

# Sustainable binders for concrete: A structured approach from waste screening to binder composition development

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**Worldwide, the building sector requires the production of 4 billion tonnes of cement annually, consuming more than 40% of global energy. Alkali activated “cementless” binders have recently emerged as a novel eco-friendly construction material with a promising potential to replace ordinary Portland cement. These binders consist of a class of inorganic polymer formed mainly by the reaction between an alkaline solution and an aluminosilicate source. Precursor materials for this reaction can be found in secondary material streams from different industrial sectors, from energy to agro-alimentary. However, the suitability of these materials in developing the polymerisation reaction must be assessed through a detailed chemical and physical characterisation, ensuring the availability of required chemical species in the appropriate quantity and physical state. Furthermore, the binder composition needs to be defined in terms of proper alkali activation dosages, water content in the mix, and curing conditions. The mix design must satisfy mechanical requirements and compliance to desired engineering properties (workability, setting time) for ensuring the suitability of the binder in replacing Portland cement in concrete applications. This paper offers a structured approach for the development of secondary material-based binders, from their identification to mix design and production procedure development. Essential features of precursor material can be determined through chemical and physical characterisation methods and advanced**

microscope techniques. Important mixing parameters and binder properties requirements are examined and some examples of developed binders are reported.

*Keywords: Geopolymer, alkali activated binder, microstructural analysis, chemical activation, binder development*

## 1 Introduction

The building sector faces an outstanding challenge on the path towards sustainability. Increase in the world population, urbanization, economic growth of developing countries, infrastructure needs, maintenance of existing structures: all these are driving factors in the rising trends in construction material needs for today and for the near future. Concrete is one of the most widely used building materials, due to its several positive features (low cost, durability, ease of utilisation on site and in factory production, transportation, availability worldwide), and its global consumption rate has been estimated at 25 gigatonnes (Gt) per year [International Energy Agency, 2009]. However, the environmental impact associated with the production of the hydraulic binder mainly used for concrete, i.e. Portland cement, is raising concern among scientists and building sector stakeholders. The most recent available data estimate the world production of cement to be about 4 billion tonnes [CEMBUREAU, 2014], which is responsible for 8% of the total CO<sub>2</sub> emissions [Olivier *et al.*, 2012]. Half of these emissions can be assigned to the combustion of fossil fuels, whereas the remaining half are due to the calcination of limestone [Metha *et al.*, 2006]. The use of alkali activated binders (AAB) and geopolymers for replacing Portland cement in some applications is gaining interest [Provis *et al.*, 2015] due to the low environmental impact that is generally associated with the utilisation of secondary materials or by-products.

Geopolymer technology is radically different from Portland cement technology because the setting of the binding system depends on a different reaction mechanism. Whereas in traditional concrete technology the raw material is activated by water which results in a mixture of hydrated calcium silicates and aluminates, in geopolymer technology the raw material is activated by an alkaline solution creating a 3-dimensional amorphous structure based on aluminosilicates. The raw materials can be used without any previous thermal treatment or calcination, thus leading to major energy savings compared to the manufacturing of Portland cement.

Energy is needed in some cases during the curing of the geopolymeric system but the reaction is completed relatively quickly and the required temperature does not exceed 100 °C.

Theoretically, any aluminosilicate material might represent a source material for geopolymerisation so that many industrial aluminosilicate by-products can be utilised as raw material. Recently, Machiels *et al.* [2014] proposed that also Fe-silicate streams with low Al can be used for the synthesis of inorganic polymers. However, in this paper only aluminosilicate precursors will be discussed.

Large numbers of residues which can potentially be precursor materials for geopolymer or alkali activation synthesis can be found in several industrial processes. However, not all the secondary material streams are “created equal” in terms of reactivity, and a screening of potential precursors is needed for the development of cement-less concrete products. When suitable raw materials are identified, an extensive optimisation has to be carried out for obtaining suitable mix “recipes”. Targeted concrete products have to be replicated and the conformity of cement-less products has to be assessed.

In the framework of the SUS-CON “Sustainable, Innovative and Energy-Efficient Concrete, based on the Integration of All-Waste Materials” project [Corvaglia *et al.*, 2012], the above mentioned steps were taken for developing geopolymer binders suitable for several targeted end products. This paper describes the methodology followed for the development of geopolymer binders, proposing a procedure spanning from the characterisation of candidate by-products to the validation of the conformity of geopolymer-based concrete products.

## **2 Analytical tools for identification and characterisation of potential materials for geopolymerisation**

Geopolymerisation is a reaction involving the dissolution of Si and Al from a raw material and their re-organisation into a 3-dimensional rigid network. The mechanism of geopolymerisation, although still not fully understood, is believed to consist of four simultaneous stages: a) Si and Al dissolution of the raw material due to the alkaline environment b) diffusion of the dissolved species into the solution c) polycondensation of Si and Al precursors and gel formation d) hardening of the gel phase and formation of the final product. It is to be underlined that these reaction stages occur simultaneously.

In order to assess the potential of a material to be used for geopolymerisation it is essential to estimate not only its Si and Al content, but also:

- The crystalline and the amorphous phases.
- The grain size distribution and the specific surface area (SSA).
- The shape of the material grains.
- The dissolution rate in alkaline environment.

These will be discussed later on in more detail. Thus, the ability to perform a preliminary screening of potential raw materials requires the application of a series of analytical techniques that can aid in the assessment of the above-mentioned material properties. In addition to characterising potential source materials, also insights in the formed reaction product are of great importance. Elemental bond structure, possible hydration compounds, reaction by-products such as zeolites and carbonates, composition and morphology of reaction products can be determined through analytical techniques and provide information on the nature and degree of the geopolymerisation process. In the following paragraphs the techniques are briefly presented and their potential in assessing important properties of raw and reacted materials is pointed out. The candidate materials were first identified and their availability across Europe assessed in the work package 1 of the project [Arena *et al.*, 2015]. Out of this list, the following were selected for their actual availability: pulverised fuel ash (pfa) and ground granulated blast furnace slag (ggbfs) from UK; red mud from Ireland; silica fume (or  $\mu$ -silica), perlite tailings (cyclones), Na-bentonite, Ca-bentonite from Greece.

It is important to observe that it is not possible to give straightforward indications concerning minimum requirements for physical and chemical features of candidate materials, as the overall reactivity is influenced by several aspects, as previously discussed. The reactivity of a specific precursor material under specific conditions might be satisfactory whereas under the same conditions another material might not perform well. Moreover, precursor materials are often investigated among by-products or wastes, with high variability and uncontrolled production features. Excluding *a priori* some candidates because of a non-compliance with general specifications might lead to underestimate the potential of particular recycling applications, which can be fulfilled even with low grade precursors. In the following sections results from screening analysis on investigated materials will be presented and discussed, and the precursors showing the best potential will be carried on for practical applications.

### 2.1 X-ray fluorescence (XRF)

The first step towards the evaluation of the geopolymerisation potential of a raw material is the determination of the presence of adequate quantities of Si and Al. The quantitative elemental analysis of a material can be performed by XRF analysis which is based on the emission of characteristic “secondary” (or fluorescent) X-rays from the material that has been excited by bombarding with high- energy X-rays or gamma rays. Via XRF analysis it is possible to receive the relative mass content of various elements (presented as oxides) that are in the raw material. However, not all the elements can be measured through this analysis. Elements like C and S cannot be detected, so usually the XRF analysis is complemented by the Loss on Ignition (LoI) test. The LoI test involves the calcination at temperatures 900-1100 °C of a pre-weighted quantity of the sample and measured relative weight loss corresponds to the mass of compounds containing carbon and sulphur. In table 1, the XRF analysis and LoI results of all the candidate materials for the SUS-CON project are presented.

*Table 1: Main oxide content (in weight, %) and loss on ignition (LoI) results of candidate aluminosilicate secondary sources*

|                                | pfa  | ggbs | Red<br>Mud | μ-Silica | Perlite<br>tailings | Na-<br>Bentonite | Ca-<br>Bentonite |
|--------------------------------|------|------|------------|----------|---------------------|------------------|------------------|
| SiO <sub>2</sub>               | 46.8 | 29.4 | 7.8        | 67.2     | 75.3                | 51.1             | 58.7             |
| Al <sub>2</sub> O <sub>3</sub> | 22.5 | 11.2 | 15.5       | 13.6     | 10.5                | 15.4             | 13.2             |
| Fe <sub>2</sub> O <sub>3</sub> | 9.1  | 0.4  | 45.3       | 2.3      | 1.2                 | 5.3              | 5.1              |
| CaO                            | 2.2  | 43.7 | 13.7       | 1.1      | 1.4                 | 9.2              | 5.8              |
| MgO                            | 1.3  | 6.9  | 0.1        | 1.4      | 0.3                 | 4.0              | 3.4              |
| K <sub>2</sub> O               | 4.1  | 0.9  | 0.1        | 4.8      | 4.3                 | 0.6              | 0.9              |
| Na <sub>2</sub> O              | 0.9  | 1.0  | 1.3        | 3.7      | 4.0                 | 3.2              | 0.6              |
| LoI                            | 3.6  | 2.4  | 10.0       | 5.5      | 2.8                 | 10.1             | 11.4             |

As it can be seen in Table 1, all the candidate materials, except red mud contain Si in excess of 30% in weight. Since the geopolymer network is based on Si-chains it is important that the raw material has high content of Si in order to be regarded as a potential raw material for geopolymerisation. Red mud in this respect does not seem to be a very promising material. Nevertheless, its relatively high content of Al, which is an element participating in the geopolymer network formation, suggests the possibility of a further investigation of this material with other analytical methods for assessing other characteristics (like

amorphous content) before excluding it from a possible candidate material in a blended system.

## 2.2 *X-Ray Diffraction (XRD)*

For the assessment of the suitability of a raw material it is not enough to determine the silicon and aluminium content but it is of high importance to identify the mineralogical phases in which the silicon and aluminium species are connected, which have strong effects on the reactivity of the compounds. XRD technique can be used as a screening method for the assessment of the compliance of candidate materials for the geopolymerisation process.

X-Ray crystallography (XRD) is a technique based on the detection of the diffraction patterns created by crystalline atoms when bombarded with a beam of X-rays. The analysis of diffraction patterns gives information on the crystallinity and crystalline phases present in the investigated materials. XRD on powder is extensively used in the characterisation of geopolymer raw materials and reaction products [Xu and Van Deventer, 2002]. Usually, source materials for geopolymerisation show an increased content of amorphous (or partially amorphous) aluminosilicates which generally allow an easier and higher dissolution of silicates and aluminates in an alkali medium. Amorphous aluminosilicates can be detected by XRD as a broad hump at 20-30  $2\theta$ , with the absence of spikes from crystal diffraction. The absence of amorphous aluminosilicates can give a strong indication that the candidate material is not suitable for geopolymerisation, but again further investigation is required to exclude the possibility that the crystalline phases can be dissolved in alkaline media, thus providing the geopolymerisation reaction with the necessary Si and Al species.

The quantification of amorphous phase content can be carried out through the Rietveld method by adding a known percentage of an internal standard (e.g. corundum) to the investigated powder. Dedicated software is used for the phase quantification (crystalline and amorphous) as well as for the comparison with a database of crystal diffraction patterns for the identification of elements present in the powder.

In geopolymerisation, XRD is not only used for the initial characterisation and evaluation of source materials but it can be a very valuable tool for the characterisation of the reaction products and aid in linking the synthesis parameters with the reaction mechanism and the reaction extent. Even though geopolymers are amorphous materials, thus cannot be identified through X-ray diffraction, the detection of new crystalline phases within the geopolymeric matrix such as calcium hydrates (in case Ca-rich pozzolanic materials such

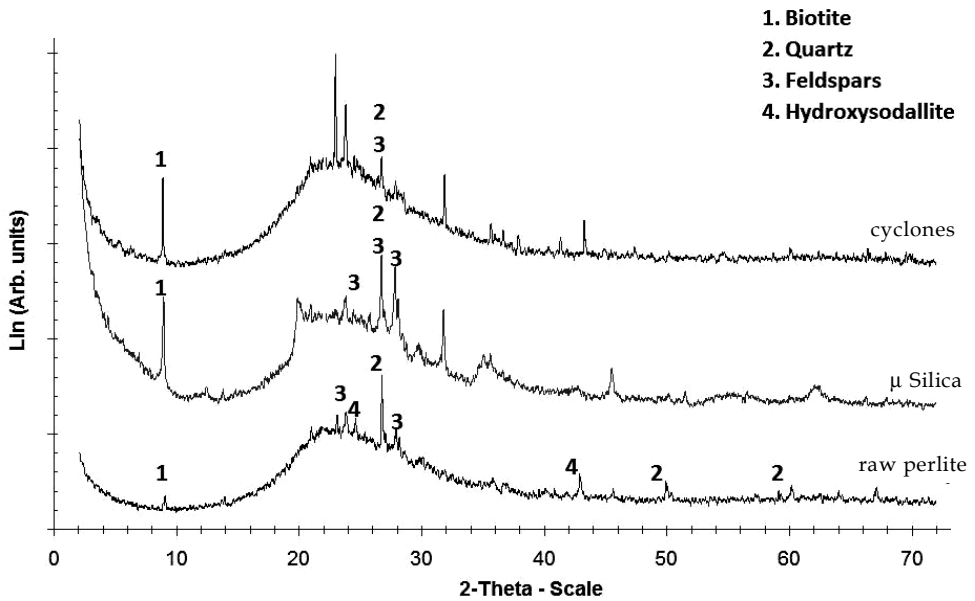
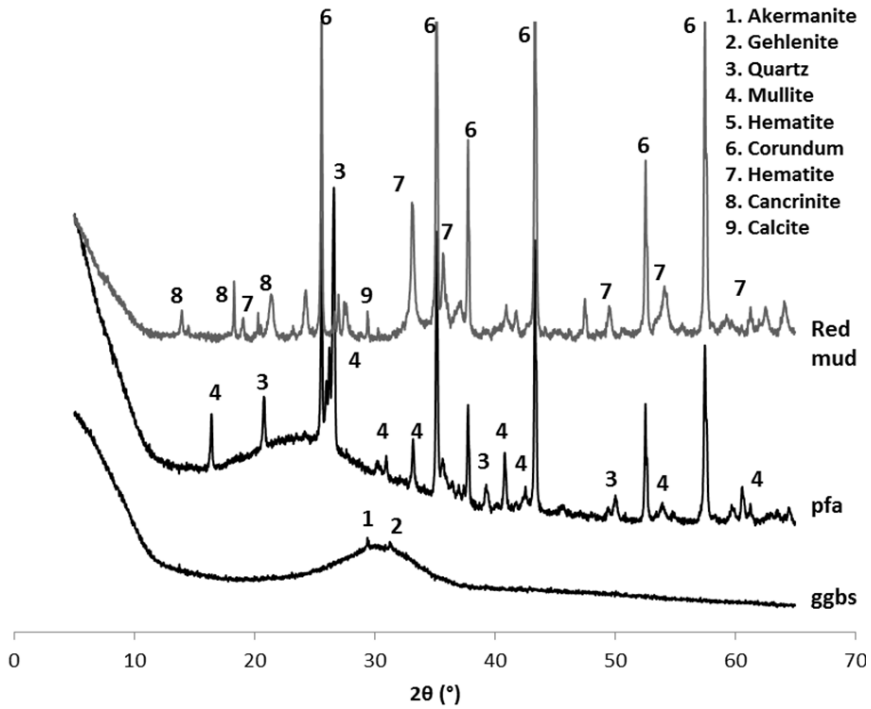


Figure 1: XRD spectra for the investigated materials

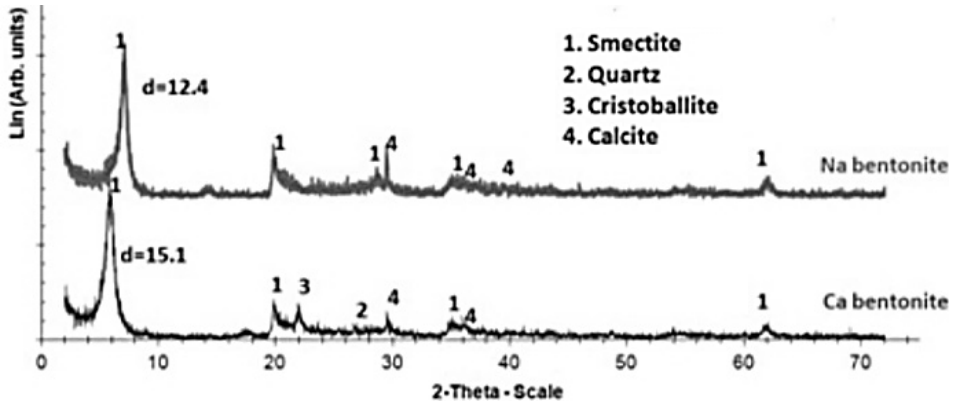


Figure 1 continued: XRD spectra for the investigated materials

as ggbs), zeolites and carbonates can give strong indication on side-reactions.

The mineralogical analysis allowed to identify the crystalline phases in each of the investigated materials. Rietveld method for the determination of amorphous content was applied for some of the candidates and the results were as follows: pfa (84%), ggbs (98%), red mud (70%). Silica fume, perlite tailings (= cyclone), Na-bentonite and Ca-bentonite were not tested for the assessment of amorphous content, although the amorphous content of silica fume and cyclone was evident from the hump of the spectra centred at about 22 – 25 °2 $\theta$ . Out of the initial list of candidate materials, the following were found satisfactory in terms of amorphous content: pfa, ggbs, silica fume, perlite tailings. Red mud on the contrary showed a low glass content that might not be enough for ensuring the release of active silicates and aluminates in an alkaline environment. Bentonite tailings contain mostly crystalline phases that generally are not easily affected by the alkaline solution as the amorphous materials. Nevertheless, the phyllosilicate structure of bentonites renders them with ion-exchange abilities, and therefore they appeared to be susceptible to the alkaline solutions.

### 2.3 Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy is utilised for obtaining the infrared spectrum of absorption or transmittance of investigated materials. FTIR can provide useful information on the chemical bonds between atoms regardless of their crystallinity, thus even for amorphous phases (present in the source material and the geopolymer matrix) significant information on their structure can be determined.



More specifically for geopolymerisation, this technique can be used for studying silicate (Si-O) and aluminosilicate (Si-O-Al) bonds in geopolymer. The focus is on the main (Si, Al-O) band. Other strong vibrations are assigned to internal vibrations of Si-O-Si and Si-O-Al [Puligilla, 2011; Pinkas, 2005]. A summary of typical peak locations for these materials can be found in Table 2.

*Table 2: FTIR Peak locations as identified by the literature. Data from [Puligilla, 2011; Özlem Çelik et al., 2008; Sakulich, 2009; Pnias and Giannopoulou, 2006; Allahverdi et al., 2010]*

| Location (cm <sup>-1</sup> ) | Origin   |
|------------------------------|--|
| 3400                         | -OH stretching vibrations of water   |
| 1650                         | -OH bending vibrations of water  |
| 1450 - 1420                  | C-O asymmetric stretching vibration of CO <sub>3</sub> <sup>2-</sup>   |
| 1100 - 900                   | Si-O-Si and Al-O-Si asymmetric stretching vibrations<br>[Aluminosilicate bonding (Si-O, O-Si-O, Al-O, etc.)] |
| 880-860                      | C-O bending vibration of CO <sub>3</sub> <sup>2-</sup>   |
| 790 - 560                    | Si-O-Si and Al-O-Si symmetric stretching vibrations  |
| 600 - 450                    | Si-O-Si, Al-O-Si and O-Si-O bending vibrations   |

The main developed peaks for raw materials are in the area of the Si-O-(Si or Al) band, which is observed at around 1000 cm<sup>-1</sup> for pfa, 925 cm<sup>-1</sup> for ggbs, 980 cm<sup>-1</sup> for red mud, 1038 cm<sup>-1</sup> for  $\mu$ -silica, 1072 cm<sup>-1</sup> for cyclone, about 1040 cm<sup>-1</sup> for Na-bentonite and Ca-bentonite. In the range 3200-3600 cm<sup>-1</sup> a hump that is due to the stretching vibration modes of H-OH groups can be observed for red mud sample. The presence of water was confirmed by the -OH bending vibrations at 1650 cm<sup>-1</sup>, indicating therefore the presence of physically absorbed and/or chemically bound water. Ggbs sample showed some signs of carbonation from the peaks at about 1450 cm<sup>-1</sup> (stretching) and 850 cm<sup>-1</sup> (bending).

The FTIR analysis carried out on investigated materials confirmed the nature of the Si-O-(Si, Al) bonds, which, due to their amorphous nature, cannot be detected by XRD analysis. The analysis of peak locations (and the peak shifts from raw material to reacted sample spectra) on reacted materials would allow the identification of the products formed by the geopolymerisation reaction.

#### 2.4 Dissolution tests

For geopolymerisation, it is of paramount importance the determination of the susceptibility of the potential raw materials in alkaline media. The investigation of the

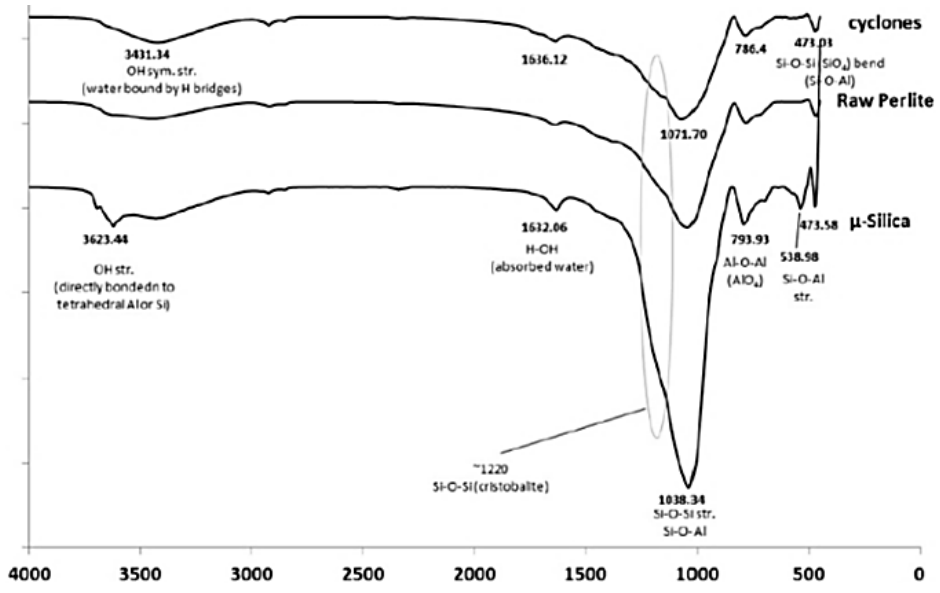
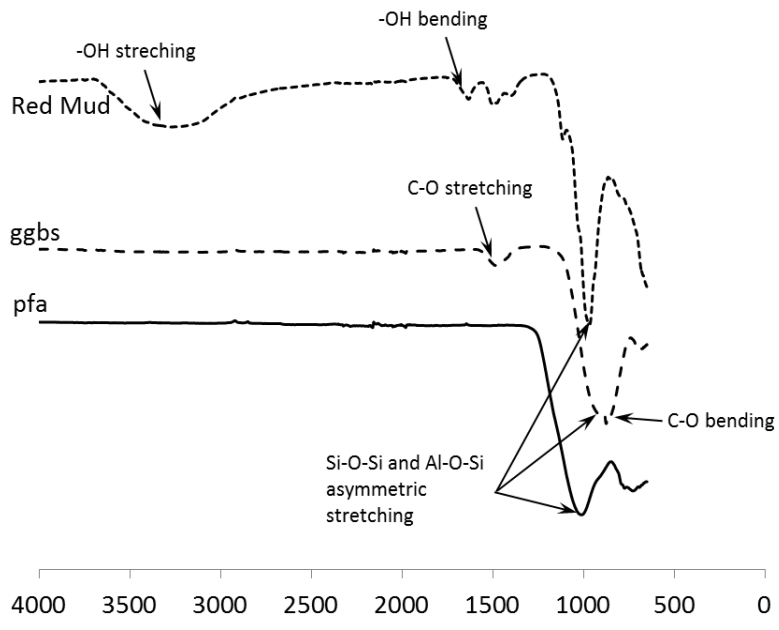


Figure 2: FTIR spectrograms of investigated materials

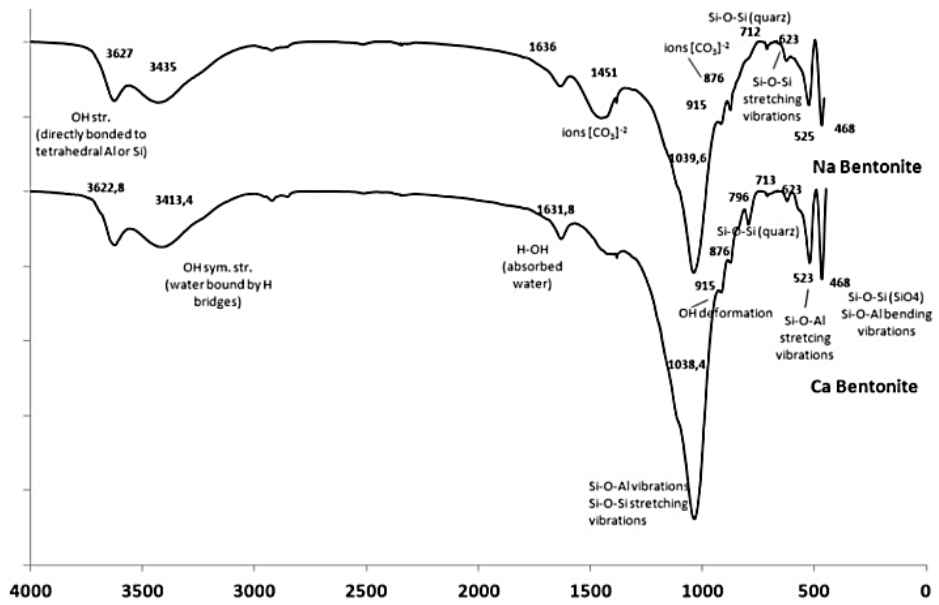


Figure 2 continued: FTIR spectrograms of investigated materials

behavior of raw materials during alkaline dissolution can give an indication about their reactivity, since the capacity of a material to provide adequate Si and Al species in an alkaline solution is crucial for the realization and progress of geopolymerisation. A general and universal methodology on the dissolution investigation however does not exist, but the main concept is to use increased liquid volumes for relatively small amounts of raw material in order to avoid as much as possible the saturation of the solution in Si and Al and the possible polycondensation or precipitation of aluminosilicates. In order to bridge this gap, a methodology used for the study of the dissolution extent of raw materials was developed for the SUS-CON project and it is presented in Figure 3.

This methodology has been tested on some of the candidate materials and confirmed the suitability of silica fume, perlite tailings, Na-bentonite, and Ca-bentonite for geopolymer synthesis, whereas red mud was found not to release enough Si and Al for its utilisation as precursor material. This evidence, along with the results from XRF, XRD and FTIR, led to the exclusion of the red mud from further investigations.

Although the detailed analysis of the obtained results falls out of the scope of this paper, this approach is mentioned for introducing it as a possible screening method. It must be noted that the degree of alkaline dissolution of the materials does not represent the exact behaviour of the materials during geopolymerisation, because the extent of the dissolution

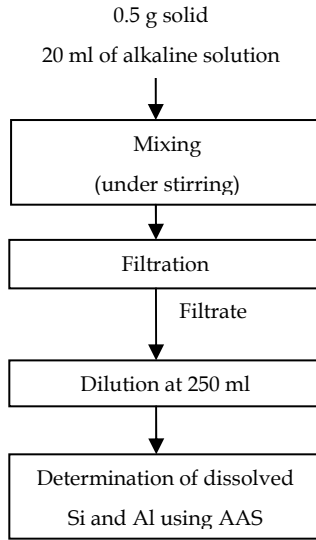


Figure 3: Schematic representation of alkali dissolution procedure

phase in real conditions can be affected by many factors. Nevertheless, the behavior of a material in an alkaline environment can provide essential information regarding the “predisposition” of the raw material to geopolymerise.

### 2.5 Grain Size Distribution (GSD)

Particle size of the precursor materials plays a significant role in its reactivity, on the paste rheological properties (viscosity, setting time etc.) and also can have a significant impact on the water demand.

In order to assess the suitability of candidate powders for reaction in an alkali medium, grain size distribution using laser diffraction particle size analyser can be carried out.

Ideally, the mean particle size should fall in the range 20 – 30  $\mu\text{m}$  [Barnett *et al.*, 2011]. The reduction of the grain size through further milling is known as mechanical activation, and it is commonly adopted for increasing the reactivity of powders [Kumar *et al.*, 2007].

Grain size distribution curves are presented in Figure 4. As it can be observed,  $\mu$ -silica and Ca-bentonite were the finest powders ( $d_{50}$  equal to 7 – 8  $\mu\text{m}$ ), followed by ggbs and pfa ( $d_{50}$  equal to 16 – 18  $\mu\text{m}$ ) and by cyclones (= perlite tailings) and Na-bentonite ( $d_{50}$  equal to 30 – 35  $\mu\text{m}$ ). All the materials can therefore be considered suitable in terms of grain fineness.

Another physical property of the material directly connected to both reactivity and workability is the Specific Surface Area (SSA). The Specific Surface Area can be measured

with Brunauer–Emmett–Teller (BET) -based methods. However, this analysis was not performed on SUS-CON candidate materials.

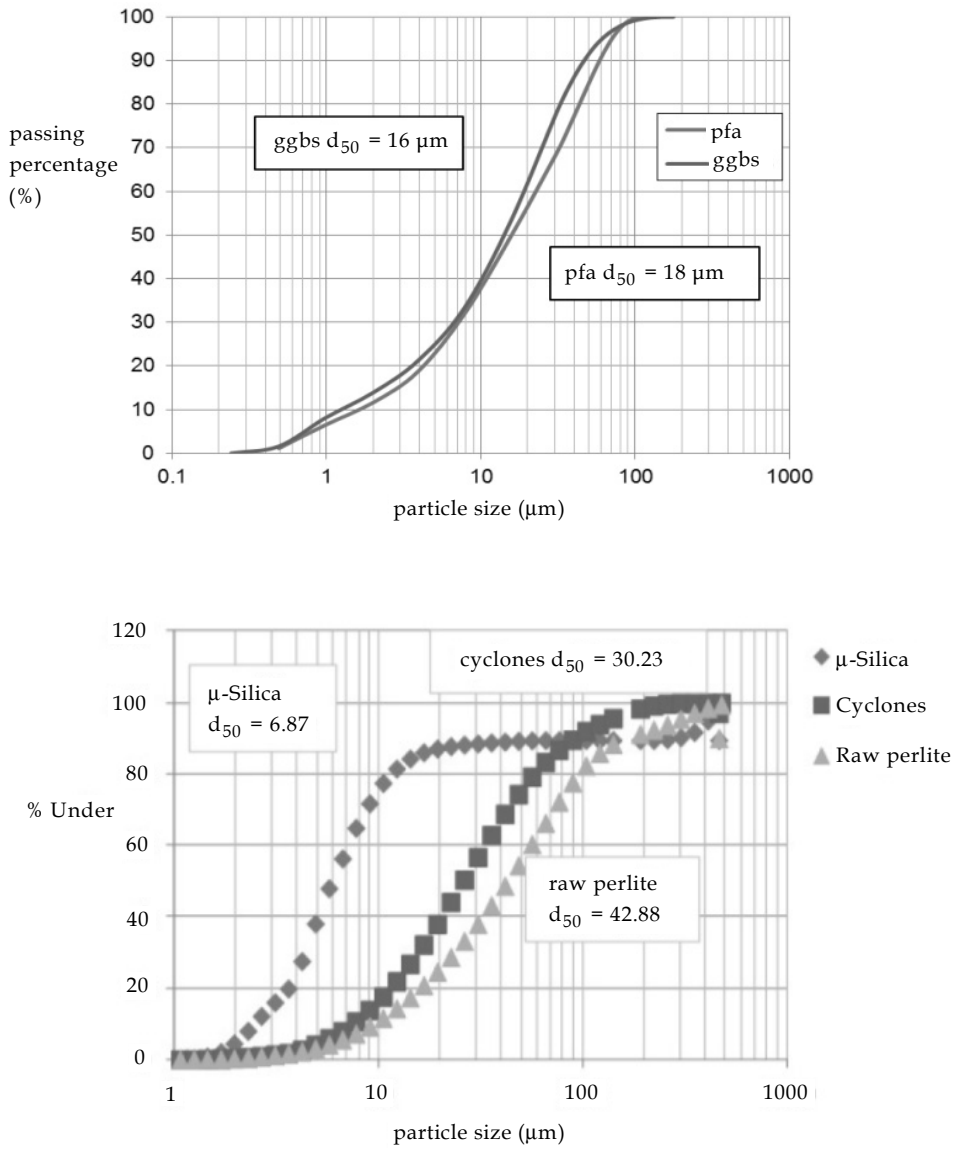


Figure 4: GSD of investigated materials

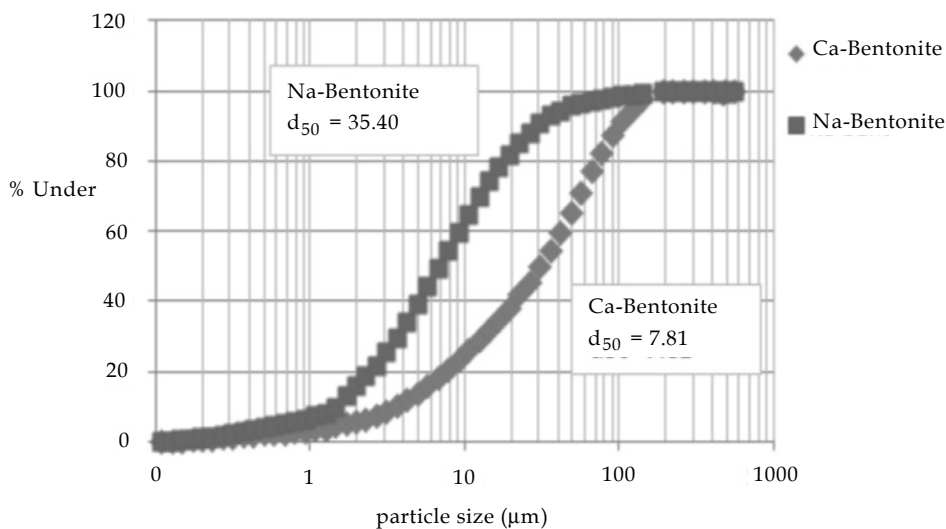


Figure 4 continued: GSD of investigated materials

## 2.6 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX)

Scanning Electron Microscopy (SEM), coupled with Energy Dispersive X-ray Analysis (EDX), is mainly used for the observation of the morphology and chemical composition of raw materials, as well as of reaction products.

Abundant literature is available on the investigation of geopolymer paste (see for example Fernández-Jiménez and Palomo [2005]). Due to the high resolution that can be achieved, amorphous aluminosilicate gel structure can be observed, as well as unreacted (or partially reacted) particles of precursor material, allowing to estimate the extent of the reaction development, the presence of crystals, cracks and other singularities in the specimen. EDX analysis allows to define the chemistry of the investigated material by detecting the presence and the quantity of chemical elements in the sample. The elemental analysis can be carried out at different scales, both on the whole SEM image as well as targeting specific points in the sample for the determination of the chemical composition of reaction products. Molar ratios of Si/Al, Si/Ca, Na/Si can be determined for understanding the nature of the gel produced by the reaction.

## 2.7 Thermogravimetric analysis (TGA)/Derivative Thermogravimetric analysis (DTGA)

Thermogravimetric analysis (TGA) is carried out on powdered samples for the assessment

of mass loss during heating (e.g. from 25° to 1000°C). The thermal decomposition of different reaction products takes place in specific temperature ranges. By observing the temperature intervals where mass loss occurs, the presence and the quantification of different reaction products (e.g. hydrated compounds, hydroxides, sulphates, carbonates) can be determined. When the system is coupled with a mass spectrometer for the analysis

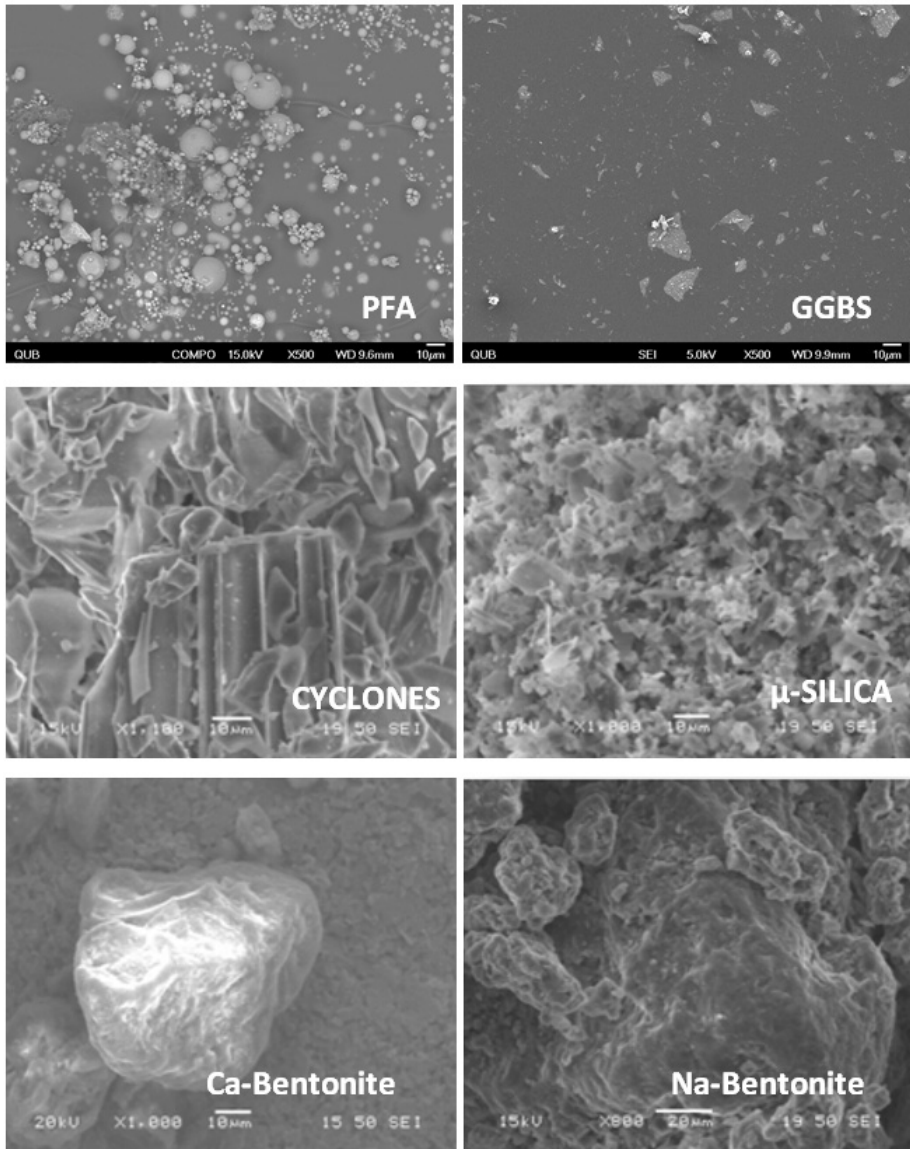


Figure 5: SEM images of investigated materials

of gases emitted during the heating process, such identification is easier and more accurate. Main mass losses occur usually in the region 50 - 150°C. This region corresponds to the dehydration of physically bound water in the gel structure. Instead, mass loss related to carbonate presence is usually observed in the range 600 - 850°C, where emissions are attributed to CO<sub>2</sub> gas. The removal of chemically bonded water is reported in the technical literature to be completed at 500°C.

As far as raw materials are concerned, it can be observed that they are, in general, very stable. A mass loss of about 5% has been observed for pfa, which is presumably due to the loss on ignition of carbon compounds, whereas ggbs showed no sign of thermal decomposition.

The dehydration of cyclones (= perlite tailings) and raw perlite occurs with a total mass loss of 3%, which is less than the mass loss of  $\mu$ -silica. No carbonates were detected. Ca- bentonite and Na- Bentonite showed more complex patterns of dehydration in several stages. The removal of absorbed moisture and the interlayer dehydroxylation were identified at different temperatures, giving information on the actual material microstructure.

When carried out on reacted paste, the amount of hydrated products is an indirect indicator for the degree of reaction, therefore the TG/DTG analysis can be utilised for assessing and quantifying the reaction of the geopolymeric system, particularly when high quantity of hydration products are expected, i.e. in Ca-rich systems such as ggbs-based binders [Ben Haha *et al.*, 2011].

## 2.8 Selection of candidate materials in SUS-CON project

The SUS-CON project carried out preliminary investigations on a wide range of possible materials, as discussed in [Arena *et al.*, 2015], from energy industry by-products, metallurgical slags, mining industry secondary materials. Analysis described in the previous paragraphs allowed the selection of promising precursors, with suitable chemical composition, amorphous state and particle size distribution. Materials showing the highest content in Si and Al, a high degree of glassy structure and fine grain size distribution were selected for further analysis. As previously discussed, it is not possible to give straightforward indications concerning minimum requirements for physical and chemical features of candidate materials, since some candidates that are non-compliant with some specifications might be suitable for particular recycling applications. However, some indications on general requirements for precursor materials (fly ash, ggbs, metakaolin) can be found in the literature [Garcia-Lodeiro *et al.*, 2015]. The precursors chosen after the first



stage of investigation were: pfa, ggbs, and perlite tailings, which showed the most promising features. A summary of the results is presented in Table 3.

Table 3: Summary of results obtained from the screening analysis

|                                    | pfa  | ggbs | Red<br>Mud | $\mu$ -Silica | Perlite<br>tailings | Na-<br>Bentonite | Ca-<br>Bentonite |
|------------------------------------|------|------|------------|---------------|---------------------|------------------|------------------|
| SiO <sub>2</sub> (%)               | 46.8 | 29.4 | 7.8        | 67.2          | 75.3                | 51.1             | 58.7             |
| Al <sub>2</sub> O <sub>3</sub> (%) | 22.5 | 11.2 | 15.5       | 13.6          | 10.5                | 15.4             | 13.2             |
| CaO (%)                            | 2.2  | 43.7 | 13.7       | 1.1           | 1.4                 | 9.2              | 5.8              |
| Amorphous<br>content (%)           | 84   | 98   | 70         | n.e.          | n.e.                | n.e.             | n.e.             |
| d <sub>50</sub> ( $\mu$ m)         | 18   | 16   | n.e.       | 7             | 30                  | 35               | 8                |

*n.e.* = not executed.

### 3 Binder composition methodology for geopolymer concrete production

Further experimental tests on the selected materials were carried out for a comprehensive assessment of the engineering properties achievable with the geopolymer binders that are desirable for the production of concrete and upscaling for industrial trials.

Geopolymerisation is a complex process that involves a series of reactions that take place simultaneously, as discussed in chapter 2. It involves two basic reactions: the dissolution of Si and Al from the raw material and the polymerization of the dissolved Si and Al species into a three dimensional aluminosilicate network. Thus the parameters that can affect the overall geopolymerization reaction are the parameters that affect one or both of the above mentioned reactions.

Important synthesis parameters are the alkali content of the activation solution, the presence of initially dissolved silicates as well as its content in the activation solution, the water content of the solution and the energy supplied during the curing phase. On the other hand, requirements for the practical utilisation of developed binder encompass engineering properties such as workability, setting time, compressive strength, thermal properties, and utilisation of admixtures for modifying rheological properties of the pastes.

#### 3.1 Strength development of geopolymer binders versus alkali activators

Chemical activation of aluminosilicate materials has been extensively investigated in the scientific literature (see Provis and van Deventer [2014] for a summary of the outcomes of

published researches regarding the suitability of different alkali sources for the activation of different precursors). The most common activators used in the synthesis of alkali activated binders are sodium and potassium hydroxides and sodium and potassium silicates or a combination of silicate and hydroxide alkalis. Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), calcium oxide ( $\text{CaO}$ ), and lime ( $\text{Ca}(\text{OH})_2$ ) have also been used. The role of alkalis during geopolymerization is twofold: they induce the dissolution of Si and Al from the raw material during the dissolution stage but they also participate in the final network by balancing the negative charge of Al. The presence of initially dissolved Si species can increase the dissolution extent of raw materials and it can also affect the polymerization reaction by providing the first nuclei for the formation of monomers. The initially dissolved Si species also participate in the final network resulting in a more dense and rigid structure.

Dosage parameters are commonly expressed as alkali dosage ( $M^+$ ), which is the mass ratio of the total  $\text{Na}_2\text{O}$  in the activator to the mass of the precursor, and the modulus of the activator, i.e. the ratio  $\text{SiO}_2/\text{Na}_2\text{O}$  in the activating solution, or its reciprocal  $\text{Na}_2\text{O}/\text{SiO}_2$  (alkali modulus, AM).

“Geopolymerization potential” requires the assessment of the maximum compressive strength that a binder based on a specific raw material can achieve if the optimum synthesis parameters are used. Optimum synthesis parameters are different for each and every precursor because they depend on the nature of the raw material, its chemical and mineralogical content, its origin, its crystallinity, its amorphous phase content and its previous thermal history. It must be highlighted that the problem with the compressive strength decrease of a specific formulation is not “numerical” but rather “chemical”.

Compressive strength is a property directly linked with the extent of reaction of the raw material. A significant compressive strength decrease would indicate poorly reacted raw material (well below its capacity) that could threaten the final product stability. A determination of the geopolymerisation potential should be carried out through a systematic variation of dosage parameters in order to define achievable compressive strength and to identify the trends. The detailed description of the results concerning alkali dosage effects on compressive strength for candidate precursors falls out of the scope of this paper. Some further description can be found in [Rafeet *et al.*, 2014; Taxiarchou *et al.*, 2012]. Outcomes can be summarised as follows:

- For 100% pfa and pfa/ggbs blend 30% / 70% strength increases with the increase of the AM, then it decreases until a residual value, presumably due to the reduced amount of available Si. The range of optimum values of AM was found

to be 0.95 – 1.25. The M+ increase led to an increase in the compressive strength, but the gain narrowed when M+ was higher than 9.5% for pfa system and higher than 7.5% for pfa/ggbs blends. Higher dosages were found to trigger fast setting behaviour. Final dosage were chosen equal to M+ = 7.5% and AM = 1.25, in order to ensure proper strength development and suitable initial setting time, also considering that high dosages imply high production costs and environmental burdens [Vinai *et al.*, 2015].

- Perlite tailings consist of a raw material that was found to be able to geopolymerise adequately. The optimum achieved compressive strength of 34 MPa classifies it as a material having medium geopolymerisation potential. The compressive strength results show that in the case of low alkalinity, equal to 4M, the effect of soluble addition is paramount: the increase of Si from 0M to 5M leads to continuous compressive strength increase up to 34 MPa. For the intermediate alkali content of 5M, Si addition from 0M to 3M leads to compressive strength increase, reaching a maximum of 34 MPa. The addition of higher quantities of Si (for 5M NaOH concentration) reaching 4M and 5M results in a significant compressive strength decrease. For higher alkalinity, the addition of Si does not affect in any way the compressive strength development, which remains at low values. Therefore, in the case of perlite tailings, the combined effect of the alkali and soluble silica content has been demonstrated: depending on the alkali content the effect of soluble silica addition varies from positive to negative and neutral. Regarding the thermal and other mechanical properties of the perlite- based geopolymers, they appear to be dependent on the utilized formulation and must be investigated specifically for each formulation. Roughly, based on the measurements of selected formulations, the apparent density of perlite-based geopolymers was found to vary from 1440-1520 kg/m<sup>3</sup>, the bending strength 6-7 MPa, and the thermal conductivity coefficient  $\lambda_{10}$  from 0.2098-0.2191 W/mK. [Ch. Panagiotopoulou *et al.*, 2013]

The full set of microstructural analysis previously described can then be carried out on selected and representative paste samples for the understanding of the reaction process [Soutsos *et al.*, 2015]. The selected activation dosages that were adopted for further work considered not only the highest strength, but also other parameters such as mix workability or initial setting time, in order to tailor the mix design to the end-use applications.

### 3.2 *Strength versus water to solid ratio relationship*

When aluminosilicate species only are present in the system, water does not participate as a reactant (only on the very initial stages of alkaline hydrolysis), but it represents the means of transportation for the reactive species. The common practice for geopolymer synthesis regarding the use of water is “utilize the minimum amount of water that can lead to an adequate wetting of the raw material”. This parameter also affects significantly the rheological properties of the pastes.

During the curing stage, the evaporation of the water (which is not consumed during the process) leaves pores and open channels that affect the compressive strength as well as other parameters influenced by the matrix porosity, such as water absorption and durability-related parameters [Zang and Wang, 2014]. Therefore, the addition of water results to an improvement of the rheological properties (increase of spread value) but usually also to a compressive strength decrease.

On the contrary, in calcium-rich alkali activated system (e.g. ggbs based system), water also participates in the hydration reaction, being partially consumed during the hardening process. Moreover, the hydration also causes a swelling of the structure, which in turns results in a denser matrix [Brough and Atkinson, 2002], increasing the compressive strength and the resistance to pore-related damaging mechanisms such as freeze-thaw attack. High-calcium binder systems are less affected by strength decrease when water is added [Hung and Chang, 2013]. However, reduction in strength is observed when added water exceeds the maximum required by the system, which needs to be determined on a case-by-case approach.

Water content also affects the setting time of high-calcium systems: the less the water to solid ratio, the faster the initial setting is. Water content needs therefore to be determined taking into consideration a) the type of precursor material; b) the targeted workability; c) the required setting time; and d) the required strength.

### 3.3 *Curing conditions*

In aluminosilicate-based systems, the geopolymerisation reaction needs external energy to develop at a faster pace, as strength development is slow at room temperature. For this reason, thermal or steam curing is usually applied [Provis and van Deventer, 2014]. As discussed in Provis and van Deventer [2014], optimal curing conditions and curing temperature are related to the mix design, precursor materials and end-product requirements. A prolonged period of sealed curing is considered necessary for producing a

dense and durable binder matrix. Carbonation issues and possible cracks on the sample surface should also be considered when specifying the curing protocol.

Sample dimensions have an impact on the effectiveness of the curing regime, as well as the potential interaction with plastic aggregates when cured at high temperatures. Large samples might need longer curing time than small samples, as well as lightweight aggregates made from plastic material can swell when heated, leading to geometrical non-compliance, stresses on the moulds and weak bonds between the binder matrix and the aggregates themselves. It is therefore necessary to carry out dedicated trials for the optimisation of the curing regime, both in terms of curing temperature and curing time. Ca-rich systems (e.g. ggbs-based binders) can harden and cure at room temperature, reaching their full potential without oven curing. Care must be taken in keeping samples in proper humidity conditions, ideally sealing them at RH > 90%, in order to allow the full development of both geopolymerisation reaction and hydration.

Curing conditions that led to satisfactory results have been defined for pfa, pfa/ggbs blend and cyclone mixes. Whereas pfa samples required a curing at 70°C, pfa/ggbs cubes were well enough cured at 20°C in air tight boxes. Cyclone (= perlite tailings) mixes required a two stage curing (70°C followed by a 55°C curing period). Details can be found in [Visser *et al.*, 2015].

### ***3.4 Industrial production upscaling***

The selection of a binder is not only related to its mechanical features, but also to engineering properties that are of paramount importance when the research results are transferred to industrial production. Workability, thermal features, and admixture addition should be investigated for optimising the binder choice.

#### *Consistence and initial setting time*

Consistence of mortars can be assessed according to the relevant European norm [EN 1015-3, 2004] for evaluating the workability. The spread of mortars is influenced by chemical dosage, water content (w/s ratio), and precursor material nature (grain size distribution and grain shape).

Initial and final setting times are influenced by chemical dosage, water content (w/s ratio), and precursor material nature (Ca-rich precursor can set at room temperature). Setting times can be assessed with the Vicat needle test, but it is worth observing that measurements on mortars can be biased by the presence of sand grain under the needle, whereas measurements on paste are of difficult execution, since the w/s ratio required for

achieving a suitable consistence is usually very low, and this influences the setting time itself (the paste might set before the actual measurement in the apparatus). Instead, the procedure described in the ASTM standard C403M – 08 - Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance [ASTM C403, 2008], is considered more suitable for the assessment of the setting time on mortars.

#### *Density and thermal properties*

Properties required for the end-use concrete product have an impact on the choice of the binder. High density binders with high thermal conductivity can lead to end-products that are not fit for the purpose. In the case of SUS-CON project, the targeted end-product was a lightweight concrete with thermal insulation properties. Therefore, high density binders (e.g. ferronickel slag) have not been selected for the industrial scale-up of the project.

#### *Effect of admixtures on geopolymer mixes*

Admixtures are used in order to improve fresh state features of the mix in order to meet the production targets. A review on the efficacy of traditional additives on the properties of alkali-activated slag systems can be found in Rashad [2013]. In SUS-CON project, various commercially available plasticizers (sodium lignosulphonate, melamine sulfonate, and polycarboxylate ethers) were examined in geopolymer binders for investigating their effect on workability of mortars produced with ground granulated blast furnace slag / fly ash binders. The system was activated with sodium hydroxide/sodium silicate, with fixed water to binder ratio of 0.43. The added solid polymer content was 1% in weight of binder. The workability was measured as mortar spread according to DIN 18555-2. It was observed that the efficiency of plasticizers very much depended on the type of alkaline activator, the silicate concentration and silicate modulus ( $\text{SiO}_2/\text{Na}_2\text{O}$  ratio) of activator solution. With ggbs binder, a drastic improvement in the efficiency of plasticizers was observed when only NaOH activator was used (activator without any readily available silicate). The spread value without any plasticizer was 14 cm, which increased to more than 25 cm (limit of our apparatus) using 1% in weight of sodium lignosulphonate. When both activators (NaOH and waterglass) were used, up to 21% increase in the spread value had been observed, whereas higher spread values were obtained using activator with lower silicate modulus (Fig. 6). Additionally, it was found that the plasticizer's efficiency depends on the ggbs/pfa ratio. The plasticizers were not effective on 100% pfa geopolymer binder system but they were for higher percentages of ggbs used. With 70/30 ggbs/pfa, an increment in spread value up to 18% was achieved.

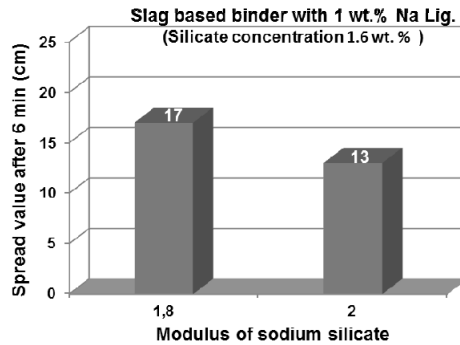


Figure 6: Spread value of fresh geopolymer mix with 1 wt.% sodium lignosulphonate plasticizer

### 3.5 Selection of binders for the replication of concrete products in SUS-CON project

The investigation of mechanical and engineering properties on the five pre-selected precursor materials allowed to identify three binder systems suitable for the production of SUS-CON concrete. It can be observed that materials such as pfa and ggbs have been extensively studied in the literature and do not actually constitute a novel proposal. However, the availability of such materials all through Europe and in general all over the world represents an opportunity for the replication of the results from the SUS-CON project, which is a key achievement. Experimental results obtained can add up the knowledge on these precursors for their better utilisation in alkali activated technology. The three binders that were selected for the next step of the project were the followings:

- 100% pfa activated with waterglass and NaOH, with dosages M+ (i.e. the mass ratio Na<sub>2</sub>O/binder) equal to 7.5% and AM (i.e. the mass ratio Na<sub>2</sub>O/SiO<sub>2</sub> in the activating solution) equal to 1.25, showed good workability (mortar flow = 180 mm), satisfactory uniaxial compressive strength (UCS) equal to 30 MPa after 7 days and no setting issues.
- Pfa/ggbs mixes with a 30% 70% blend activated with waterglass and NaOH, with dosages M+ = 7.5% and AM = 1.25, gave satisfactory workability (mortar flow = 150 mm), UCS = 50 MPa after 7 days, and initial setting time (around 60 min) when water to solid ratio of 0.43 was used.
- Cyclones (perlite tailing)  $\mu$ -Silica mixes showed improved rheological properties and satisfactory co-geopolymerisation of the raw materials. 90% Cyclones-10%  $\mu$ -Silica mix was recommended as binder for the production of SUS-CON concrete, since it was light weight (1484 - 1598 kg/m<sup>3</sup>), it had good insulation properties ( $\lambda \approx 0.20$

W/mK), and good workability and UCS = 20 MPa. Formulations for two types of binders were provided for the production of SUS-CON concrete: one containing waterglass and a second activated only by NaOH solution.

#### **4 Conformity tests: replication of concrete products**

After the definition of suitable binder mixes, concrete products were targeted for assessing the product conformity and the technical feasibility of a complete substitution of Portland cement with geopolymer binders without compromising the required properties.

##### *4.1 Lightweight GP concrete*

Two recipes of lightweight geopolymer concrete (GPC) were designed with alkali activated binder. Pfa and pfa + ggbs were used for the two formulations respectively. Expanded clay and natural sand were utilized as aggregates. Two homogeneous lightweight concrete mixtures were developed with good rheological properties. In the case of recipe 2 (pfa + ggbs), a retarder additive was added after observing a fast setting of the fresh concrete. Consistency test was carried out according to the standard UNE 83313:90, and in both cases a flowing consistency was obtained. Mechanical performance was assessed via the measurement of compressive strength, indirect tensile strength and modulus of elasticity at 28 days. Results showed that recipe 1 produced a light-weight GPC with properties similar to a conventional light-weight concrete (density between 1600–1800 kg/m<sup>3</sup> and compressive strength in the 20–35 N/mm<sup>2</sup> range), but it needed thermal curing. Recipe 2 (cured at room temperature) produced samples with higher mechanical properties than conventional light-weight concrete.

Durability tests were carried out according to the American standard ASTM C666/666M. Each cycle was completed within 2 hours, and the dimension and elastic modulus variation were used for the determination of a durability factor. Samples underwent more than 300 cycles. Both materials showed very similar dimensional variation after the cycles. However, the weight change was slightly higher in Recipe 1, presumably due to a higher porosity. Both lightweight recipes resisted well 320 freeze-thaw cycles. After 420 cycles deterioration was observed on top of the specimen for the recipe with 100% pfa.

In order to compare lightweight GPC to commercial lightweight concrete, façade panels of 62.5 x 25 x 7 cm dimensions were produced. Concerning the surface finish, best specimens were obtained with the Recipe 2, see Figure 7. Neither segregation nor voids in the mix





Figure 7: (Left) Recipe 1 after 420 freeze-thaw cycles. (Right) Recipe 2 panels. [Chozas *et al.*, 2015]

were observed. The result was a very compact finish. Nevertheless, areas of different colour were observed [Chozas *et al.*, 2015].

#### 4.2 Geopolymer building blocks

The replication of building blocks followed 2 laboratory phases: the first one was focused on the preliminary assessment of strength achievable with different binder contents and different pfa/ggbs blends. The effects of different curing conditions on the strength development and on the occurrence of efflorescence were also studied. Selected binder blends and contents were then investigated in more detail in a second phase, in order to choose the binder composition to be used during the factory trial. The compressive strength tests at 7 and 28 days on samples cured under different conditions allowed to define the binder mix that ensured full compliance to the technical requirements for the product, which was a minimum compressive strength of 7 MPa.

A 30%/70% pfa/ggbs blend was therefore recommended for factory trials, which were carried out in a block production factory in Northern Ireland (UK). More than 500 blocks were produced with factory machinery. The geopolymer blocks showed strength comparable (or superior) to a control batch of blocks prepared with Portland cement, and no issues emerged during the production. The geopolymer mix proved to be fully suitable for block production [Rafeet *et al.*, 2014].

#### 4.3 Concrete with conventional aggregates

Concrete mix designs with conventional aggregates and geopolymer binder from perlite tailings (cyclones) and  $\mu$ -silica were successfully produced. The concrete recipes were aimed for lightweight and conventional concrete specifications for precast concrete blocks and facades as well as lightweight precast concrete elements. The aggregates used in the



Figure 8: Replication of building blocks. (Left) Laboratory production. (Right) Factory trials

mix designs were commercial expanded perlite and quartz sand and gravel. The main targets set for the concrete specimens concerned density, mechanical strength and workability. Concrete formulations with silicate aggregates had constant binder/aggregate ratio of 0.37 and NaOH/binder ratio of 0.10, while the water/binder ratio varied between 0.58 – 0.65 depending on the workability requirements. It should be noted that small changes in water content have a high effect on workability. Additionally, the use of a plasticizer was required in some of the formulations. The geopolymeric concrete was cast in prisms (4 x 4 x 16 cm) and cubic moulds (15 x 15 x 15 cm). Both types of specimens went through a two stage curing protocol. Prisms required 2 days (1<sup>st</sup> stage) at 70°C before demoulding and 3 days (2<sup>nd</sup> stage) of additional curing at 70°C, while the respective times for the cubes were 5 and 7 days. These silicate aggregate mix designs provided concrete of 1700 – 1800 kg/m<sup>3</sup>, a compressive strength of 6 – 7 MPa and a slump between 39 – 145 mm. These results complied with the specification set by the concrete producers for precast blocks and facades.

The lightweight formulations also had a constant binder/aggregate ratio of 0.98 (w/v) and NaOH/binder ratio of 0.10 and a varying water/binder ratio of 0.71 – 0.75. Similar to the formulations with silicate aggregate, a two stage curing protocol was followed. 8 days (1<sup>st</sup>



Figure 9: Concrete mixer (Left), Slump measurement (Centre) Cubic moulds covered for curing (Right)

stage) at 70°C before demoulding and 7 days (2<sup>nd</sup> stage) of additional curing in 70°C. The lightweight expanded perlite concrete mix designs resulted, as expected, in a lighter concrete (density of 800 – 1000 kg/m<sup>3</sup>) with lower compressive strength (3 – 4 MPa) and higher slump (75 – 160 mm). These formulations also proved to be suitable for lightweight precast concrete elements.

#### *4.4 Proposed procedure for geopolymeric binder development from secondary material streams*

The experience gained during the SUS-CON project in the synthesis of geopolymeric binder from secondary material streams allowed to develop a general procedure that can be applied also when other streams or concrete end products are considered. The proposed approach has been summarised in the flow chart presented in figure 10.

## **5 Conclusions**

Geopolymeric binders represent a promising alternative for the reduction of the environmental impact of the construction industry. The use of secondary material streams is even more tempting for the reduction of our dependence on Portland cement whilst reducing waste disposal in landfills. However, not all the candidate materials are suitable for geopolymerisation purposes. A screening is required for ensuring that the materials are reactive and that the binder can be tailored according to the requirements of the final product to be achieved.

This paper proposed a methodology and described the steps that could be followed for assessing all the properties that candidate materials should have before being considered ‘precursors’. The analytical tools used for the screening, the methodology for the definition of the reactivity as well as the parameters to be checked in view of developing a suitable binder for concrete product replication have been described. Some examples of concrete product replication have also been presented and discussed. A structured procedure for the implementation of the methodology has been developed.

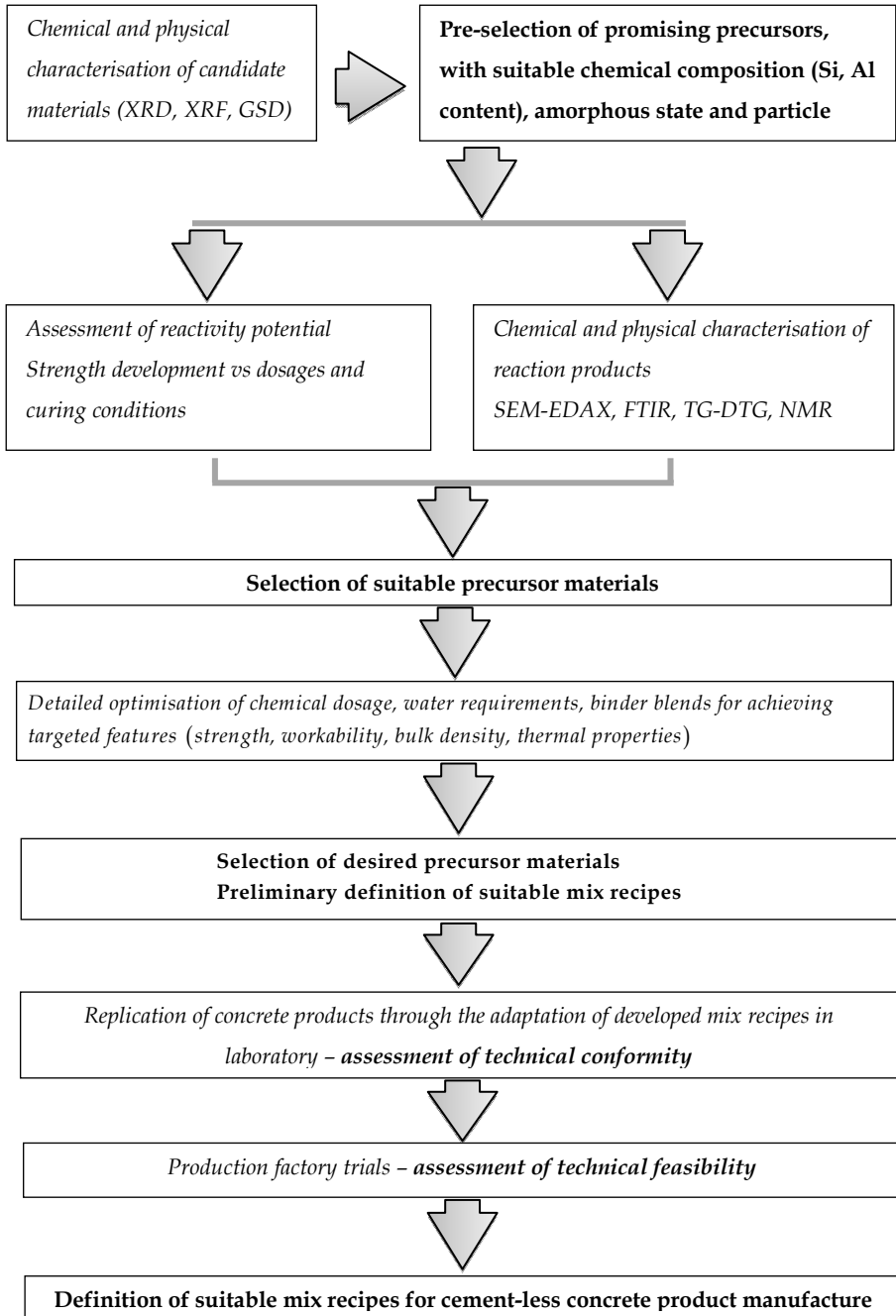


Figure 10: Flow chart of the proposed procedure

## Literature

- Allahverdi, A., Shaverdi, B., & Kani, E. N. (2010). Influence of sodium oxide on properties of fresh and hardened paste of alkali-activated blast-furnace slag. *Int. J. Civ. Eng.*, 8, 304-314.
- ASTM C403 / C403M-08 (2008). Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance. ASTM International, West Conshohocken, PA, 2008
- Barnett, S. J., Hadjierakleous, A., and Soutsos, M. N. (2011). Alkali Activated Binders from UK Fly Ashes. 31st Cement and Concrete Science Conference, London (UK) 12-13 Sep. 2011
- Ben Haha, M., Le Saout, G., Winnefeld, F. and Lothenbach, B. (2011). Influence of activator type on hydration kinetics, hydrate assemblage and microstructural development of alkali activated blast-furnace slags. *Cement and Concrete Research* 41(3): 301-310
- Brough, A. R., and Atkinson, A. (2002). Sodium silicate-based, alkali-activated slag mortars: Part I. Strength, hydration and microstructure. *Cement and Concrete Research*, 32(6), 865-879.
- Çelik, Ö., Erdem, D., Pişkin, S. (2008). Characterization of fly ash and its effects on the compressive strength properties of Portland cement. *Indian Journal of Engineering & Materials Sciences*, 15: 433-440.
- CEMBUREAU (2014). The European Cement Association, key facts & figures, <http://www.cembureau.eu/about-cement/key-facts-figures>, accessed on 22/05/2015.
- Chozas, V., del Val, I., Vera, J., Larraza, I. (2015). Alternative concrete materials from industrial waste. Concrete 2015, 27th Biennial National Conference of the Concrete Institute of Australia, 30th August – 2nd September 2015, Melbourne, Australia.
- Corvaglia, P., Largo, A., Soutsos, M. (2012). Sustainable, innovative and energy-efficient concrete, based on the integration of all-waste materials: the SUS-CON project. *fib Symposium 2012: Concrete Structures for Sustainable Community - Proceedings* pp. 499 - 502
- EN 1015-3:1999/A1 (2004). Methods of test for mortar for masonry - Part 3: Determination of consistence of fresh mortar (by flow table). European committee for standardisation.
- Fernández-Jiménez, A. and Palomo, A. (2005). Composition and microstructure of alkali activated fly ash binder: Effect of the activator. *Cem. and Conc. Res.* 35(10): 1984–1992.

- Garcia-Lodeiro, I., Palomo, A., & Fernández-Jiménez, A. (2015). Crucial insights on the mix design of alkali-activated cement-based binders. *Handbook of Alkali-Activated Cements, Mortars and Concretes*, pp. 49-73.
- Hung, C. C., & Chang, J. J. (2013). The influence of mixture variables for the alkali-activated slag concrete on the properties of concrete. *J. Mar. Sci. Technol*, 21(3), 229-237.
- IEA, WBCSD (2009) *Cement Technology Roadmap 2009 – Carbon emissions reductions up to 2050*. Paris, France: International Energy Agency [IEA], World Business Council for Sustainable Development [WBCSD].
- Kumar, R., Kumar, S., and Mehrotra, S. P. (2007). Towards sustainable solutions for fly ash through mechanical activation. *Resources, Conservation and Recycling* 52(2): 157-179.
- Machiels, L., Arnout, L., Jones, P.T., Blanpain, B., Pontikes, Y. (2014). Inorganic polymer cement from fe-silicate glasses: Varying the activating solution to glass ratio. *Waste and Biomass Valorization*, 5 (3), pp. 411-428.
- Mehta, P.K., and Monteiro, P.J.M. (2006). *Concrete: microstructure, properties, and materials* (3rd. ed.) McGraw-Hill, New York, NY
- Olivier, J. G. (2012). Trends in global CO<sub>2</sub> emissions: 2012 Report (p. 40). Hague: PBL Netherlands Environmental Assessment Agency.
- Panagiotopoulou, Ch, Taxiarchou, M., Panias, D., Paspaliaris, I., (2013). Mechanical, Thermal and Chemical Properties of Geopolymer Pastes based on Perlite tailings, Oral Presentation, *13th International Conference of the European Ceramic Society*, 23-27 June 2013, Limoges, France
- Panias, D., Giannopoulou, I. P. (2006). Development of inorganic polymeric materials based on fired coal fly ash. *Acta Metallurgica Slovaca*, 12, 321-327.
- Arena, W., Attanasio, A., Marseglia, A., Pascale, S., Ristoratore, E., Rocco, B., Saracino, S. and Urbano, G. (2015), Market availability and mapping of waste streams across the EU27, SUS-CON publication, available from [www.sus-con.eu](http://www.sus-con.eu).
- Pinkas, J. (2005). Chemistry of silicates and aluminosilicates. *Ceramics– Silikáty*, 49, 287-298.
- Provis, J. L., Hanafi, R., and Garcia Trinanes, P. (2015). Valorisation of wastes by alkali activation – progress, opportunities and pitfalls. Keynote lecture at the 4th Slag Valorisation Symposium, Leuven, 15 – 17 April 2015.
- Provis, J.L., and van Deventer, J.S.J. (2014). Alkali Activated Materials: State-of-the-Art Report. RILEM TC 224-AAM, RILEM Reports 13, DOI 10.1007/978-94-007-7672-2\_4
- Puligilla, S. (2011). Understanding the role of slag on geopolymer hardening and microstructural development. University of Illinois at Urbana-Champaign.

- Rafeet, A., Vinai, R., Sha, W., and Soutsos, M. (2014). Alkali activated fuel ash and slag mixes: optimization study from paste to concrete building blocks. 34th *Cement and Concrete Science Conference*, Paper Number 179, 14-17 Sep. 2014, University of Sheffield (UK)
- Rashad, A. M. (2013). A comprehensive overview about the influence of different additives on the properties of alkali-activated slag – A guide for Civil Engineer. *Construction and Building Materials*, 47, 29–55. doi:10.1016/j.conbuildmat.2013.04.011
- Sakulich, A. R. (2009). *Characterization of Environmentally-Friendly Alkali Activated Slag Cements and Ancient Building Materials*. Thesis Ph.D., Drexel University, September 2009.
- Soutsos, M.N., Vinai, R., and Rafeet, A. (2015). Effect of alkali dosage and modulus on strength development and microstructure of alkali-activated binders. *14th International Congress on the Chemistry of Cement (ICCC 2015)*, 13-16 October 2015, Beijing, China
- Taxiarchou, M., Pantias, D., Panagiotopoulou, C., Karalis, A., & Dedeloudis, C. (2012). Study on the suitability of volcanic amorphous aluminosilicate rocks (perlite) for the synthesis of geopolymer-based concrete. In *Proc., ASTM Int. Symp. on Geopolymer Binder Systems*, San Diego, CA.
- Vinai, R., Rafeet, A., Soutsos, M., Sha, W. (2015). The role of water content and paste proportion on physico-mechanical properties of alkali activated fly ash-ggbs concrete. *Journal of Sustainable Metallurgy*, Thematic section: Slag Valorisation Today. DOI: 10.1007/s40831-015-0032-6
- Visser, J., Couto, S., Gupta, A., Larraza Alvarez, I., Chozas Ligero, V., Sotto Mayor, T., Vinai, R., Pipilikaki, P., Largo, A., Attanasio, A., Chao-Lung Huang, M. & Soutsos, M. (2015). Sustainable concrete: design and testing. *HERON* 60 (2015) Vol. 1/2, pp. 59-91.
- Xu, H., and Van Deventer, J.S.J. (2002). Microstructural characterisation of geopolymers synthesised from kaolinite/stilbite mixtures using XRD, MAS-NMR, SEM/EDX, TEM/EDX, and HREM. *Cement and Concrete Research* 32, 1705–1716.
- Zhang, Z., and Wang, H. (2014). Analysing the relation between pore structure and permeability of alkali-activated concrete binders. *Handbook of Alkali-Activated Cements, Mortars and Concretes*, pp 235-264.

