PON Nº 156 - GEOPOLYTILE : "ECOFRIENDLY CERAMIC TILE DEVELOPMENT BY GEOPOLYMERIZATION"

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ABSTRACT

The aim of the project proposed in the framework of the 6th Joint CORNET is to develop low cost energy saving methods for manufacturing ceramic tile by using geopolymerization as a new ceramic processing technique. Geopolymers are non-crystalline aluminosilicate polymers that are formed by mixing of alkali-silicate solutions with reactive aluminosilicate materials under normal temperature conditions. The geopolymerization reaction contains dissolution and a polycondensation-step. Different raw materials, including primary raw materials such as metakaolin and other meta-clays as well as secondary raw materials such as fly ashes, slags and ceramic wastes are generally suitable for geopolymerization.

The properties of the geopolymers differ significantly due to the reactivity of the raw materials, the activator composition and the setting conditions. The cold setting behaviour offers the possibility of energy saving in the ceramic manufacturing process; a high temperature firing step is not necessary to obtain materials that are ceramic-like in their structures and properties. Water-resistant ceramic tiles could be fabricated without firing. The possibility of using cost efficient and simple raw materials to build and glaze castable and extrudable geopolymer bodies in the form of tile geometry will be tested. The project work includes the questioning of the European raw material situation due to geopolymerizaion as well as the technological needs of geopolymer tile production. The prototype tile samples will be processed for demonstration and tile standard testing will be applied.

1. INTRODUCTION

CORNET is an ERANET project and stands for **CO**llective **R**esearch **NET**working. It is a network for information exchange and collaboration between national and regional programmes. The project consortium for this project consists of three different partners from three different countries that have a funding agency participating in CORNET. 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 (GHI) and Bauhaus-Universität Weimar (BUW). The partners and research performers, having considerable expertise in the field of "Geopolymer" have submitted a project proposal in response to a call published in the framework of CORNET entitled: *"Ecofriendly ceramic tile production by geopolymerization"*. The CORNET selection committee has recommended the proposal for funding. Main purpose of cooperation among the associations is to develop an ecofriendly manufacturing tile technology and disseminate this technology to their members. Each research performer has specific experiences. BUW has experience in raw materials and their geopolymerization behaviour, GHI has experience in geopolymer design and geopolymer composites. ITC has experience in glazing and ceramic technology. SAM also has experience in tile manufacturing technology and characterization.

Geopolymers [1,2] are made of reactive aluminosilicate raw materials by alkali activation (Figure 1). The alkali activation is a singular procedure in which the aluminosilicate material (raw materials or by-industrial products) is mixed with certain alkaline activators; the resulting paste is then cured at particular conditions producing hardened materials. In a previous research, it was found that the main reaction product formed in such systems is an amorphous aluminosilicate gel with short-range order in its three-dimensional structure.

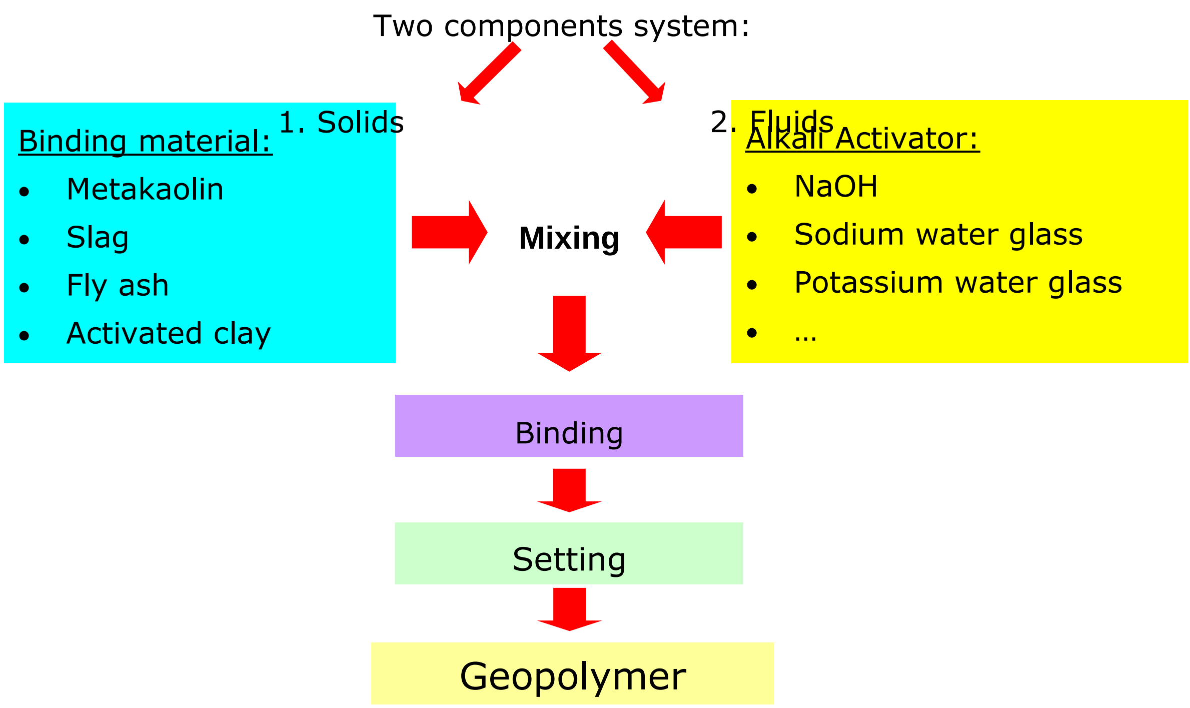

Figure 1. Production steps of geopolymer [3].

Depending on the raw material selection and processing conditions, the resultant material can exhibit a wide range of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity. However, these properties are not necessarily inherent to all type of formulations. Alkaline inorganic polymers should not be considered an universal through for all material selection problems, but rather a solution that may be tailored by correct mix and processing design to optimise properties and/or reduce cost for a given application. Most of the papers in the literature concern the metakaolin and fly ashes (industrial by-product of the thermal power stations that use coal like fuel) as source material [4,5]. Commercially available metakaolin is a highly technical product obtained by several cleaning steps to reach definite colourless for the use as filler in plastics, etc. On the other hand, pure metakaolin is an expensive material for that to make binders materials with it is not a realistic idea. Secondary raw materials such as fly ash promise high ecological benefit and lower cost, but their use bring difficulties in availability, handling and especially product quality. The search for alternative low cost or highly available materials may lead among other things [5] to "normal clays". This material is widely available all over the world and may show certain reactivity after a thermal activation process as well [7-9].

Geopolymers are energy efficient ceramic-like materials which form and harden at ambient temperatures, yet are sufficiently durable and stable at high temperatures for using in building and fireproof insulating applications as well as for immobilization and storage of hazardous heavy metal containing and radioactive materials. Major efforts have been dedicated to greenhouse CO_2 mitigation with the development of low CO_2 geopolymer cements. There are a lot of studies published on geopolymer technology for different applications, but it is not possible to see any substantial studies about the use of geopolymer technology into the ceramic tile manufacturing or any successful industrials implementation in recent years.

Geopolymer based ceramic tile processing may eliminate the main energy intensive processing steps. Ceramic tiles are produced at 1100-1250°C. As a result, not only a high amount of energy is consumed and CO_2 is emitted (around 0.2kg CO_2/kg final product or 3kg CO_2/m^2 final product) during the production process, but also the energy cost is a significant percentage of the total production costs; around 25-30%. Geopolymers require temperatures around 25-150°C to obtain the desired strength. Geopolymer based ceramic tile processing will save substantial energy cost and reduce CO_2 emission.

This new processing method is expected to have immediate applications in the ceramic tile industry, where raw material and fuel costs are significant. As ceramic tile is used in both residential and commercial floor and wall coverings, the technology will likely have mass-market appeal. The project starts using established shaping technologies of the ceramic tile processing to enable an easy exploitation of the R&D results in the European ceramic tile production. The raw material situation will be view from a European perspective.

Advantages due to the state of the art:

1. Energy saving: Geopolymers hardens under normal climatic conditions and do not need a high temperature heat treatment. Therefore, the potential of energy saving is substantial. Drying and firing steps use around 65% of the total ceramic process energy.
2. Alternative raw materials: Generally a wide range of raw materials is possible to be employed, beside highly pure metakaolins different meta-clays as well as industrial by-products such as fly ashes are usable. The geopolymer binder works as a binding phase and can be diluted to about 30% by several types of fillers. Other clay materials might be utilisable that are restricted so far in ceramic tile production due to rheological or drying problems.
3. Reduction of CO_2 emission: Since ceramic tiles are fired at 1100-1200 °C, there is a huge amount of CO_2 emission. By using geopolymers which harden at lower temperatures (25-150°C), it is possible to reduce CO_2 emission remarkably.

2. TECHNICAL AND SCIENTIFIC METHODOLOGY

As much as possible technology steps (excluding firing) should be kept due to a low investment. For instance; the usual practices of shaping technology like pressing of free flowing powder will be kept. This will be a new path in both materials for ceramic industry as well as for geopolymers. Material and technology development is needed to show the possibilities, borders and obstacles of such a technology. In the end, only a glaze firing process at low temperatures or even no firing may be needed. The project has to show if tile produced will have the required properties via the geopolymeric route.

The problem will be solved by developing geopolymer materials that can be shaped by powder pressing and hardens without a high temperature treatment. The following questions will be essential for a successful forthcoming:

1. Which raw materials are suitable for the tile production? Technical, ecological and economic needs are required to meet. The material has to be widely available in a certain amount and quality.

2. How has the geopolymer mix to be designed using the identified raw materials? The geopolymer mix has to consider the raw material reactivity (amount of reactive phase and reaction kinetic) as well as technical and technological needs (required strength, workability due to shaping technology).

3. Can the usual shaping technology be adapted for shaping a geopolymer tile?
- The primary path that has to be investigated is the granulation and pressing of free flowing powders.
- As a second alternative, the extruding of a paste will be taken into consideration.

4. How can a decorative surface material be adjusted preferably without heat or with low energy consumption? Two possible ways will be followed during this investigation:
- The glazing with frits that melts at very low temperatures.
- Development of a decorative layer made of a geopolymer as well.

5. Does the developed geopolymer tile fulfil the technical requirements in accordance with the European standards? An extensive testing program has to be completed to answer this fundamental question.

Therefore, the following work packages (Figure 2) were built to solve the problem. The research performer in charge with the work package is identified by its acronym set in brackets.

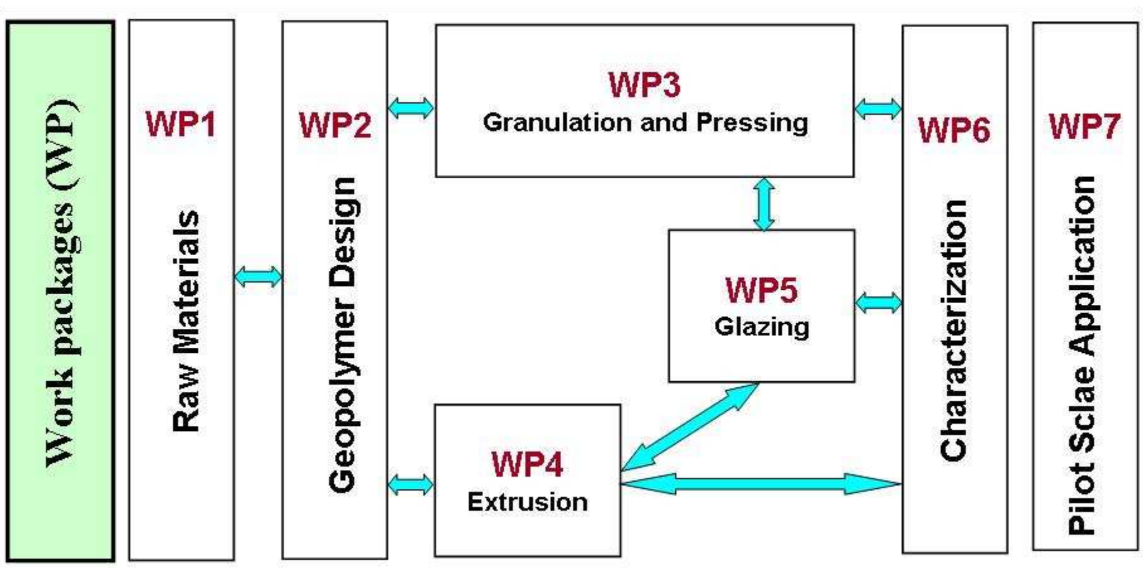

Figure 2. Correlations between each work package.

2.1. Work packages

WP1: Raw material identification and modification

This work package contains the identification, characterisation and modification of suitable raw materials. Due to the definition given above, a large number of primary and secondary raw material is suitable for preparing a geopolymer. Geopolymer properties are mostly influenced by different properties of the raw materials. Thus, mixing design and preparation need fundamental data about raw material properties.

Different possible raw materials (Metakaolin, other meta-clays, fly ash, slags, and fillers) will be taken into consideration. A material catalogue will be prepared from the most promising raw materials according to their reactivity.

Metakaolin (and other meta-clays respectively) will be synthesized by dehydroxylation of phase pure kaolin clays (or normal clays respectively) for the metakaolin (meta-clay) based geopolymer compositions. Calcination of clay is essential for aluminate dissolution into the liquid phase to solidify geopolymers. The effect of calcination time and temperature of clay on surface area, degree of dehydroxylation and the reactivity of the meta-clay will be investigated. Calcination process is an energy consuming process, so fast calcinations will be worked out to obtain desired meta-clays by TG-DTA facilities.

WP2: Geopolymer design of the substrate and decorative layer

According to the raw material reactivity and the technological needs of the shaping technology, the geopolymer mix has to be designed by using different types and concentration of activators as well as employing different filler materials. The different shaping technologies need special material properties related to workability that has direct influence on the geopolymer composition and mixing procedure. For instance a granulated free-flowing material is needed for rapid dry pressing. Raw material surface area directly influences the required moisture content to reach the necessary consistency. The surface area of suitable raw materials varies between 3 and 15 m^2/g. The consequence of this is strongly differing moisture content to reach a comparable consistency. This different moisture content has to be harmonised with the needed activator concentration and absolute amount that influences geopolymerization reaction. All changes in the geopolymer composition will influence the consistency. Therefore, the interdependence of technological relevant properties, geopolymer composition and reactivity of the raw material has to be in the focus of investigation within this work package.

WP3: Granulation of geopolymer mix to a free flowing powder and their pressing behaviour

Joining particles within a given granulation process will improve flow and compression characteristics, reduce segregation, improve content uniformity, and eliminate excessive amounts of fine particles. The first objective of the process is to combine the starting raw materials into an optimised formulation and obtain granules with good flow behaviour and compression characteristics. In the process, the powder granulation using a suitable granulator will be done by the addition of alkaline solution into the optimised composition (type and the amount of added alkaline solution and optimum composition will be determined in WP2). The main variables for granulation step will be investigated including particle size of the starting powders, granulation chamber temperature, time needed to obtain with required properties. The general processing flow diagram is given below.

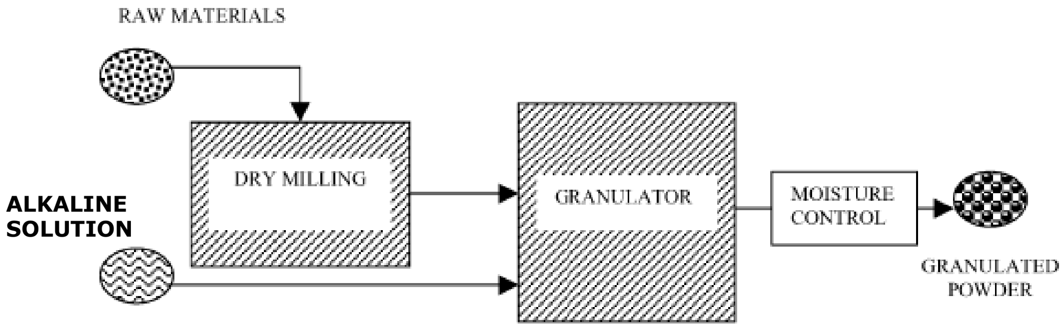

Figure 4: Dry granulation process

Almost all ceramic tiles are produced by means of dry forming, using pressing to give the product its desired shape. A high pressed density is essential for reasons of green strength higher off-the-press strength and a lower firing shrinkage. Density uniformity is also required to minimize shape distortion on firing. A reproducible pressed density and low firing shrinkage are required to maintain low variation in fired dimensions, especially for larger tile sizes. The pressed product should be free of surface and edge defect and internal laminations. The second objective of this process is to dry-press the granulated powders to obtain a desired shape and to investigate the pressing behaviour of the granules. The geopolymer based dry granulated powder characteristics will be expected to have different properties than those of the traditional ones. For geopolymer based granules, because of the alkali activation, will be expected to harden with time, and the pressing behaviour will be changed. In this task, the granules will be kept in a closed container with a different residence time and than pressed. The flowability and the pressing behaviour will be controlled. The maximum residence time will be investigated before pressing in order to design suitable industrial application scheme.

WP4: Extrusion of geopolymer mix as paste

A suitable paste for extrusion requires an accurate formulation. Paste will be prepared using raw materials studied in last work packages. The particles fed to a paste extrusion process have a size, size distribution, shape, crystal form, internal structure and mechanical properties that are determined by earlier preparation processes. In traditional extrusion, liquid and processing additives are added to the powder otherwise shaping requires very high pressures. Liquid is mixed with the powder in order to separate the particles and to lubricate both relative particle movement and motion along the wall of the die land or other surfaces in the flow path.

Chemical properties of the liquid added to the solid phase may be of significance and this will be particularly true if the undried extrudate is the final product. Besides, in geopolymer extrusion process, liquid is important because of the alkaline dissolution. The alkaline solution is used as activating agent in the reaction. Processing additives: In some cases, it is necessary to use additives as lubricant and in other cases as plasticizer. The geometrical properties of the layer will result in a spatial distribution of distances between particles and wall. A lubricant is used to improve the extrusion process. Amorphous aluminosilicates do not behave well in extrusion. This is why certain amount of additive should be introduced to improve the plasticity property in the paste.

Experiments on a laboratory scale should have quantitatively defined the paste, the process requirements, the extrusion conditions, the extrudate quality and the range of these that is permissible. This step has important benefits since the critical parts of the process are clear and it allows the potential purchaser to communicate to manufacturers with some insight. With the optimum paste formulation and using an adequate liquid/solid ratio and some processing additives, small geopolymer samples will be shaped by laboratory extrusion equipment.

WP5: Glazing

Glazes are used on a wide diversity of ceramic products. While the glaze layer has a negligible thickness compared to that of the body, its real purpose is to ennoble the product by improving its density, hardness, gloss, colour, etc. The great variety of products uses places equally multi-various demands on the outward appearance and surface qualities of the glaze, i.e. on its colour and characteristic properties (mechanical, optical, electrical, etc.). Consequently, it can be quite difficult to design for a particular product a glaze of the desired quality and utility value. In order to produce such a glaze, a number of technological and economic dictates should be satisfied. One may say that modern glaze manufacture constitutes a blend of science and art, handicraft and industry.

The objective of this task is to develop an engobe and a glaze that could be used using "traditional techniques". In order to be consistent with the aim of the project the engobe and the glaze have to be fired at the lowest temperature possible.

In order to develop the engobe and the glaze composition it is compulsory to know the properties of the body, mainly the ones related to its behaviour with increasing temperature. The main properties such as thermal expansion behaviour of the body, glaze and angobe will be determined. To avoid the problem of crazing, the expansion coefficients of the engobe and the glaze should, in general terms, be similar to, or slightly lower than those of the body. In order to perform the dilatometric fit, the thermal expansion curves of the glaze, body and engobe were made to coincide at the temperature which is defined for the glaze as the fit temperature.

The engobe layer has to be opaque, in order to hide the colour of the body, and has to have nearly zero water absorption at the maximum firing temperature and the correct thermal expansion in order to avoid problems of crazing. An engobe and a glaze composition will be developed taken into account the properties required by these layers and the firing cycle. Both compositions will have to have a very high fluxing behaviour in order not to use high firing temperatures. As a consequence, it is going to be more feasible to obtain a glaze with a matt finish (crystalline phases inside a glassy matrix) than with a glossy finish (glassy matrix mainly). The main problem with this subtask will be to find raw materials, with a low solubility in water (required when a glaze suspension is prepared), and with a very fluxing behaviour.

WP6: Characterisation of the tile according to valid European standards

Dimensional and surface quality requirements and physical and chemical properties will be studied. The standard tests given below will be done on the final products in two different laboratories (ITC and SAM) for comparison. The tests will be carried out according to EN ISO 10545 series standards and evaluated according to the EN ISO 14411 standards.

3. ECONOMIC IMPACT OF THE PROJECT

Traditionally, the high cost of a quality ceramic tile has made it difficult for the tile industry to compete with other flooring options. The new geopolymer based tile processing methods will have a great potential to lower energy costs related to the conventional method of manufacturing ceramic tile. Therefore, this new processing method should allow the tile industry to compete effectively against the other covering materials.

According to recent figures, fossil fuel cost is around 1€ /m^2 during tile production and there are over 1,5 billion m^2 tile production in Europe (about half of which is wall tile). Thus, potential advantage is substantial. Ecofriendly production and reduced energy cost will put tile industry into more competitive position against other covering materials.

Moreover, the tile manufacturing process produces carbon dioxide (CO_2), which is a greenhouse gas. The gas is produced in two different stages:

- The combustion of natural gas in the firing and drying steps.
- The decomposition of carbonates in the raw materials during the firing step.

The emission of carbon dioxide is regulated by the European Emission Trading Scheme. Some ceramic manufacturing industries are affected by this scheme, and are involved in the reduction of their CO_2 emissions. Any decrease in energy consumption will produce a reduction in CO_2 emissions and also manufacturing costs.

Job security in tile industry will be maintained due to increased competitiveness.

Nowadays energy saving and global warming are the most important issues in all over the world. This project brings totally a new approach to the ceramic production to reduce energy need and decrease CO_2 emission to a great extent. Less tile use of fossil fuels will reduce CO_2 emission due to the tile firing process and the environment will be protected and impact of tile industry. This also has direct impact on life quality by protecting the environment. Reduced firing temperatures will also create better working atmosphere for the workers.

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Keywords: geopolymers, ceramic wall tiles, alkali-activated materials, low-temperature process

Type of contribution: oral