic wastes that today are not re-introduced in the cycle, reducing contributions of material to landfill extending their working life and saving territories leaving them uncontaminated.

(d) At the end of life of the geopolymeric tile, the material can be milled and reused by alkali activation creating other object or tiles using geopolymerization.

(e) Preserve natural stocks of virgin rocks and important minerals in Europe such as clay, limestone and feldspar; preserving the uncontaminated lands from deforestation.

(f) Reduce the imports of minerals for ceramic mixture from overseas, considering that naval transport, used for raw materials, is the most important pollution factor regarding CO_2 emissions and fine dust emissions.

PRODUCT FINAL DESTINATION

In general, in the Italian market, "sustainable" tiles are not always recognizable, only in few shops these products are identified with environmental brand such as LEED, Ecolabel, EPD or Carbon Footprint. In any case, the most part of customers are not interested in these kinds of product, especially in the south part of Europe. The attention of this part of the market is focused on the aesthetic appearance and low price.

On the other hand, in the north of Europe customers shows more interest in "sustainable" tiles, especially designer, architects and sector experts. This part of market is growing up and the tile sector has to be ready to satisfy the request from the market.

The finals destinations for geopolymeric tiles can be floor and wall covering like ceramic tiles. The best pressed samples belong to the BIIa class and can cover a great market slice.

To the BIa category-class belong the high-range porcelain tiles, but the large market slice in all the world is composed by products for paving and wall covering of all the other classes like the BIIa products. Only in Italy the BIa class is the best-selling category.

In the table 9.3 is possible to see the categories to which the geopolymeric tiles obtained belong.

CLASS	**Water Absorption**	**Flexural strength**	**Modulus of rupture**
BIa	≤ 0.5%	Thickness < 7.5 mm: ≥ 700 N Thickness ≥ 7.5 mm: ≥ 1300 N	≥ 35 N/mm^2
BIb	0,5%< X ≤3,0 %	Thickness < 7.5 mm: ≥ 700 N Thickness ≥ 7.5 mm: ≥ 1100 N	≥ 30 N/mm^2
BIIa	3 %< X ≤6 %	Thickness < 7.5 mm: ≥ 600 N Thickness ≥ 7.5 mm: ≥ 1000 N	≥ 22 N/mm^2
BIIb	6%< X ≤10 %	Thickness < 7.5 mm: ≥ 500 N Thickness ≥ 7.5 mm: ≥ 800 N	≥ 18 N/mm^2
BIII	> 10%	Thickness < 7.5 mm: ≥ 500 N Thickness ≥ 7.5 mm: ≥ 800 N	≥ 12 N/mm^2
Geopolymer parameters			
PRESSING METHOD	BIb	BIa	BIIa
CASTING METHOD	BIIa	Not Classifiable	BIII

Table 9.3 – category class for the geopolymeric tiles obtained.

FUTURE DEVELOPMENTS

The main development in the future of this research is the optimization of the mix design and curing process to obtain a geopolymer tile that belong to the BIa class according to the ISO 13006.

One other important point of this research is the development of the decoration process to reach a harder and more resistant surface. To reach these points the building of a prototype production line for geopolymer tiles is needed.

So, beyond the designated experimental program, some further developments may be carried out:

1) Water-to-solid ratio optimization: geopolymers requires extra water not only for dissolution purpose but also to compensate quick-evaporated water from its self-generated heat but we know that less water permit a higher pH with more dissolution. To achieve maximum strength, the optimum water-to-solid ratio should be extendedly studied.

2) Concentration of alkaline activators optimization: the dosage of alkaline activators used in this study was based on recent geopolymer literatures and experimental tests. Optimum alkaline concentration might be investigated to improves geopolymers reactivity and reach higher mechanical strength and lower water absorption.

3) Fineness of raw materials: smaller particle and higher surface area increase the level of both physical and chemical reactions of geopolymerization, such as dissolution rate, ions transportation, forming alumina-silicate species. The synthesis of geopolymers with high fineness materials could enhance the setting time, increase the geopolymeric gel phase and lead to higher strength values.

4) Heat and moisture loss protection: The protection of moisture loss is strongly recommended to geopolymers. Maintaining moisture could significantly maintain and improve curing regimes for the mixtures to achieve the designated properties of construction materials and applications. To complete the industrial process for production of geopolymer tile there is the need to develop the technology to achieve the best heating process that could prevent moisture loss.

5) Life Cycle Assessment (LCA): LCA of geopolymer tiles could be considered and studied in order to demonstrate its environmental benefits as sustainable alternative materials.

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