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"Multifunctional inorganic foams based on

alkali – activated materials"

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"Niente nella vita va temuto, dev'essere solamente compreso. Ora è tempo di comprendere di più, così possiamo temere di meno."

-MARIE CURIE

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INTRODUCTION

INTRODUCTION

The fabrication of inorganic foams with a porosity gradient is widely desired from scientists in order to achieve enhanced performances, mainly due to their low density, high strength and specific functional properties. Multifunctional inorganic foams represent innovative systems thought for specific and advanced functions, in which a spatial gradation in structure and/or composition lends itself to tailored properties and for this reason they find application in a broad range of high–tech fields such as energy, building, aerospace, filtration and bioengineering.

Supporting or shaping zeolites can represent a challenge to obtain this kind of systems. In fact, structuring a porous powder, as a zeolite, permit to obtain an optimized structure with high mass transfer, low pressure drops and high mechanical and chemical stability. Different methods have been developed to achieve this technological goal, by using porous ceramic binders, polymer foams, or permeable bags. Pelletization and extrusion are the most frequently used methods to shape powdery zeolites, but they require a binder that can partially obstruct the active sites of zeolite. Recently, Additive Manufacturing (AM) approach has been also tested to obtain binder-less shaped zeolite monoliths. Geopolymer Gel Conversion (GGC) represents an economic and sustainable alternative to obtain a selfsupporting zeolite. Several studies confirms that it is possible to promote the nucleation of a zeolite inside a geopolymeric matrix by tuning pH, temperature, pressure, and time of the geopolymerization reaction. In fact, the geopolymers can be considered the amorphous counterpart or precursor of crystalline zeolites. The hydrothermal treatment is the traditional method to promote the crystallization of zeolites in the geopolymer framework. More recently a one-step procedure is developed, during which geopolymerization and zeolites formation can take place simultaneously. The two-step method is useful to drive the crystallization of a specific zeolite inside the matrix, with the aim to functionalize the self – supported foam.

These geopolymer – zeolite composites find application in different technological fields, e. g. purification of wastewater, gas adsorption and separation, catalysis.

The zeolites have excellent ion-exchange and sorption properties, that depend on their physical–chemical features. For these reasons, the geopolymer – zeolite composites can be proposed as water softeners, solving the problem of structuring powder zeolites. In particular,

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Na–LTA and FAU–X zeolites are excellent candidates for these systems, because they can easily exchange their sodium ions with "hard water ions", such as calcium and magnesium.

Zeolite, in particular FAU–X zeolite, is largely used for CO₂ capture, thanks to high performance in gas adsorption. FAU-X zeolite is industrially produced as a microcin powder, therefore shaping it represents a technological challenge. Also in this case, the geopolymer gel conversion represents an innovative method to obtain a self-standing FAU-X porous monolith without the use of a binder and, moreover, the presence of the geopolymer backbone ensures mechanical strength and mesoporosity level.

This research activity was focused on hybrid foams based on zeolite–geopolymer materials and characterized by hierarchical porosity.

The activity first centered on the analysis of the state of the art. Then, the research focused on the design of a multifunctional porous material, obtained by GGC with a one-step method, combining the microporosity of the zeolites, the mesoporosity of the geopolymer matrix and the macroporosity obtained by adding a foaming agent. In particular during the first year, the optimization of the operating conditions, by studying the effect of the foaming agent (Silicon powder) content, relative humidity, and curing time on zeolite content in the sample, was performed.

After the optimization phase and the consequently choice of the best sample, the activity of the second year focused on the study of main relevant properties for industrial applications. In particular the selected samples were characterized in terms of chemical, physical and morphological analysis. Then the "water properties" of the softeners were evaluated by measuring Cation Exchange Capacity (CEC), softening, regeneration and reusability performance.

In addition, to obtaining a controlled and homogeneous foaming process, an under vacuum curing process was performed by studying the effect of curing temperature and foaming agent (Silicon powder) content. At the same time the addition of a foaming stabilizer or the use of a new foaming agent (Hydrogen Peroxide) was investigated to determine the effects in terms of crystalline phase and porosity.

Finally, a two steps method to favour the crystallization of only FAU–X zeolite was carried out. After chemical, physical and morphological analysis, the self–standing FAU–X porous

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monoliths were tested for gas adsorption of several molecules (nitrogen, carbon dioxide, water vapor, acetic acid and ethanol).

The collected results suggest the possibility of using geopolymer – zeolite hybrid materials as bulk–type adsorbent (both in gaseous and aqueous system), self–supporting membranes and gas separation.

1. GEOPOLYMERS

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1.1 ORIGIN AND HISTORY

The term 'geopolymer' was coined in the 1970s by the French scientist and engineer Prof. Joseph Davidovits, and applied to a class of solid materials synthesised by the reaction of an aluminosilicate powder with an alkaline solution [1] – [3].These materials were originally developed as a fire–resistant alternative to organic thermosetting polymers [4], as a resin in high–temperature carbon-fibre composites [5], in thermal protection of wooden structures [6], as a heat-resistant adhesive [7, 8], as a monolithic refractory [9, 10], and in various other niche applications. However, the primary application for geopolymer binders has since shifted to uses in construction. This is primarily due to the observation, first published by Wastiels [11], that it is possible to generate reliable, high–performance geopolymers by alkaline activation of fly ash, a by–product of coal combustion.

Geopolymers are a subset of the broader class of alkali–activated binders [12], which also includes materials formed by alkali–, silicate–, carbonate– or sulfate– activation of metallurgical slags and giving a product that is predominantly calcium silicate hydrate. The defining characteristic of a geopolymer is that the binding phase comprises an alkali aluminosilicate gel, with aluminium and silicon linked in a three–dimensional tetrahedral gel framework that is relatively resistant to dissolution in water [13].

The principal means of synthesising geopolymers is to combine an alkaline solution with a reactive aluminosilicate powder, in particular metakaolin (calcined kaolinite clay) or fly ash (a by–product of coal combustion). This results in the formation of a disordered alkali aluminosilicate gel phase, known as the geopolymeric gel binder phase. Embedded within this phase are unreacted solid precursor particles, and the pore network of the gel contains the water that was used in mixing the precursors (usually supplied via the alkaline activating solution). Unlike in a calcium silicate hydrate gel, the water does not form an integral part of the chemical structure of a geopolymer binder; from a practical perspective this presents both advantages and disadvantages. The fundamental framework of the gel is a highly connected three–dimensional network of aluminate and silicate tetrahedra, with the negative charge due to Al³⁺ in four–fold coordination localised on one or more of the bridging oxygens in each

aluminate tetrahedron and balanced by the alkali metal cations provided by the activating solution.

It has also been shown that the geopolymeric gel binder displays structural similarities, on an atomic to nanometre length scale, to zeolitic materials. Since geopolymers can be regarded as the amorphous counterpart or precursor of crystalline zeolites and zeolite crystallization can be promoted inside a geopolymer matrix choosing suitable operating conditions such as pH, humidity conditions, time and temperature of curing.

1.2 SYNTHESIS AND CHEMICAL STRUCTURE

Davidovits, while naming the material, also named the 'building blocks' of geopolymers. These 'polymer' constructs originated from his training as an organic chemist and look like carbon polymers with silicon and aluminium replacing the carbon atoms. He continues to name these 'polymers' poly–sialate, poly–sialate–siloxo, and poly–sialate–disiloxo for the ratio of silicon to aluminium being one, two and three respectively [14] as in Figure 1.1:



Figure 1.1 Representation of the oligomer units according to the Davidovits model

Geopolymers, according to Davidovits, are 3D structures consisting of tetrahedra of $(SiO_4)^{4-}$ and $(AIO_4)^{5-}$ connected together through the sharing of an oxygen atom (Figure 1.2):



Figure 1.2 Geopolymer structure according to Davidovits model

Alkaline ions are present in the framework cavities to balance the negative charge of Al³⁺in the (IV) coordination (Figure 1.3) [15]:



Figure 1.3 Balance of charge with potassium ions

Geopolymers have the following empirical formula:

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

- $M = \text{monovalent cation } (K^+, Na^+, \text{ et al.})$
- n =degree of polycondensation
- w =amount of bound water
- z = Si/Al molar ratio.

The process through which geopolymers are formed consists of 3 main phases: dissolution, condensation and solidification as seen in Figure 1.4:



Figure 1.4 Reaction mechanism of geopolymerization

In the first stage of geopolymerization, aluminate and silicate tetrahedral monomers are generated by alkali dissolution of solid aluminosilicate precursors [16]. The soluble species released as a result of this alkaline dissolution, $Si(OH)_4$ and $Al(OH)_4^-$, form oligomers leading to the formation of the *sol*. The second step is condensation in aqueous phase. The *gel*, a non – regular three–dimensional lattice, is formed: the oligomer chains, previously formed, condense with consequent release of water molecules.

The solidification of the gel is the final stage; following the evaporation of water molecules, the geopolymer, an amorphous structure, is formed (Figure 1.5).



Figure 1.5 Amorphous structure of geopolymer

An important role in the microstructure plays the ratio Si / Al; in fact, the interconnected porosity is dependent on the value of z. When Si / Al \approx 1 the pores vary between the 1 µm and the 10 nm, they are lower than this value for Si / Al \approx 1.65 and became really fine (\approx 5nm) for values Si / Al \approx 2.5 [17, 18]. Moreover, for high values of z, the final structure turns out to be more homogeneous with isolated pores; while, for low values, the structure may not have reacted completely and results heterogeneous.

In the geopolymer synthesis the water, while not remaining within the structure, has different roles providing the dissolution of aluminosilicates, the transfer of various ion and polycondensation of hydroxyl-aluminate and hydroxyl-silicate species. The water, produced by the condensation phase, evaporates and acts, in this way, as poring agent.

In addition to this intrinsic porosity, additional porosity can be added. Into the geopolymer slurry different poring agents could be added as:

 Hydroxide peroxide: it is a thermodynamically unstable species and decomposes according to the following reaction:

$$2H_2O_2(liq) \rightarrow 2H_2O(liq) + O_2 \uparrow (gas)$$

The oxygen bubbles remain trapped into the geopolymeric slurry and expand its volume.

 \checkmark Metal silicon: gaseous hydrogen, H₂, is produced through the redox reaction of Si powder in the alkaline media:

$$Si + 4H_2O \rightarrow 2H_2 + Si(OH)_4$$

This reaction leads to an increase in volume during the curing period. Metal aluminium powder could also be used as pore agent.

 Surfactant: the process consists in mixing the slurry containing the surfactant to generate wet foams, trapping and stabilizing the air bubbles.

Another important parameter in the geopolymer synthesis is the ratio M / Al, where M is the alkaline ion present in the aluminosilicate source or added with the alkali activating solution. Good polymeric proprieties are obtained when M / Al = 1; if the quantity of alkaline ions is excessive and therefore uncompensated ions are present, an atmospheric carbonation can occur leading sometimes to the formation of fractures and tensions. In addition to this phenomenon, the residual ions not compensated by the aluminium tetrahedrons, in the

presence of water, can exchange with the ion H⁺ generating a tensile stress in the material [19].

The last factor to consider is the temperature of curing (T_{curing}), after the solidification phase, geopolymer is subjected to a period of curing at a certain temperature. Generally, a temperature lower than 90 °C leads to obtain an amorphous product. If the temperature is higher than this value ($\approx 150 - 200$ °C) crystalline phases can be obtained.

1.3 RAW MATERIALS

The first step in the synthesis of geopolymers is the selection of the raw materials. Based on this choice, different end products can be obtained. During geopolymerization process an alkaline activating solution reacts with a solid aluminosilicate source, with solidification possible within minutes and very rapid early strength development [20]. In some cases, additives and/or fillers of various form and chemical nature may also be added to improve some features or to add new properties.

1.3.1 ALUMINOSILICATE SOURCE

The most common aluminosilicate powders used in the field of geopolymer are fly ash and metakaolin (from kaolin calcination); but other sources can also be used such as: blast furnace slag, residues of the bauxite process, some clays, rise husk ash, pozzolan, clayey lake sediments.

In general, we refer to chemical compounds that are composed predominantly of aluminium oxide, Al₂O₃, and silicon dioxide, SiO₂, which may be anhydrous or hydrated, naturally occurring as minerals or synthetic. Their chemical formula is often expressed as

$$xAl_2O_3 \cdot ySiO_2 \cdot zH_2O$$

1.3.2 ALKALINE ACTIVATOR

In geopolymer synthesis a chemical activator of the aluminosilicate powder is required. Strong bases are required to activate silicon and aluminium present in the powder. The most common activating solutions, used in this field, are sodium and/or potassium hydroxides; but also, others have been used as Na₂SO₄, Na₂CO₃, K₂CO₃, K₂SO₄, Na₂SiO₃, K₂SiO₃.

The choice of the solution depends on the nature of aluminosilicate source and on the type of final product desired. Hydroxide is used for modifying the ratios M_2O / Al_2O_3 and M_2O / H_2O (where M is the alkaline ion present in the aluminosilicate source or added with the alkali activating solution); the former is important for balancing the negative charge that is generate on the Al atom, the second is important to adjust the pH to reach the ideal value for dissolving the aluminosilicate powder during the first step of geopolymerization. The silicate is used to increase the Si / Al ratio of the reactive source in order to obtain the desired value in the final product. Very often both the silicate and the hydroxide are used. The factor that most influences the mechanical resistance of the final product is pH: at low values of pH the mixture is viscous and behaves like a cement; at high values of pH the viscosity decreases, and the slurry is more workable [21]. The choice of the cation also plays an important role. Smaller alkaline cations and cations with higher charge density lead to a greater dissolution of the aluminosilicate powder (alkaline hydrolysis) while polymerization and hardening are favoured by larger-sized cations which help the finalization of the geopolymerization process and consequently the mechanical resistance. In addition, larger alkaline cations increase the refractoriness of the geopolymer [22] – [25]. Even if all the alkaline or alkaline earth cations can be used in the polymer synthesis process, the studies focused mainly on sodium and potassium cations.

1.4 PROPERTIES AND APPLICATIONS

The properties of geopolymers depend strongly on their microstructure, which in turn depends on the chemistry of the process and not only on the composition and nature, crystalline or otherwise, of the powders from which it starts [18]. The main properties can be summarized as follow:

- High compressive strength and rapid forming and gripping times
- Good resistance to abrasion, above all with the addiction of fibres
- Fire resistance (up to 1000 °C) without the emission of harmful gases
- Low thermal conductivity
- Excellent chemical resistance to numerous chemical agents
- Low shrinkage and excellent surface definition in replicating relief structures in molds
- Absence of unwanted reactions between matrix and aggregate

• Cost less than Portland cement, especially if waste is used as raw material.

The high mechanical resistance of geopolymers can be attributed to a high degree of polycondensation and the factors that influences the process are time and temperature of curing, type of alkaline activator solution and water content. By appropriately choosing the process conditions, a final product can be obtained which could be used instead of Ordinary Portland Cement (OPC). Geopolymer cements differ from traditional cements as they have a three–dimensional and complex structure while in the concrete there are linear chains (Figure 1.6):



Figure 1.6 Differences of traditional cement and geopolymer cement

There are several advantages of geopolymer cement: the production temperature is lower than in production of OPC (\approx 1500 °C) and this aspect leads to a lower energy consumption, wastes as fly-ash could be used as raw materials, there is a higher chemical durability, and a lower density. But the most relevant aspect concerns the emissions of carbon dioxide (CO₂) [26]: 1 ton of CO₂ is produced to produce 1 ton of cement, while the production of 1 ton of geopolymer concrete leads to the production of 170 kg of carbon dioxide. Then, this type of material is part of the development of eco–sustainable market policies. The geopolymers discovered recently are reported to possess excellent fire–resistant performance due to their ceramic like characteristics. Geopolymeric cement is superior to Portland cement in terms of heat and fire resistance, as Portland cement experienced a rapid deterioration in compressive strength at 300 °C, whereas the geopolymeric cements were stable up to 600 °C [27]. Other

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typical applications, in this area, are molds for foundry, insulating panels and insulating walls, fire–resistant materials for cars and planes, expanded geopolymer panels for thermal insulation, refractories, adhesives, binders and coatings for high temperature.

The tetrahedra present in the structure of the geopolymers create cavities, inside which substances can be incorporated. Indeed, geopolymer can be used as a medium for the encapsulation of hazardous or low/intermediate level radioactive waste. Geopolymeric matrix acts as binder to convert the waste into a solid substance that can be easy stored. Furthermore, transition metal ions can be incorporated as centres for catalytic reactions [28].

Finally, an important sector where geopolymers are making their way is restoration of cultural heritage. Being inorganic material, geopolymer can create new materials for the restoration works of artefacts made in natural and artificial stone materials, ranging in the field of architecture, statuary, the ceramic, and glass. Coloured geopolymers can also be created by inserting inorganic pigments [29].

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2. ZEOLITES

2.1 ORIGIN AND HYSTORY

The term *"zeolite"* was first used by the Swedish mineralogist Cronstedt in 1756, when he discovered the first zeolite mineral: stilbite [1].

The term derived from two Greek words: *zeo* and *lithos*, meaning "to boil" and "stone", in fact he observed that upon heating this mineral released steam, as water evaporated, and the zeolite seemed to be boiling because of the rapid water loss [2]. In 1862 St. Claire Deville tried to synthetize in laboratory *levynite* zeolite through a hydrothermal process. Between 1989 and 1909 Friedel and Grandjean observed that dehydrated zeolites adsorbed liquids like alcohol, benzene, chloroform and molecules as ammonia, air and hydrogen [3, 4].

The first crystal structures of zeolite were described by Taylor and Pauling in 1930 and, after that, they concluded that zeolites have aluminosilicate frameworks with loosely bonded alkali or alkali–earth cations, or both, and molecules of H₂O occupying extra-framework positions [5]. In 1932 McBain coined the term *molecular sieve* to define porous solid materials that acts as sieves on a molecular scale [6]. In the 30s various properties of zeolites began to be described as ion exchange, adsorption and molecular sieves.

Milton and Donald discovered important types of zeolites, called A, X and Y; but an important step was taken in 1959 when T.B. Reed and D.W. Breek reported the structure of the synthetic zeolite A. From this point on, there were several industries that used zeolites in commercial applications. In 1959 a zeolite Y–based catalyst was marked by Carbide as an isomerization catalyst [7], in 1974 Henkel introduced zeolite A in detergents as a replacement for the environmentally suspect phosphates. In 1977 Union Carbide introduced zeolites for ion-exchange separations. Currently, both natural and synthetic zeolites can be marketed. Synthetic zeolites are used mainly as detergent builders, catalysts, and absorbents/desiccants, while natural zeolites are used for feed additives, soil amendment, water treatment, environmental uses, and construction. Most natural zeolites are formed as a result of volcanic activity. The magma produced by volcanoes eruption breaks through the earth's crust and flows out in form of lava accompanied by gases, dust and thick ash. If the volcanoes were in proximity of sea, the ejected lava and ashes could flow into sea; the hot lava, the water and the salt of the sea, over the course of thousands of years, could reacted leading to the

formation of crystalline solids knows as zeolite [8] – [10]. Instead, synthetic zeolites are generally produced through a hydrothermal synthesis; amorphous silico-aluminate systems tend to evolve, in an alkaline environment and in hydrothermal conditions, towards tectosilicate phases, in particular of a zeolitic type [11].

2.2 SYNTHESIS AND CHEMICAL STRUCTURE

According to the CNNMN (Commission on New Minerals and Mineral Names):

"A zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting of four oxygen atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. These are usually occupied by H₂O molecules and extra-framework cations that are commonly exchangeable. The channels are large enough to allow the passage of guest species. In the hydrated phases, dehydration occurs at temperatures mostly below about 400 °C and is largely reversible. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedral [5]".

This is a general definition which allows to consider as zeolites many both natural and synthetic compounds characterized by a three-dimensional anionic scaffolding, called framework, which has the TO₄ tetrahedron as the primary constructive unit [12]. Indeed, primary building units (PBUs) can be distinguished in the crystal structure of zeolites (Figure 2.1):



Figure 2.1 Primary building units

The PBUs are $(SiO_4)^{4-}$ and $(AIO_4)^{5-}$ tetrahedra; they connect each other by sharing all the vertices of the tetrahedra represented by the oxygens and form a spatial arrangement of simple geometric forms: the SBUs. Some Si⁴⁺ ions are substituted by Al³⁺ ions leading to a net negative charge in the network; this negative charge is balanced by the presence of counterions, which are generally alkaline or alkaline earth metals, as Na⁺, K⁺, Ca²⁺ et al. (Figure 2.2).



Figure 2.2 Counterions present in zeolite framework

At present, 23 types of SBUs are known to exist [13] (Figure 2.3).

Figure 2.3 Secondary Building Units (number in parentheses indicates frequency of occurrence)

Depending on how PBUs are interconnected, different forms are formed as single rings, double rings, polyhedral or even more complex units which are linked together in a variety of ways to produce a unique system of channels and cages [2] (Figure 2.4):



Figure 2.4 Evolution of the zeolite structure

As shown in Figure 2.4, the size of the rings in the framework determines the pore size in different zeolites. Zeolites are classified as micro-porous materials; indeed, the cavities have openings smaller than 2 nm. Figure 2.5 shows different zeolitic structures with respective channels and cavities.



Figure 2.5 Examples of channels and cavities in zeolite framework

A generic formula for these tectosilicates is:

$$(M, D_{0.5})_x \cdot \left[Al_x \cdot Si_y O_{2(x+y)}\right] \cdot nH_2 O$$

- *M* = monovalent ions (K, Na, Li, ...)
- D = bivalent ions (Mg, Ca, Ba, ...)
- $y/x \ge 1$ (Loewenstein rule)
- *n* = number of water molecules in unit of formula.

Loewenstein rule (1954) regulates the replacement of silicon with the aluminium according to which two adjacent tetrahedral sites that share an oxygen at the vertex cannot be occupied simultaneously by Al. Then the substitution maximum of Si by Al may be 50% and therefore the minimum ratio Si / Al equal to 1. In addition to conventional zeolites, several new classes of zeolitic materials have been prepared such as AIPO (aluminophosphates), SAPOs (Aluminophosphates Si Substituted) and many others.

Natural zeolites can be found as great deposits of mineral and can be procured at low costs; while synthetic zeolites are produced through a hydrothermal process which can be described as follow:

- Amorphous silica and alumina sources are mixed with an aqueous medium, in alkaline pH condition.
- 2. The mixed solution is sealed in autoclave and heated to promote synthesis reactions.
- 3. Following the time of crystallization, the obtained crystals undergo processes of filtration, washing and drying.

Natural zeolites are normally not pure, is contaminated by other elements, metals and crystals (such as quartz which is found in most of the clinoptilolite deposits) [2]. Actually, about 60 species of natural zeolites are known to exist occurring naturally in soils, sediments, and rocks and the most common are analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite. On the other hand, the advantage of synthetic zeolites is that they can be produced with the desired chemical composition for their subsequent use. About 200 synthetic zeolites are reported in literature. Synthetic zeolites have higher surface areas, higher micro–pore volumes, lack impurities and can be specially manufactured for a specific task [14].

2.3 NA-LTA AND FAU-X

Above all, the structure of NaLTA (Linde Type A) and FAU–X (Faujasite type X) zeolites are interesting for this research activity.

The structure of many zeolites is based on the unit of 24 tetrahedra of Si or Al, linked together, called "sodalite cage" or " β -cage"; consisting of rings with 4 or 6 sides interconnected to each other so as to form a closed three-dimensional structure, having the shape of a truncated octahedron (Figure 2.6). The interconnection of eight sodalitic cages determines the formation of a larger cavity, called " α cage" (Figure 2.7).



Figure 2.6 Sodalite cage

The first commercially interesting zeolite to be synthesized was the Linde Type A, from the Linde Division of the Carbide Union, with chemical formula $Na \ Al \ Si \ O_4 \cdot 2.25 \ H_2O$. It has a three-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes, and is made of secondary building units 4, 6, 8, and 4-4 (Figure 2.3). The pore diameter is defined by an eight-member oxygen ring and is small 4.2 Å. This leads into a larger cavity of minimum free diameter 11.4 Å. The cavity is surrounded by eight sodalite cages (truncated octahedra) connected by their square faces in a cubic structure. The unit cell is cubic (a = 24.61 Å) with Fm-3c symmetry. Na–LTA zeolite (Figure 2.7) has a void volume fraction of 0.47, with a Si / Al ratio of 1.0. It thermally decomposes at 700 °C [15, 16].



Figure 2.7 Na-LTA zeolite

SEM micrograph (Figure 2.8) shows the characteristic cube shape of the Na–LTA zeolites [17, 18].



Figure 2.8 SEM micrograph of the Na–LTA zeolite [17]

While Na–LTA zeolite is obtained only through a synthetic process, FAU–X zeolites can be found in nature. The name of this structure derives from the name of the mineral which presents this framework, faujasite (Figure 2.9).

2. ZEOLITES



Figure 2.9 Faujasite

The faujasite framework consists of sodalite cages which are connected through hexagonal prisms. The pores are arranged perpendicular to each other. The pore, which is formed by a 12–membered ring, has a relatively large diameter of 7.4 Å. The inner cavity has a diameter of 12 Å and is surrounded by 10 sodalite cages. Y zeolite has a void fraction of 48% and a Si / Al ratio of 2.43. It thermally decomposes at 793 °C. Synthetic X and Y zeolites have the same framework of faujasite, but in FAU–X zeolite the Si / Al ratio is between 1 and 1.5 while in the FAU–Y zeolite it is between 1.5 and 3 [15, 16].

SEM micrograph (Figure 2.10) shows the characteristic morphology of octahedral crystalline structure of FAU-X zeolite [19, 20].



Figure 2.10 SEM micrograph of the FAU-X zeolite [19]

2.4 PROPERTIES AND APPLICATIONS

The most interesting property of zeolites is due to their microporous crystal structure. Inside the framework there are large cavities and uniform channels with dimension between 3 and 10 Å (Figure 2.11).



Figure 2.11 Microporous zeolite structure

This structure corresponds to a very wide specific surface. The different types of zeolites correspond to different percentages (from 20 to 50%) of the volume of empty spaces (channels and cavities) with respect to the volume of the entire crystal and different surface areas. Normally, there are water molecules inside these cavities; but, treating the zeolites thermally, the water evaporates and leaves free space for other molecules, preferably polar molecules. Another characteristic is the presence of extra-reticular cations; these are used to balance the negative charge deriving from the presence of aluminium in tetrahedral coordination, replacing the silicon. Due these characteristics zeolites can be used in different applications:

1. Adsorption and molecular sieving:

The adsorption is a surface phenomenon consisting in the adsorption of liquid or gaseous molecules on the surface of a solid. The earliest use of zeolites was in their application as adsorbents in 1777 by Fontana and Scheele [2]. In fact, after a thermal treatment, in order to eliminate water molecules, if the zeolite is put into contact with a solution in which there are molecules, whose critical diameter is smaller than the diameter of the zeolite channels, these molecules could be adsorbed. The water present in the structure is weakly linked and its release is reversible. Molecules are attracted to the surface by presence of residual electric

charges and therefore the absorption is more active on the polar molecules (such as water) rather than non-polar molecules. This ability to select molecules based on their size is called "molecular sieving" [21]. The use of zeolites as adsorbent is aimed at separation and purification processes as: purification of industrial or municipal wastewater and treatment of drinking water [22].

2. Cationic exchange:

The ion bonds existing between zeolitic framework and the cations results strongly weakened due to the dielectric action exerted by the water molecules; this makes it possible to replace the extra-framework cations with others present into a solution putted in contact with the zeolite. The maximum substitution amount is defined as "Cation Exchange Capacity" (CEC), expressed in milliequivalents of cations exchanged per gram of substance (meq g⁻¹) (Figure 2.12):



Figure 2.12 Representation of Cationic Exchange Capacity

This parameter depends above all on the ratio Si / Al. CEC is maximum when Si / Al = 1, that is when the replacing of Al to Si is 50%. In this case, in fact, the presence of counterions is maximum. Also, as cationic exchangers the zeolites are strongly selective, in the sense that they show strong preferences for some cations instead of others [21]. The uses of zeolites as cation exchangers find application in the field of detergency, the production of soil improvers and fertilizers for agricultural soils, the removal of pollutants from waste water [23], the production of nanostructured pigments [24].

3. Catalysis:

The catalytic properties of zeolites are due to the enormous extension on their internal surface and to the presence on it of active sites that lower the energy of activation of the reaction of interest. In fact, within the structure, it is possible to find acid sites that can be reached by the reacting molecules through the passage in the cavities and in the channels. For this, the zeolites have been extensively used for long, either in standard industrial processes or in emerging fields, such as biogas upgrading and CO₂ capture [25].

In petrochemical processing, zeolites are used, for example, as catalysts for Fluid Catalytic Cracking (FCC process) [26], a process which transforms long–chain alkanes into shorter ones.

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3. GEOPOLYMER – ZEOLITE COMPOSITES

Since the zeolite is generally synthetised as micronic powder (0.5-5 µm), shaping it has become necessary for most industrial processes. Different methods have been developed to achieve this technological goal, by using porous ceramic binders, polymer foams, or permeable bags [1]. Pelletization and extrusion are the most frequently used methods to shape powdery zeolites, but they require a binder that can partially obstruct the active sites of zeolite [2, 3]. Recently, additive manufacturing (AM) approach has been also tested to obtain binder-less shaped zeolite monoliths [4]. Geopolymers can be considered the amorphous counterpart or precursors of crystalline zeolites [5] – [8], therefore it is possible to promote the nucleation of a zeolite inside a geopolymeric matrix by tuning pH, temperature, pressure, and time of the geopolymerization reaction. Provis et al. [9] reported that an important part of the binder phase formed in geopolymerization is likely to be consisted of nanometer-sized crystalline structures, resembling the nuclei around which zeolites crystallize. Agglomeration of these nano-crystallites by the remaining aluminosilicates material in the form of an amorphous gel produce a high-performance mineral binder. So, under suitable conditions, geopolymer gel should convert in zeolites: depending on starting materials and process conditions, different types of zeolites can be produced such as Na–LTA zeolite [10], Na–X zeolite [11], FAU zeolite [12]. Recently, a one-step procedure is successfully carried out realizing geopolymerization and crystallization under mild operating conditions [13].

Many authors have drawn comparisons between zeolites and geopolymers since there are a lot of similarities between the two systems as much as the geopolymeric gel phase recently has been described as "zeolitic precursor" [9, 14, 15]. Geopolymerization is regarded as the analogue of zeolites synthesis since the chemistry involved is similar, although the resulting products are different in composition and structure. Actually, geopolymeric products do not have stoichiometric composition and comprise mixtures of amorphous to semi–crystalline structure and crystalline Al–Si particles [5]. During geopolymerization, once the alumino – silicate powder is mixed with the alkaline solution a paste forms and quickly transforms into a hard geopolymer. Therefore, there is no sufficient time and space for the gel or paste to grow into well crystallized structure; this is the fundamental difference between zeolites and geopolymers. Moreover, starting materials as well as the condition of

synthesis are similar, even if the key difference between zeolites and geopolymers is their respective relative levels of matrix phase crystallinity.

The first method carried out for production of zeolites from geopolymers was based on the hydrothermal synthesis. Yan et al. [16] used this method starting from an amorphous Al₂O₃-SiO₂ powder, first prepared through a sol-gel method using tetraethylortosilicate (TEOS), aluminium nitrate nonahydrate (ANN), and anhydrous ethanol (EtOH) (Figure 3.1). This hydrothermal process leads to a self-supporting Na–LTA zeolite membrane with a nano-scale structures, already present within the Al₂O₃–2SiO₂–Na₂O amorphous geopolymer. These structures were zeolite nuclei, that turn into zeolite crystals after the hydrothermal process. The self-supporting zeolite membranes, produced in this way, were proposed for organic solvent dehydration processes or seawater desalination, thanks to their high compressive strength (approximately 57 MPa) and good ions rejection capacity.



Figure 3.1 Preparation of zeolite monoliths

3.1 SYNTHESIS OF GEOPOLYMER – ZEOLITE COMPOSITES

With regard to the synthesis' mechanism of geopolymer – zeolite composites, three macro categories can be identified [17]:

- 1. Zeolites as raw materials
- 2. Direct zeolites formation in the matrix of geopolymer
- 3. Hydrothermal treatment of geopolymers.
3.1.1 ZEOLITES AS RAW MATERIALS

The use of zeolite as raw material doesn't ensure obtaining a geopolymer – zeolite composite. In fact, during the synthesis, due to the high alkalinity, the zeolite can disappear as confirmed by X–ray diffractogram of final sample [18] – [23]. This is the simplest method and both natural and synthetic zeolites can be used. The zeolite dissolution strongly depends on alkaline activator, in terms of chemical composition and concentration [19, 24]. The unreacted zeolites give several properties to geopolymeric framework, heavy metal removal [25], CO₂ capture [26], formaldehyde adsorption [27]. These composites also exhibit interested mechanical properties [28].

3.1.2 DIRECT ZEOLITES FORMATION IN THE MATRIX OF GEOPOLYMER

The formation of zeolites occurs simultaneously with the geopolymeric reaction. The birth and growth of zeolites strongly depend on raw materials, alkaline activator and curing conditions. In fact, as these parameters vary, different types of zeolite can be formed, such as LTA, FAU, CHA, SOD, ANA, CAN [29] – [34].

The choice of raw materials influences the Si / Al ratio and consequently the type of zeolite. In fact, by using metakaolin as raw material, it is possible to promote the formation of Na–LTA and/or FAU–X zeolites. If the Si / Al ratio is 1, only Na–LTA zeolite crystallizes in the geopolymeric matrix [29, 30]. When the Si / Al ratio slightly increases (up to 1.25), only FAU– X zeolite [31, 32] or a mixture of FAU–X and Na–LTA zeolites [30] crystallizes.

At the same time, the choice of alkaline activator influences the type of zeolite. Its role depends on chemical composition and concentration. Sodium hydroxide is the most widely used alkaline activator along with sodium silicate solution. However, the latter increases the Si / Al ratio. In fact, a metakaolin-based matrix activated with sodium hydroxide promotes the crystallization of Na–LTA zeolite, but if it activated with sodium silicate solution no zeolite crystallizes [29]. The same happens with fly ash–based geopolymers [35, 36]. Therefore, the use of an alkaline activator with low silica content and higher alkalinity promotes the formation of crystalline zeolitic phase [41]. In general, the use of sodium silicate solution as alkaline activator influences the type of zeolite, too. For example, Moon et al. [42] obtained Y zeolite and sodalite by activating natural pozzolan-based geopolymers with NaOH solution, and phillipsite and little quantity of Y zeolite with a mixture of NaOH and sodium silicate. About that, the choice of an alkaline activator with a higher silica content involves the crystallization

of less ordered zeolite [43]. The system alkalinity influences the type of zeolite that crystallizes in the framework, due to the different stability of zeolite building units in various conditions of alkalinity. In particular, lower alkalinity promotes the crystallization of Na–LTA and FAU–X zeolite in metakaolin-based and fly ash-based geopolymers, on the contrary, high alkalinity conditions favour the crystallization of hydroxysodalite [40] – [43].

The role of curing condition (e.g., time, temperature) is strongly related with choice of raw material and alkaline activator. For example, setting the Si / Al ratio at 1.12, during the activation of metakaolin-based geopolymer, FAU–X zeolite crystallizes at 80 °C and Na–LTA zeolite at 95 °C, while setting the Si / Al ratio at 1.25, no zeolite crystallizes at 80 °C and FAU–X zeolite at 95 °C [30]. Using a 3 M solution of sodium hydroxide as alkaline activator of lime and metakaolin mixture, A zeolite crystallizes at 20 °C and 80 °C. Conversely, with 5 M solution of sodium hydroxide, no zeolite crystallizes at 20 °C and FAU–X zeolite at 80 °C [48]. The zeolites crystallization is promoted by increasing curing temperature, as several studies show [45] - [47]. As curing time increases, the crystallization is promoted and the quantity of zeolite rises [48] - [51]. In general, considering the synergistic effects of the various factors, it can be concluded that a long time is required to obtain well crystallized zeolites, while the amorphous zeolite precursor is obtained in a short time and at low temperatures.

3.1.3 HYDROTHERMAL TREATMENT OF GEOPOLYMERS

The traditional method for the synthesis of zeolites is the hydrothermal treatment This process increases the conversion rate of geopolymeric framework into zeolite [56]. During the hydrothermal treatment Si – Al radical ions depolymerize, zeolite grains form and zeolite crystals grow [57]. It is usually carried out in a Teflon-lined hydrothermal reactor (Figure 3.2).



Figure 3.2 Teflon-lined hydrothermal reactor (Autoclave)

The hydrothermal treatment can be done with a one- or two-steps procedure. The first involves a single synthesis interval. The geopolymeric slurry is immediately subjected to hydrothermal treatment, during which zeolites crystallizes directly from some aluminosilicate oligomers and the other form the geopolymeric framework. During the two-steps procedure, a bulk geopolymer is first synthesized, which is subjected to hydrothermal treatment and it is converted into crystalline zeolites [58].

Qing Tang et al. [59] synthesized and characterized ZSM–20 zeolites from metakaolin–based geopolymers. ZSM–20 zeolite is considered to resemble faujasite in certain structural aspects, but it has a higher Si / Al ratio. ZSM–20 zeolite could be used as an adsorbent or employed as a catalyst in a wide variety of hydrocarbon conversion reactions, such as polymerization, aromatization, cracking and hydrocracking because of its large pore capacity. The geopolymer sample was first prepared and after submitted to the hydrothermal treatment. Metakaolin, obtained by kaolin calcination at 800 °C for 2h, and a sodium silicate solution (Modulus = 1.1) were fully mixed to obtain a slurry. This was then cast into cylindrical moulds and cured at 40 °C for 3 days. At last, the geopolymer gels were placed in a Teflon hydrothermal reactor with distilled water at 140 °C for 10 hours. Under these operating conditions ZSM–20 zeolite was yielded; the crystallinity was calculated to be 71.6%, with no unrelated zeolite crystals produced, as SEM images show (Figure 3.3).



Figure 3.3 SEM images of (a) ZSM-20 zeolite; (b) magnified image of (a) [59]

Hongquan Wang et al [11] produced self–supporting zeolite monoliths from a metakaolinbased geopolymer gels. The geopolymer gel precursors were prepared via sol–gel method by mixing metakaolin and an alkaline activator as combination of sodium silicate solution (Modulus = 1) and sodium hydroxide (10 M). The Al₂O₃ / SiO₂ molar ratio was 1 : 4 and the Na₂O / SiO₂ molar ratio was 1. The resulting gel was cast into cubic moulds and then cured in an oven for 30 min; at last, the hydrothermal treatment was carried out. The synthesis of Na– X zeolite was affected by several parameters as Na₂O / SiO₂ molar ratio, H₂O / Na₂O molar ratio, time and temperature of hydrothermal treatment. The optimal conditions for a good degree of crystallization were Na₂O / SiO₂ = 1, H₂O / Na₂O = 70, hydrothermal synthesis time of 18 h, and reaction temperature of 90 °C. The compressive strength of zeolitic monoliths obtained with the previous conditions was 38.46 MPa. This type of zeolite has high capacity either for separations of different heavy metal cations by filtration or water vapour for use as a desiccant.

Although the hydrothermal treatment is the traditional method for the synthesis of zeolite, long crystallization time (from few hours to several days) in sealed autoclave are sometimes required. About that, some authors have tried to produce zeolite crystals without hydrothermal condition. Jianxia Duan et al [60] synthesized bulk zeolite by one-step method through geopolymer gels without surfactants and autoclave. The one-step procedure allows to realize simultaneously geopolymerization and crystallization using mild operating conditions, without secondary processing. Metakaolin and a sodium hydroxide solution were used as starting materials. These were mixed and the obtained slurry was poured in cubic mould and cured for a certain time in an oven. Curing time and temperature, Na / Al and water / binder ratio are important parameters for the crystallization of Na-LTA zeolite. Best results have been obtained with a Na / Al ratio of 1, water / binder ratio of 0.7, curing time of 16 h at 70 °C. The geopolymer gels bonded the microparticles of Na–LTA zeolite with each other, which made the bulk samples has certain strength. By nitrogen adsorption analysis micropores and mesopores have been observed because of the coexistence of Na-LTA zeolite phase and geopolymer phase. Figure 3.4 shows the formation mechanism of the bulk zeolite and the morphology evolution under different synthesis conditions.



Figure 3.4 The formation mechanism of the bulk zeolite and the morphology evolution under different synthesis conditions

3.2 HOW DETECT ZEOLITES

Thanks to their unique crystalline structure, the zeolites can be detected by XRD, SEM, FT–IR and MAS NMR analysis.

As regards the geopolymeric framework, some studies confirm the presence of a characteristic XRD spectrum with a broad hump (at around 27-29° 20), whatever the chemical nature of the raw materials and the conditions of synthesis, attributed to the amorphous aluminosilicate gel [5], [9], [61]–[63]. This gel, as confirmed by SEM analysis, consists of nanometer-sized aluminosilicate crystals [64], [65]. These nanocrystals, thanks to the alkalinity of solution, curing temperature and time, relative humidity, can be converted into zeolites, which have a characteristic diffraction pattern. When the synthesis conditions are favourable, well–crystallized zeolites can be observed with Scanning Electron Microscopy. Liu et al. [66] show as geopolymeric gel can be transformed in well-crystallized FAU-X zeolite thanks to the hydrotermal treatment (Figure 3.5).



Figure 3.5 SEM images (c) and XRD pattern (f) of faujasite block

At the same time, Infrared Spectroscopy can be used to identify the type of zeolite that crystallize inside the geopolymeric framework. In fact, several studies confirm that the vibrations in the range 800 – 500 cm⁻¹ give structural information on zeolites secondary building units (SUB) [38], [45], [46]. More recently, FT–IR is also used to determine the Si / Al ratio of zeolites [67].

Zeolites are composed of some nuclei (e.g., ²⁹Si, ²⁷Al, ¹H, ²³Na) with a magnetic moment and therefore suitable for NMR investigation. Tracing the type of zeolite to a specific vibration is not trivial but became possible considering the number and type of units that make up the zeolitic framework [68]–[70].

3.3 APPLICATION OF GEOPOLYMER – ZEOLITE COMPOSITES

The geopolymer – zeolite composites can be used in various application field such as energy, building, aerospace, filtration and bioengineering.

Several studies show the high performance of geopolymer – zeolite composite as bulk type adsorbent in aqueous system to remove different types of pollutants from urban and / or industrial wastewater.

Recently, Pimraksa et al. produced geopolymer – zeolite pellets for dye removal. The geopolymer acts as binder to confer mechanical strength (26.9–20.4 MPa) and zeolites functionalize composite giving it the adsorption capacity. Methylene blue ($C_{16}H_{18}N_3SCI$) is used as reference dye and the removal efficiency is assessed at70% [71].

A geopolymer – zeolite membrane, with an efficient ability to separate Cr(VI) pollutants from aqueous solution, was prepared by hydrothermal treatment of circulating fluidized bed fly ash solid waste. This membrane was first characterized in terms of chemical, physical and morphological analysis, then the separation experiment was conducted by analysing the effect of the transmembrane pressure, Cr(VI) concentration, pH value, ionic strength and coexisting anions. The promising results and the low production cost suggest the real possibility of using the geopolymer – zeolite membrane in removal of hypertoxic Cr(VI) from wastewater [72].

Salam et al. developed a diatomite / kaolinite geopolymer to remove phosphate and ammonium ions in sewage water and groundwater. The experiment was carried out in batch and the effect of time, pH, concentration, dosage, coexisting anions was investigated. The composite shows high sequestration capacities (206.6 mg g ⁻¹ for PO_4^{3-} and 140 mg g ⁻¹ for NH_4^+), therefore can be used effectively in the purification of water [73].

Na–LTA zeolite microspheres, prepared by alkaline activation of metakaolin based geopolymer, were used for static and dynamic Pb (II) removal (Figure 3.6). The main removal mechanism is the ions exchange between Na (I) and Pb (II) and the removal rate is assessed at 74.5% for dynamic test and 99.99% for static test [74].



Figure 3.6 Schematic diagram of the preparation NaA-ZMs and their Pb (II) static and dynamic removals [74]

A zeolite – carbon composite, obtained by hydrothermal conversion of high carbon fly ash, was proposed as petroleum substances (e.g., engine oil) adsorbent. The presence of well– defined zeolite crystals, confirmed by X–ray analysis, gives the highest sorption capacity, therefore these composites can be classified as the most effective adsorbents for the oil spills removal in the group of mineral adsorbents [75].

At the same time, different studies confirm the possibility of using geopolymer – zeolite composites ad bulk type adsorbent in gaseous system. Geopolymer–hydrotalcites composites, synthetised by geopolymer gel conversion, were proposed for CO_2 adsorption at low (35 °C) and intermediate temperature (200 °C). The high mechanical strength (25–27 MPa) and CO_2 sorption capacity (0.141 mmol g⁻¹ at 200 °C and 0.154 mmol g⁻¹ at 35 °C) allow the use of these composites in different working temperatures [76].

The geopolymer – zeolite composite, prepared by hydrothermal treatment of metakaolin / diatomite based geopolymer, was used as catalyst in the transesterification of spent cooking oil. This innovative research shows the promising activity to achieve 99% biodiesel yield. Therefore the geopolymer – zeolite composites become optimum candidates also as solid basic catalysts [77].

Li et al. produced a mesoporous faujasite from the fly ash solid waste by one-step method for the application in low-temperature solid oxide fuel cells. This composite shows a high ionic transport process (shown in Figure 3.7) and the power density and the open circuit voltage are evaluated at 286 mW cm⁻² and 0.98 V, respectively. These promising results suggest the possibility of developing mineral–based energy technologies [78].



Figure 3.7 The schematic of the ionic transport process in composite material [78]

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4. SELF – SUPPORTING ZEOLITES BY GEOPOLYMER GEL CONVERSION

For several industrial applications supporting or shaping powdery zeolites is a technological urgency. In fact, structuring a porous powder, like a zeolite, allows attaining better performances in terms of mass transfer, chemical and mechanical stability. Nowadays, zeolite membranes are principally obtained by grow crystal seeds previously deposited on a proper substrate. The technological problem linked to this method is to obtain a uniform distribution of the crystallization seeds on the substrate which therefore causes some defects. To decrease these defects, a self–supported zeolite membrane could be a good choice [1]. Therefore, the present research activity aims to achieve self–supported zeolites by Geopolymer Gel Conversion method, analysing the effect of the synthesis parameters on the birth and growth of crystalline phases.

The first part of this research focused at designing a multifunctional porous bulk–type system combining the microporosity of zeolite, the mesoporosity of the geopolymer matrix and the macroporosity induced by the foaming process. A one–step procedure was selected to realize simultaneously geopolymerization and crystallization using mild operating conditions, without hydrothermal treatment. The optimization of the operating conditions was carried out by studying the effect of the foaming agent content, relative humidity, and curing time on zeolite content in the sample [2]. The resulting self–supporting zeolite was chosen as water softener and its properties were investigated.

Afterwards, a procedure to obtain a self–standing FAU–X zeolite monolith was developed. Starting from previous findings, a two–steps geopolymer conversion process to obtain a self– standing FAU–X monolith was set up. The resulting self–supporting zeolite was proposed as bulk type adsorbent in gaseous system and its sorption properties were evaluated.

4.1 RAW MATERIALS

To obtain the geopolymer – zeolite composites the following raw materials were chosen:

1. metakaolin, provided by Neuvendis, as alumino-silicate source. Its composition is reported in Table 4.1.

Table 4.1 Metakaolin composition (wt%)

| | Al ₂ O ₃ | SiO ₂ | K ₂ O | Fe ₂ O ₃ | TiO ₂ | MgO | CaO |
|------------|--------------------------------|------------------|------------------|--------------------------------|------------------|------|------|
| Metakaolin | 41.90 | 52.90 | 0.77 | 1.60 | 1.80 | 0.19 | 0.17 |

Metakaolin is ideally synthesized by dehydroxylation of pure kaolin. While the calcination temperature and duration of treatment affect the final surface area, the degree of dehydroxylation and the reactivity, the base structure is that of a highly disrupted phyllosilicate structure containing only silicon and aluminium.

The XRD spectrum of the metakaolin (Figure 4.1) confirmed the mainly amorphous nature of the sample, which shows traces of quartz, montmorillonite, halloysite and titanium oxide as crystalline phases.



Figure 4.1 XRD spectra of metakaolin (° = Halloysite, * = Kaolinite – Montmorillonite, + = Quartz and # = Titanium Oxide)

For this reason, metakaolin is very reactive in alkaline environments. Another important parameter to take in consideration is its specific surface area, because it can give precious information about the reactivity of powder. The producer has provided the value of the specific surface area of metakaolin: 12.69 m² g⁻¹.

The average value of particle size is $d_{50} = 3.64 \ \mu m$, determined by particle size analysis performed by a Malvern Mastersizer 3000 laser particle size analyzer.

The microstructure of the metakaolin powder was evaluated using SEM analyses. Figure 4.2 shows the SEM images of metakaolin: the layered microstructure deriving from the decomposition of kaolinite is still detectable.



Figure 4.2 SEM images of metakaolin

2. 10 M sodium hydroxide (NaOH) solution as alkaline activator. It was prepared using suitable amount of NaOH pellets (Carlo Erba Reagenti) dissolved in deionized water. Alkaline solution is necessary to dissolve metakaolin into Si(OH)₄ and Al(OH)₄-: these species will lead to the formation of the geopolymeric framework.

3. A foaming agent.

Nowadays, different foaming procedures based on gas evolution in the viscous matrix have been widely exploited. A chemical foaming process is based on a redox reaction of Al or Si in alkaline solution, which induces porosity by H₂ evolution. In the present work the chemical foaming was obtained by hydrogen produced through the redox reaction of Si powder in alkaline medium [3]:

$$Si + 4H_2O \rightarrow 2H_2 + Si(OH)_4$$

Silicon powder was purchased by Riedel De-Haen (purity 97.5 %).

At the same time some authors proposed hydrogen peroxide (H_2O_2) as chemical blowing agent for the foaming of the geopolymeric pastes [4]. In fact, it easily reacts in alkaline environment by producing oxygen gas, according to the following equation [5]–[7]:

$$H_2 O_2(l) \to 2 H_2 O(l) + O_2(g)$$

Therefore, a hydrogen peroxide solution (30% by weight) provided by Titolchimica S.P.A. was used as pore agent in alternative to silicon powder.

4. A foam-stabilizer. Vegetal surfactant provided by Isoltech S.R.L. was added to the slurry to stabilize the macroporosity obtained by silicon–promoted foaming.

4.2 PREPARATION OF GEOPOLYMER – ZEOLITE COMPOSITES

Geopolymer gel could turn into zeolites by several methods (see Chapter 3). The Geopolymer Gel Conversion (GGC) method directly promotes the growth of zeolites inside the geopolymeric matrix [8]. Its efficiency strongly depends on raw materials and synthesis conditions. Usually a hydrothermal treatment is used to promote the crystallization of zeolite inside the matrix and it can be done with one- or two-steps method [9]–[11].

In this research activity a GGC method using mild operating condition was proposed. This was carried out by one- or two-treatments, then the difference in terms of crystalline phase was analyzed.

4.2.1 ONE – STEP METHOD

The geopolymeric paste was obtained by mixing metakaolin, silicon powder and sodium hydroxide solution. The slurry was cured in a single synthesis run at specific conditions, in terms of relative humidity, curing time and temperature. The final properties of geopolymer – zeolite composites, in terms of quantity of crystalline zeolite, porosity and morphology, are influenced by several parameters. First, the role of silicon amount, relative humidity and curing time were investigated.

The Design of Experiments (DOE) approach was used in the experimental program since it can help to detect the impact of input factors on the output response of the synthesis. The space of the experiments was explored using a fractional factorial design (an orthogonal array was used [12]), considering two factors that can vary on two levels (silicon w%, time), and one factor that can vary on three levels (relative humidity of curing). The resulting matrix of experiments, containing the different levels used for each parameter, is shown in Table 4.2.

Each sample is labelled as follows: ZEOP/x/y/t, where x is the silicon content expressed as a percentage by weight, y is a relative humidity and t is the curing time expressed in days.

| Sample name | Si, % | RH, % | t, d |
|----------------|-------|-------|------|
| ZEOP/0.5/50/1 | 0.5 | 50 | 1 |
| ZEOP/0.5/75/1 | 0.5 | 75 | 1 |
| ZEOP/0.5/100/1 | 0.5 | 100 | 1 |
| ZEOP/1/50/1 | 1 | 50 | 1 |
| ZEOP/1/75/1 | 1 | 75 | 1 |
| ZEOP/1/100/1 | 1 | 100 | 1 |
| ZEOP/0.5/50/3 | 0.5 | 50 | 3 |
| ZEOP/0.5/75/3 | 0.5 | 75 | 3 |
| ZEOP/0.5/100/3 | 0.5 | 100 | 3 |
| ZEOP/1/50/3 | 1 | 50 | 3 |
| ZEOP/1/75/3 | 1 | 75 | 3 |
| ZEOP/1/100/3 | 1 | 100 | 3 |

 Table 4.2 DOE matrix of experiments

Once the operating parameters were chosen, metakaolin and silicon powders were homogeneously dry mixed, then sodium hydroxide solution was added. The slurry was cast into cylindrical moulds and cured in oven at 40 °C. Figure 4.3 shows a geopolymer – zeolite composite sample after curing.



Figure 4.3 Geopolymer – zeolite sample after curing (a) top view and (b) front view with cylindrical mould

The properties of geopolymer – zeolite composites depend on the quantities of zeolites that crystallize in the matrix. These can vary significantly depending on the reaction parameters. The effect of the silicon content, relative humidity (RH), and synthesis time on the zeolite content were investigated. To study the effect of silicon as pore forming, two mixtures with different percentage of silicon (0.5% and 1%) were produced and cured in oven at 40 °C at the same time. Silicon amount affects the volume increase (Table 4.3), by using 1% of silicon the volume triplicates, while in the case of 0.5% the volume almost doubles.

| Si, % | Initial Volume, ml | Final Volume, ml | Volume Increase, % |
|-------|--------------------|------------------|--------------------|
| 0.5 | 9 | 20 | 122.22 |
| 1 | 10 | 35 | 250 |

Table 4.3 The effect of silicon amount on final volume

On the other hand, the amount of silicon does not modify the foaming kinetic. In fact, the expansion starts (about at t = 30min) and ends at the same time (about at t = 39min) for each sample (Figure 4.4).



Figure 4.4 The effect of silicon amount on foaming kinetics

4.2.2 TWO-STEPS METHOD

With the aim to obtain a self-standing FAU-X zeolite, firstly, a metakaolin–based geopolymer precursor was obtained [2], inducing the formation of macropores by silicon–promoted foaming. Then, the porous geopolymer precursors, containing nanometer–sized crystalline structures resembling the nuclei around which zeolites crystallize [13], were converted into FAU–X monoliths by means of an alkaline treatment at different temperatures and times.

The influence of NaOH concentration (0.1 to 2 M), treatment temperature (40 to 80 °C) and time (1 to 20 days) on the FAU–X crystallization was studied. Therefore, 7 post–treatment tests were performed, during which the effect of one parameter was evaluated while keeping the other two constants (Table 4.4).

| Test | с _{NаОН} , М | t, d | т, °С |
|------|-----------------------|------|----------------|
| Α | 2 | 1 | 40, 50, 60 |
| В | 1.5 | 1 | 40, 50, 60 |
| С | 1 | 1 | 40, 50, 60, 80 |
| D | 0.5 | 1 | 40, 50, 60 |
| E | 0.5 | 3 | 40, 50, 60 |
| F | 0.2 | 1, 3 | 40 |
| G | 0.1 | 1, 3 | 40 |

Table 4.4 Planning of post-treatment experiments

In each sample, the zeolitic phase was checked by means of X–ray diffraction and Scanning Electron Microscopy (SEM), and the crystallization kinetic of FAU-X inside the geopolymer slurry was investigated by means of X–ray diffraction quantitative phase analysis (XRD–QPA).

4.2.3 SYNTHESIS UNDER VACUUM

In this case, the geopolymer – zeolite composites were prepared with the same one–step method described in the previous paragraph, but the synthesis was carried out under vacuum by using a vacuum glass desiccator (Figure 4.5). Samples were produced by fixing relative humidity at 100%, curing temperature at 40 or 60 °C, curing time at 1 or 3 days, amount of silicon at 0, 0.5 or 1%.



Figure 4.5 Vacuum glass desiccator

4.2.4 FOAMING WITH HYDROGEN PEROXIDE

Several mixtures were prepared by varying the amount of H_2O_2 . Table 4.5 reports the composition of mixture and the corresponding increase in volume.

| Sample | Pore agent | Increase in volume, % |
|--------|--|-----------------------|
| 1 | 10 vol% H ₂ O ₂ | 240 |
| 2 | 5 vol% H ₂ O ₂ | 200 |
| 3 | 2.5 vol% H ₂ O ₂ | 150 |
| 4 | 1 vol% H ₂ O ₂ | 100 |
| 5 | 1 wt% H ₂ O ₂ | 100 |
| 6 | 1 wt% H ₂ O ₂ + 1 wt% Si | 60 |

Table 4.5-The effect of H₂O₂ on final volume

The samples with higher amount of H_2O_2 (indicated in the Table 4.5 as 1, 2 and 3) show a too coarse porous texture: as shown in Figure 4.6, there are big voids in the sample, that would lead to a poor contact surface and time with gaseous or liquid phases under dynamic conditions.



Figure 4.6 Sample number 3 after 3 days of curing at 40 °C

The right balance was obtained with 1% of hydrogen peroxide (samples indicated as 4, 5 and 6 in Table 4.5). In particular, Figure 4.7 shows the sample with 1 vl% of H_2O_2 .



Figure 4.7 Sample number 4 after 3 days of curing at 40 °C

4.3 CHARACTERIZATION OF GEOPOLYMER – ZEOLITE COMPOSITES

The properties of geopolymer – zeolite composites strongly depend on the presence of zeolites that crystallize and grow inside the geopolymeric framework. The presence and the type of zeolites were investigated by means of X–ray diffraction analysis, scanning electron microscopy and infrared spectroscopy. Then the physical and mechanical properties were analysed.

4.3.1 ONE – STEP METHOD

The properties of geopolymer – zeolite composites depend on the quantities of zeolites that formed in the matrix. These can vary significantly depending on the reaction parameters. To study the effect of the silicon content, relative humidity (RH), and synthesis time on the zeolite content, different mixtures were investigated. When the conditions are favourable, the crystalline seeds of the geopolymeric framework may transform into zeolite and can be detected by X-ray diffraction (Table 4.6). The presence of crystalline zeolite was detected by using a Panalytical X'Pert Pro diffractometer equipped with PixCel 1D detector (operative conditions: Cu K $\alpha_1/K\alpha_2$ radiation, 40 kV, 40 mA, 20 range from 5 to 80°, step size 0.0131° 20, counting time 40 s per step).

| Sample name | Si, % | RH, % | t, d | Detected Zeolite |
|----------------|-------|-------|------|------------------|
| ZEOP/0.5/50/1 | 0.5 | 50 | 1 | - |
| ZEOP/0.5/75/1 | 0.5 | 75 | 1 | - |
| ZEOP/0.5/100/1 | 0.5 | 100 | 1 | - |
| ZEOP/1/50/1 | 1 | 50 | 1 | - |
| ZEOP/1/75/1 | 1 | 75 | 1 | - |
| ZEOP/1/100/1 | 1 | 100 | 1 | - |
| ZEOP/0.5/50/3 | 0.5 | 50 | 3 | Na–LTA, FAU-X |
| ZEOP/0.5/75/3 | 0.5 | 75 | 3 | Na–LTA, FAU-X |
| ZEOP/0.5/100/3 | 0.5 | 100 | 3 | Na–LTA, FAU-X |
| ZEOP/1/50/3 | 1 | 50 | 3 | Na–LTA, FAU-X |
| ZEOP/1/75/3 | 1 | 75 | 3 | Na–LTA, FAU-X |
| ZEOP/1/100/3 | 1 | 100 | 3 | Na–LTA, FAU-X |

Table 4.6 Zeolites detected by X–ray diffraction

The XRD analysis reveals that, for a synthesis time of 1 day, crystallization did not occur in every sample family. On the contrary, for a synthesis time of 3 days, all samples showed the presence of two distinct crystal phases, identified as zeolites Na–LTA ([LTA], ICCD ref. code n. 00-039-0222) and FAU–X ([FAU], ICCD ref. code n. 01-083-2319), detected at different amounts, depending on the sample family. As an example, Figure 4.8 reports the XRD patterns of 1 day and 3 days sample.



Figure 4.8 XRD pattern of ZEOP/1/100/1 (lower pattern) and ZEOP/1/100/3 (upper pattern) (X = FAU-X zeolite, A = Na–LTA zeolite, Q = Quartz, T = Titanium Oxide and K = Feldspar)

The XRD pattern of the crystallized sample shows different peak widths for both zeolites: in particular, FAU-X peaks appear broader, suggesting the presence of crystals sized at the nanoscale. The patterns of the zeolite-containing samples were also elaborated to evaluate the content of both zeolites: as an estimation parameter, the integrated area of the most intense peak for both zeolites was used ([200] plane, located at 7.178 °20 for the zeolite Na–LTA, and [111] plane, located at 6.094 °20 for the zeolite FAU–X). Patterns were thus elaborated over a range spanning from 5 to 8 °20, modelling the peak shape as a pseudo–Voigt function corrected for the low angle asymmetry, and the background as a second order polynomial function. Figure 4.9 shows the result of the modelling for a sample obtained with a Si content of 1% at a relative humidity RH = 100% (ZEOP/1/100/3).



Figure 4.9 Peak modelling of the crystallized phases for ZEOP/1/100/3 sample

The collected data are correlated to the synthesis process, and two surface plots (Figure 4.10) were obtained, describing the dependence of each zeolite content on the process parameters (silicon amount, relative humidity).



Figure 4.10 Surface plots

The obtained figure reveals a positive correlation of both silicon addition and relative humidity on the FAU–X growth, while it seems that the growth of Na–LTA negatively depends on both the added silicon and relative humidity.

With the aim to maximize the FAU–X content in the obtained geopolymer – zeolite sample, the ZEOP/1/100/t family was selected to follow the system evolution with time at 40 °C. Namely, starting from a single batch mixture, five samples were produced, which were allowing to react for 1, 3, 8, 20 and 30 days, respectively. After that, samples were collected, washed, crushed and analyzed to evaluate their zeolite content. Peak areas evolution over time was modelled with the following equation:

$$A = A_{MAX} (1 - e^{-Kt^n})$$

where A and A_{MAX} [arbitrary units] are the peak area and the maximum peak area, respectively, K [days⁻ⁿ] a kinetic constant, and n an arbitrary constant. To be noted that, for n = 4, such equation reduces to the Avrami equation, which describes the kinetics of crystallization in the case of random and homogeneous nucleation and growth rate constant with time and in all directions. Figure 4.11 shows the results for both zeolites, while the model parameters and the coefficient of determination R² are reported in Table 4.7.

| | FAU–X | Na–LTA |
|--------------------------|--------|--------|
| А _{мах} , а. и. | 949.33 | 636.97 |
| K, days⁻ ⁿ | 0.02 | 0.08 |
| n | 4 | 1 |
| Reaction time, days | 2.62 | 12.40 |
| R ² | 0.990 | 0.922 |

 Table 4.7 Model parameters for the crystallization kinetic of FAU–X and Na–LTA zeolites in

 the ZEOP/1/100 sample



Figure 4.11 Fitting between experimental results and model values

Concerning the FAU–X, the modelling is successful using a n value = 4, which suggests an Avrami–like crystallization process, while for the Na–LTA case such constraint led to poor agreement between the curve model and the experimental data: probably, this discrepancy arises because the Na-LTA zeolite nucleates as a "parasitic" phase, which crystallizes at a much lower rate. Nevertheless, another modelling is performed using n = 1, which produced a much better fitting (Figure 4.11). For both cases, even if the latter one lacks physical meaning, a "reaction time" was calculated as the time to reach the maximum amount of crystallization (i.e. the time at which A = A_{MAX}). Such reaction time turned out to be of 2.6 days (about 60 hours) for the FAU–X zeolite, and around 12 days for the Na–LTA zeolite.

Samples morphologies were assessed by scanning electron microscopy (SEM) using a Phenom Pro X Microscope. SEM images confirm that the zeolites crystallization inside the geopolymer matrix occurs after about 3 days of curing. In fact, at 1 day of curing the sample shows amorphous structure typical of geopolymer (Figure 4.12 a). At longer curing time the presence of a significant amount of nanometer-sized zeolite crystals is verified, as shown for the sample ZEOP/1/100/3 in Figure 4.12 b.



Figure 4.12 Microstructure of ZEOP/1/100/1 (a) and ZEOP/1/100/3 (b)

The microstructure (Figure 4.13) presents well-developed zeolite Na–LTA crystals with cubiclike morphology and a mean dimension of 800 nm. Na–LTA crystals seem to be surrounded by smaller nanometric crystals with the typical morphology of FAU–X zeolites.



Figure 4.13 Cubic crystal of zeolite Na–LTA in the ZEOP/1/100/3 sample

The crystallization of each zeolitic phase occurs preferentially along the pore wall, whereas the struts are completely constituted by a geopolymer gel (Figure 4.14). It seems that the porosity generated by foaming process promotes the zeolite nucleation mainly on the surfaces of the pores, whereas the struts remain amorphous.



Figure 4.14 Morphological differences between wall pores and strut

The geopolymer conversion approach allows to produce a hierarchical system characterized by macroporosity (generated by the hydrogen evolution), mesoporosity (typical of the geopolymer matrix) and microporosity (characteristic of the zeolitic phases) (Figure 4.15).



Figure 4.15 Hierarchical structure of the foamed geopolymer – zeolite composites

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded using a Thermo Nicolet 6700 mod. Nexus spectrometer (with parameters: resolution of 4 cm⁻¹, spectral range of 400–4000 cm⁻¹). FTIR spectrum of 1 day sample (Figure 4.16) is typical of an amorphous or poorly crystallized hydrated aluminosilicate. It shows six main contributions in the range 4000 – 800 cm⁻¹. A broad absorption band at ~ 3456 cm⁻¹ and a sharper band at 1653 cm⁻¹ can be reasonably attributed to O–H stretching and bending modes of adsorbed molecular water [14]. The absorption band at 1464 cm⁻¹ is attributable to CO_3^{2-} species [7, 8]. The band at 1385 cm⁻¹ is attributable to stretching vibrations of Al–OH [17]. A band at \sim 1032 cm⁻¹ is attributable to T-O (T = Si or Al) in plane stretching [14] or to Si-O stretching vibrations [18]; this second attribution is more likely to be correct as this band will disappear in the 3 days sample. In the range 800 – 400 cm⁻¹ where the Si–O–Al vibrations are active, several broad and not well resolved absorption bands are observable. Quite different is the spectrum of the 3 days sample (Figure 4.16). In fact, in the range 4000 – 800 cm⁻¹ the absorption bands remain quite unchanged, except that the band at 850 cm⁻¹ has disappeared. This last finding is likely related to a higher polymerization degree in samples cured for longer times and to the presence of a lower number of non-bridgeable oxygens. In the range 800 – 400 cm⁻¹ several sharp bands appeared, indicating that some of the amorphous phase has crystallized. As evidenced, this is the range of the Si-O-Al vibrations and is considered as the fingerprint region of zeolites. In particular, the bands at 670, 557 and 465 cm⁻¹ can be likely attributed to Na – LTA type zeolite and the band at 746 cm⁻¹ together with the shoulder at \sim 700 cm⁻¹ to FAU–X or ANA zeolites [11–13]. Spectra of 12– and 20–days samples do not greatly differ from that of 3 days sample.



Figure 4.16 FTIR spectra of the geopolymer – zeolite composites at different curing time

The determination of density and porosity of geopolymer – zeolite composites were carried out according to the European Standard UNI 11060:2003 and UNI EN 1936:2001. At first a weighted amount of the sample was immersed in water under vacuum at room temperature ($22 \pm 3 \,^{\circ}$ C). The system was maintained under vacuum for 2 hours. At the end of the period, the sample was weighted in air and by hydrostatic balance. So, apparent density and open porosity were calculated. Real density can be evaluated by pycnometer method. Accordingly, it is necessary to grind the sample (0.063 mm). The test portion was immersed in the water contained in the pycnometer at room temperature ($22 \pm 3 \,^{\circ}$ C) and with a slight rotation and shaking of the pycnometer, the trapped air bubbles were removed. Subsequently the pycnometer was put under vacuum in the desiccator, until no more bubbles form (15 - 30 minutes). The desiccator was reported at atmospheric pressure, the pycnometer was filled with water and closed with the cap, taking care not to trap the air inside, therefore, the equipment was dried outside and weighted.

The water vapor permeability was evaluated according to the European Standard UNI EN 1015–19:2008 and UNI EN 12086:2013. The samples were placed in plexiglass vessels over a saturated solution of potassium nitrate (KNO₃), that maintains a constant relative humidity (RH) of 93.2% at T = 20 °C. Then, the containers were sealed and placed in a climatic chamber at T = 20 ± 2 °C and RH = 50 ± 5%. The water vapor flow through the specimen was

evaluated by measuring, every 24 h, the mass change of the vessels. The test is considered completed when the above mass change is constant for at least three consecutive weights. By processing the data obtained from the test, it is possible to calculate:

1. Water vapor permeability:

$$W_{vp} = \Delta \cdot t$$

where Δ is the average value of the permeation to water vapor [kg m⁻²·s⁻¹ Pa⁻¹], and t is the thickness of the samples [m]

2. The resistance factor to the diffusion of water vapor (μ) which allows for the relative resistance of the material to be overpassed by the vapor:

$$\mu = \delta_{air}/\delta$$

where δ_{air} is the permeability of water vapor in the air [kg m⁻²·s⁻¹ Pa⁻¹] and δ is the permeability of water vapor in the sample [kg m⁻²·s⁻¹ Pa⁻¹]

3. The thickness of the equivalent air layer (s_d) which indicates the thickness of the still air layer and offers the same resistance to the diffusion of water vapor of the examined material:

$$s_d = \mu \cdot d$$

where μ is the resistance factor to the diffusion of water vapor, and d is the thickness of the sample [m].

The water absorption by capillarity was evaluated according to the European Standard UNI EN 15801:2010. Once constant mass was reached, the samples were weighed and the surface under investigation was placed on the bedding layer, water was added until this last was saturated. For measuring water absorption, the specimens were weighed at specific time intervals. The end of the test was reached when the difference between two successive weighings 24 hours apart was not more than 1%. Therefore, the capillary absorption coefficient (CA, mg cm⁻² s^{-1/2}) can be evaluated as the slope of the straight line in the first 30 minutes of the capillarity test, if there is a quite linear relationship between the water adsorbed (Q, mg cm⁻²) and the square root of time during shorter times.
The water physical properties, now described, were investigated to evaluate how the zeolitic content modify the geopolymer – zeolite composites behaviour. Each experimental test was performed in triplicate and data are reported as average values in Table 4.8. The water absorption by capillary test was carried out on cubic sample with side 5 cm, showed in Figure 4.17 a. On the other hand, 12.5×12.5×2 cm slabs were prepared for vapor permeability tests (Figure 4.17 b).

| | ZEOP/1/100/1 | ZEOP/1/100/3 |
|---|-------------------|--------------------|
| Water Absorption, % | 112.83 ± 6.76 | 128.62 ± 8.85 |
| Open Porosity, % | 64.56 ± 1.96 | 68.49 ± 2.54 |
| Apparent Density, g ml ⁻¹ | 0.57 ± 0.02 | 0.53 ± 0.03 |
| Real Density, g cm ⁻³ | $2.34~\pm~0.04$ | 2.12 ± 0.02 |
| W_{vp} , (10 ¹²) kg m ⁻² s ⁻¹ ·Pa ⁻¹ | 122.7 ± 8.49 | 78.52 ± 17.39 |
| μ | 1.93 ± 0.14 | 3.00 ± 0.53 |
| <i>s_d</i> , m | 0.053 ± 0.001 | 0.068 ± 0.016 |
| Water Absorption by capillary, % | 79.97 ± 10.07 | 92.37 ± 1.59 |
| CA, mg cm ⁻² s ^{-1/2} | 7.11 ± 0.61 | 6.75 <u>+</u> 1.17 |

 Table 4.8 Water physical properties of the geopolymer – zeolite composites

Collected data show a slight increase in the water absorption and open porosity for the 3 dayssample. This indicates that the zeolite growth does not reduce the macroporosity, but, on the contrary, enhances the capillarity of the sample, suggesting an increase in the specific surface of the sample, which could in turn improve its adsorption behaviour.



(a) (b) Figure 4.17 Water absorption by capillary (a) and vapor permeability (b) tests

The mechanical properties of the samples were analyzed by use of Tensometer 2020. Data related to the sample geometry were inserted in the software that collect and process all measures made by the testing machine; the tests were conducted with a 5 kN load cell and a displacement rate of 1.0 mm min⁻¹.

A three-point flexural test was carried out. The specimen with rectangular section was placed on two parallel supporting pins. The loading force was applied in the middle by means loading pin. The distance between supporting pins, denoted as "span", was equal to 100 mm. Because of the flexure imposed, there was a compressive stress on the top and a tensile stress on the bottom. The flexural strength, σ_f , is calculated with the following equation:

$$\sigma_f = \frac{M \cdot c}{I};$$
 $M = \frac{F \cdot L}{4};$ $c = d/2;$ $I = \frac{b \cdot d^3}{12}$

where M is the maximum bending moment, c is the maximum distance between most external fibers and the center, I is the moment of inertia of the transversal section, F is the applied load and L is the span. According to the geometry:



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So, flexural strength becomes:

$$\sigma_f = \frac{3F \cdot L}{2b \cdot d^2}$$

The two parts in which each sample was broken after the bending test were used for compressive tests. The same testing machine was used. A support with a fixed base and a tilting head was implemented in the machine. In this way, the tilting head grant a good adhesion to the sample. Compressive strength was simply calculated dividing the load for the resistant section.



(a) (b) **Figure 4.18** Bending (a) and compressive (b) tests

Bending and compressive tests were made on prismatic molds with the dimension of 4x4x16 cm (Figure 4.18) and the results are summarized in Table 4.9. Firstly, each sample was weighed and measured, and density was calculated. Collected data demonstrate that the crystallization of zeolite inside the geopolymer sample does not significantly affect its physical and mechanical properties. In fact, the geopolymeric amorphous framework is responsible of mechanical features. For this reason, it is possible to make a positive comparison with highly porous geopolymers with the same porosity (70 – 80%) and obtained in the same condition (direct foaming) [22].

| Table 4.9 Physical and mechanical properties of the geopolymer – zeolite composites at two |
|--|
| different curing time |

| Sample | Density, g cm ⁻³ | Compressive strength, MPa | Flexural strength, MPa |
|--------------|-----------------------------|---------------------------|------------------------|
| ZEOP/1/100/1 | 0.36±0.015 | 0.39±0.072 | 0.33±0.068 |
| ZEOP/1/100/3 | 0.39±0.014 | 0.39±0.071 | 0.31±0.015 |

4.3.2 TWO – STEPS METHOD

Concerning the FAU–X porous monoliths, the presence of zeolite and the type of zeolite that crystallizes in the geopolymer precursor depend on alkaline concentration, temperature and time of post-treatment and were detected by X–ray diffraction analysis. 7 tests were planned to investigate the simultaneous effect of each parameter. For all prepared samples, Na–LTA and FAU–X zeolites were detected. For both zeolites, the integrated area (*A*) of the most intense peak ([200] plane, located at 7.178 °20 for the zeolite Na–LTA, and [111] plane, located at 6.094 °20 for the zeolite FAU–X) was used as quantitative estimator parameter. At higher alkaline concentration, further increase in post-treatment temperature results in crystallization of Na–LTA instead of FAU–X zeolite (Table 4.10 – Test A). When the alkaline concentration decreases, the crystallization of FAU–X zeolite is favoured, and its amount increases as post–treatment temperature increases (Table 4.10 – Test B to D). The further decrease in alkaline concentration does not crystallize any zeolite (Table 4.10 – Test F and G). The best condition in terms of least quantity of Na–LTA zeolite is obtained during tests E. Looking at the post–treatment temperature, the greatest amount of FAU–X zeolite is reached at 60 °C.

| Test | с _{NаОН} , М | t, d | т <i>,</i> °С | A [Na–LTA] | A [FAU-X] |
|-------|-----------------------|------|---------------|------------|-----------|
| A (1) | 2 | 1 | 40 | 59 | 492 |
| A (2) | 2 | 1 | 50 | 362 | 583 |
| A (3) | 2 | 1 | 60 | 544 | 268 |
| B (1) | 1.5 | 1 | 40 | - | 90 |
| B (2) | 1.5 | 1 | 50 | 325 | 610 |
| B (3) | 1.5 | 1 | 60 | 396 | 511 |
| C (1) | 1 | 1 | 40 | - | 230 |
| C (2) | 1 | 1 | 50 | 44 | 441 |
| C (3) | 1 | 1 | 60 | 51 | 1225 |
| C (4) | 1 | 1 | 80 | 189 | 1151 |
| D (1) | 0.5 | 1 | 40 | 0 | 0 |
| D (2) | 0.5 | 1 | 50 | 0 | 57 |
| D (3) | 0.5 | 1 | 60 | 0 | 154 |
| E (1) | 0.5 | 3 | 40 | 0 | 117 |
| E (2) | 0.5 | 3 | 50 | 30 | 595 |
| E (3) | 0.5 | 3 | 60 | 8 | 1464 |
| F | 0.2 | 1, 3 | 40 | - | - |
| G | 0.1 | 1, 3 | 40 | - | - |

Table 4.10 Zeolite detected by X-ray diffraction

Collected data (Table 4.10) show that the best condition to favour the crystallization of FAU– X zeolite is alkaline concentration of 0.5 M and post-treatment temperature of 60 °C. In fact, FAU–X zeolite is already detected in the sample after 3 days of post–treatment (Figure 4.19).



Figure 4.19 XRD spectrum of sample after 3 days of post-treatment (X = FAU–X zeolite, A = Na–LTA zeolite, Q = Quartz)

Thus, the crystallization kinetic of FAU–X zeolite was investigated by increasing the posttreatment time (up to 20 days) and the amount of crystalline phase were measured by X–ray diffraction quantitative phase analysis (XRD–QPA). The experiment was performed at the Elettra MCX beamline in Trieste. Data were collected in transmission mode packing the powders in a borosilicate capillary with a diameter of 500 µm. The patterns were collected at room temperature using a monochromatic wavelength of 1.549 Å (8 keV), with a 1*0.3 mm² spot size using a scintillator detector. 10 wt% of a standard powder (Silicon 640c-Nist) was also mixed to the powdered samples with the aim to evaluate the amorphous amount possibly present in the samples. The phase identification was conducted with High Score Plus software, while the QPA was performed by means of the Rietveld method [23] using the GSAS package.

Figure 4.20 shows the results of XRD–QP analysis. Starting from 3 days, a significant amount of amorphous phase was converted into zeolite (55% FAU–X and 2% Na–LTA). Thanks to the alkaline treatment at 60 °C the zeolite content increased during the crystallization kinetics, reaching an amount of 80% of FAU–X and 6% of Na–LTA after 20 days.



Figure 4.20 Crystallization kinetic of FAU–X zeolite

SEM analysis confirms the results obtained by X–ray diffraction. In fact, the presence of a well crystallized FAU–X zeolite can be detected already in the sample after 7 days of post–treatment (Figure 4.21).

At the same time, the water adsorption test was carried out on the sample at 3 days of post-treatment (FAU–X). The higher amount of crystalline phase (as confirmed by X–ray diffraction analysis) significantly increases the physical properties, in terms of water absorption (188.30 \pm 12.4%), open porosity (75.42 \pm 1.15%), apparent density (0.40 \pm 0.03 g ml⁻¹) and real density (2.18 \pm 0.02 g ml⁻¹).

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Figure 4.21 SEM images of sample after 7 days of post treatment at different magnifications: (a) 1000X (b) 2500X and (c) 10000X

(b)

(c)

4.3.3 SYNTHESIS UNDER VACUUM

The X–ray diffraction patterns confirm that the same crystalline phases occur in the samples synthetized under vacuum. Figure 4.22 shows the XRD spectra of samples with 0.5% of silicon powder. No differences appear in 1 day–samples (Figure 4.22 a–b): both are amorphous; and there are no differences in terms of crystalline phases (Na–LTA and FAU–X zeolite) in the 3– day samples (Figure 4.22 c–d).



Figure 4.22 XRD spectra of (a) ZEOP/0.5/100/1, (b) ZEOP/0.5/100/1/vacuum, (c) ZEOP/0.5/100/3, (d) ZEOP/0.5/100/3/vacuum (X = FAU–X zeolite, A = Na–LTA zeolite, Q = Quartz, S = Sodium Carbonate Hydrate, K = Feldspar and T = Titanium Oxide)

The same holds for the samples with 1% of silicon powder. No zeolite in the 1 day–samples (Figure 4.23 a–b) and Na–LTA and FAU–X zeolites in the 3 day–samples (Figure 4.23 c–d), but the higher amount of Si favours the crystallization of FAU-X instead of Na–LTA zeolite, especially for the under vacuum produced sample.



Figure 4.23 XRD spectra of (a) ZEOP/1/100/1, (b) ZEOP/1/100/1/vacuum, (c) ZEOP/1/100/3, (d) ZEOP/1/100/3/vacuum (X = FAU-X zeolite, A = Na-LTA zeolite, Q = Quartz, S = Sodium Carbonate Hydrate, K = Feldspar and T = Titanium Oxide)

To study the effect of temperature, the samples with 0.5% and 1% of silicon powder were cured under vacuum at 60 °C. The higher curing temperature promotes the crystallization of Na–LTA instead of FAU–X zeolite, as shown in Figure 4.24. Furthermore, Na–LTA and FAU–X zeolites already appear in the 1 day–samples (Figure 4.24 a and c).



Figure 4.24 XRD spectra of (a) ZEOP/0.5/100/60/1, (b) ZEOP/0.5/100/60/7, (c) ZEOP/1/100/60/1 and (d) ZEOP/1/100/60/7 (X = FAU–X zeolite, A = Na–LTA zeolite and Q = Quartz)

Indeed, more Na–LTA zeolite crystallizes in the silicon-free sample instead of FAU–X, as confirmed by the XRD spectra of 3–day samples cured under autogenous pressure (Figure 4.25 a) and under vacuum (Figure 4.25 b).



Figure 4.25 XRD spectra of (a) ZEOP/0/100/40/3, (b) ZEOP/0/100/40/3/vacuum (X = FAU–X zeolite, A = Na–LTA zeolite and Q = Quartz)

At the same time, SEM micrographs of 3 day–samples (Figure 4.26) confirm the presence of well crystallized zeolites (Na–LTA and FAU–X) both in 0.5% Si–sample and in 1 %Si and show that the under vacuum synthesis (Figure 4.26 a and c) leads to the formation of larger crystals.



Figure 4.26 SEM images of (a) ZEOP/0.5/vacuum, (b) ZEOP/0.5, (c) ZEOP/1/vacuum, (d) ZEOP/1 at 2500X magnification

In order to verify the effect of the under vacuum–synthesis on the physical properties, all samples were subjected to water absorption test.

| | ZEOP/1/100/1 | ZEOP/1/100/3 | ZEOP/0.5/100/1 | ZEOP/0.5/100/3 |
|---|--------------|--------------|----------------|----------------|
| Water Absorption, % | 141.3±1.59 | 148.2±0.88 | 110.4±4.65 | 106.7±6.99 |
| Open Porosity, % | 71.39±2.73 | 69.53±1.96 | 61.13±2.86 | 62.46±4.29 |
| Apparent Density, g ml ⁻¹ | 0.48±0.03 | 0.51±0.04 | 0.55±0.01 | 0.59±0.04 |
| Real Density, g cm ⁻³ | 2.37±0.05 | 2.16±0.08 | 2.37±0.02 | 2.01±0.04 |

Table 4.11 Water physical properties of under vacuum-samples

Collected data (Table 4.11) show that the under vacuum synthesis significantly increases the physical properties of geopolymer – zeolite composites, in terms of water adsorption and open porosity. These results, combined with XRD and SEM analysis, allow to conclude that the under vacuum synthesis actually stabilize the macroporosity obtained by silicon-promoted foaming.

4.3.4 FOAMING WITH HYDROGEN PEROXIDE

The presence of hydrogen peroxide (in several percentage) as pore agent does not affect zeolites crystallization. In fact, X–ray diffraction analysis confirms the presence of FAU–X and Na–LTA zeolites in all samples after 3 days of curing at 40 °C (Figure 4.27).



Figure 4.27 XRD spectra of samples with H_2O_2 (a) 10%, (b) 5%, (c) 2.5% and (d) 1% by volume (X = FAU-X zeolite, A = Na-LTA zeolite and Q = Quartz)

The absence of silicon powder as pore agent leads to the formation of a greater quantity of Na–LTA than FAU–X zeolite. Therefore, with the aim to maximize the FAU–X zeolite content, the sample with 2.5% of H₂O₂ was cured for 1 day at 40 °C and then subjected to a 3–day post treatment (0.5 M NaOH solution, 60 °C). At the same time, 1% of H₂O₂ was added to the slurry which contains 1% of silicon powder. The sample was cured for 3 days at 40 °C (100% RH). Figure 4.28 shows the XRD spectra of these two samples. The best condition, in terms of greater amount of FAU–X zeolite, is reached with the post treatment (Figure 4.28 b).



Figure 4.28 XRD spectra of samples with (a) 1% H₂O₂ and 1% Si and (b) 2.5% H₂O₂ after 3 days of post-treatment (X = FAU-X zeolite, A = Na-LTA zeolite and Q = Quartz)

4.3.5 USE OF A FOAM-STABILIZER

Several mixtures were prepared by adding different amount of vegetal surfactant to the slurry with the aim of stabilizing the macroporosity. The first test was performed by adding 8% by volume of vegetal surfactant in the slurry, but after 3 days of curing at 40 °C, the specimen does not consolidate. Therefore, the following tests were performed by reducing the percentage of foam–stabilizer. In particular, the second test was carried out adding 5% by weight of pre–foamed vegetal surfactant. After 3 days of curing at 40 °C, the sample is well consolidate compared to the previous test and the X–ray diffraction analysis confirms the presence of zeolitic phases (Figure 4.29). Moreover, the quantity of zeolites present is much higher than a sample obtained under the same conditions but without vegetal surfactant. For this reason, the foam–stabilizer was diluted (30% by volume), foamed and added (2% by weight) to the slurry. After 1 day of curing at 40 °C the sample is completely amorphous (Figure 4.30 a). On the contrary, by subjecting the 1 day–sample to 3 days of post–treatment (0.5 M NaOH solution, 60 °C), only FAU–X zeolite crystallizes (Figure 4.30 b).



Figure 4.29 XRD spectrum of geopolymer – zeolite composite with 5 wt% of vegetal protein (X = FAU–X zeolite, A = Na–LTA zeolite and Q = Quartz)



Figure 4.30 XRD spectra of samples with 2 wt% of vegetal protein (a) at 1 day and (b) at 3 days of post-treatment (X = FAU–X zeolite, A = Na–LTA zeolite, Q = Quartz, T = Titanium Oxide, S = Sodium Carbonate Hydrate and K = Feldspar)

The greater amount of crystalline phase present in these samples confirms that the addition of the surfactant stabilizes the macroporosity induced by the silicon-promoted foaming and consequently the zeolites have a more uniform surface on which to crystallize. Furthermore, the better resolution of the peaks confirms the presence of larger crystals.

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5. GEOPOLYMER – ZEOLITE COMPOSITES AS BULK TYPE ADSORBENT

Basing on the promising results of the chemical, physical and morphological analysis (described in Chapter 4), the water and gas adsorption properties of the produced geopolymer – zeolite composites were investigated, to explore their possible application as bulk type adsorbent (both in aqueous and gaseous systems). In particular, the geopolymer – zeolite composites obtained by one–step method, thanks to the simultaneous presence of both zeolites Na–LTA and FAU–X, are proposed as bulk type adsorbent in aqueous system to remove hardness from tap water, while the geopolymer – zeolite composites, obtained by two–steps method, are proposed as bulk type adsorbent in gaseous system, due to the higher adsorption properties of FAU–X zeolite.

5.1 HARDNESS REMOVAL FROM TAP WATER

The total concentration of magnesium and calcium in water, known as water hardness, represents a great problem for all the industrial processes which use water for steam generation, such as textile, paper, dying industry. Direct feed of hard water to the boiler reduces the steam production due to the presence of such cations, which, forming scale and sludge, priming and foaming, can greatly reduce the heat transfer efficiency [1]. Moreover, the scale formation during industrial activities produces boiler corrosion and blockage of membranes and pipes [2]. Hence the necessity to soften the water prior to use in such application.

Water softening can be mainly performed by means of several processes, which can be classified according to the removal mechanism [3].

The phase change mechanism allows to remove salts and ions from water due to a liquidvapor or liquid-solid transition. Typical liquid-vapor transition processes are based on thermal desalination, that consists in several procedure: multi-stage flash, multiple effect distillation, vapor compression, humidification and dehumidification, membrane distillation [4]–[6]. On the other hand, a typical liquid-solid transition process is freezing desalination [7], [8], that is more competitive than the liquid–vapor one in terms of lower energy and corrosion, even if the complexity of the plant still precludes the industrial scale up [9]. Long–range interactions-based mechanism exploits an electric field to move ions towards an opposite charged surface. The processes based on these interactions are ion exchange membranes [10], electrodialysis [9], capacitive deionization [11].

Short–range interaction-based mechanism adopts selective porous media [12]–[16], ultrafiltration [17] and adsorption or chelating agents [18] to remove calcium and magnesium ions from water stream.

The chemical precipitation mechanism, e.g. lime soda process [19], is frequently used in water purification and treatment plant [20], [21]. This involves the use of specific compounds that help in precipitation of Ca²⁺ and Mg²⁺ ions by removing water hardness.

Zeolites have excellent ion—exchange and sorption properties, that depend on their physical – chemical features [22]. For these reasons, such materials are employed to a large extent as water softeners [23], [24]. In particular, Na—LTA and FAU—X zeolites can exchange their sodium ions with "hard water ions", such as calcium and magnesium [25]. It has been also demonstrated that a synergistic effect can be reached using a mixture of them [26].

In this regard, the geopolymer – zeolite composite, obtained by one–step method (see Chapter 4), is proposed as softener to remove the hardness of tap water. Therefore, the Cation Exchange Capacity and the Point of Zero Charge were first evaluated. Then, the softening performance was determined through kinetic tests under pH–controlled and real conditions. In order to evaluate how zeolite nucleation affects the water softening process, the sample with the highest content of crystalline phase (Na–LTA and FAU–X zeolites) and a pure geopolymeric sample (no zeolite present) are selected. From now on, the first, obtained after three–days of curing, will be indicated as ZEOP and the second, obtained after a one–day curing, as GEOP.

The Cation Exchange Capacity (CEC), i.e. the maximum amount of cations as milliequivalents exchanged per gram of substance, was evaluated by means of the Cross-Exchange method reported in De Gennaro et al. [27]. Accordingly, a complete Na \rightarrow K exchange was performed by contacting a suitable amount of sample with 1 M KCl solution at a solid–to–liquid ratio = 2 g L⁻¹ for 3 h at 40 °C under continuous stirring, then the liquid phase was separated by centrifugation, and sampled for further analysis. Such procedure was repeated 10 times. After that, the sample was washed, dried, and the total amount (meq g⁻¹) of exchanged Na⁺ cations was then calculated as the sum of the amounts exchanged after each cycle. A complete K → Na reverse exchange was then performed on the same sample and under the same operating conditions (using a 1 M NaCl solution), obtaining the total amount of exchanged K⁺ cations. The CEC was finally evaluated as the average of the two values. The cationic amount was evaluated by ICP atomic emission spectroscopy (ICP–OES, Perkin-Elmer Optima 2100 DV). Concerning the GEOP sample, the CEC value turns out to be 3.22 meq g⁻¹. This is not surprising, because, even if no zeolite nucleated in the sample, some extra-framework sodium cations, weakly bonded to the framework, are present anyway. The CEC of the ZEOP sample, on the contrary, results to be 4.43 meq g⁻¹: such increase is certainly due to the presence of the aforementioned zeolites. Inglezakis [28] compared the cation exchange capacity of some natural zeolites. Collected data shows that the proposed samples have the same exchange features of natural ones and in particular ZEOP shows higher exchange capacity.

The study of surface charge is useful to determine the condition in which geopolymer – zeolite composites can be regenerated. Indeed, the reversal of the surface charge related to the pH of the solution allows the release of previously adsorbed cations. The Point of Zero Charge (PZC) is the condition of surface charge density equal to zero, which does not mean the absence of any charges, but rather the presence of equal quantities of positive and negative charge [29]. The determination of PZC was carried out by using powder addition method. Powdered sample was put in contact, under continuous stirring for 24 h, with 0.01 M solution of KNO₃ at different pH (4 to 13), at a solid–to–liquid ratio of 5 g L⁻¹. The addition of powder changes the solution pH. In fact, if the initial pH is lower than the PZC of the sample, the surface will absorb the protons and the final pH will be higher[29], [30]. The surface charge was determined by calculating the PZC, by measuring the initial pH (pH_i) , before adding powdered sample, and the final pH (pH_f), after 24 h under continuous stirring. For both samples, the pH variation ($\Delta pH = pH_f - pH_i$) is reported as function of initial pH (Figure 5.1). The PZC is determined when $\Delta pH = 0$ and it corresponds to 9.88, so at this pH value the surface charge is zero. Therefore, after adding the geopolymer – zeolite composite in tap water, whose pH is about 7, the pH will rise, inducing the possibility to remove cations, beside by ion exchange, also by precipitation.



Figure 5.1 Determination of PZC with powder addition methods

To investigate the ability of geopolymer – zeolite composites to purify tap water, each sample was put in contact with tap water at a solid–to–liquid ratio of 2.5 g L⁻¹ under continuous stirring. The kinetic of Ca⁺⁺ and Mg⁺⁺ removal was evaluated. 10 mL withdrawals were taken at fixed times from 0 to 1440 minutes, the liquid was separated, and both cations concentration was determined by ICP. The pH was monitored during each kinetic test with Orion Star A211 Thermo Scientific pH Meter. Figure 5.2 shows the kinetic tests equipment.



Figure 5.2 Kinetic tests equipment: magnetic plate and pH meter(a) and filtration device (b)

To study the performance of the water hardness removal, for each of the two samples three kinetic tests were carried out, and then the average of the results was calculated.

Firstly, the softeners were tested in real condition using tap water. The percentage of Ca^{2+} (or Mg^{2+}) removed by each sample was obtained as:

$$\frac{C_0 - C(t)}{C_0} \times 100$$

where C(t) and C₀ [mg L⁻¹] are the cation concentration at time t and time t=0, respectively. The uptake of calcium and magnesium is reported in Figure 5.3.

The behaviour of each softener seems very similar as regards calcium removal. In fact, both samples showed good performance: after 240 minutes the uptake of calcium is about 55 and 60% for GEOP and ZEOP respectively, while after one day both systems were able to remove about 90%. On the contrary magnesium removal seems to be strictly related to the presence of zeolites inside the exchanger matrix: after 240 minutes the uptake of magnesium is about 14 and 33% for GEOP and ZEOP respectively, while after one day about 29 and 54% for GEOP and ZEOP respectively.



Figure 5.3 Uptake of calcium (a) and magnesium (b)

Considering the pH of the solution during the softening process (ranging from 7 to 9), precipitation phenomena may occur which contribute to the cations reduction. In order to discriminate between precipitation and exchange phenomena, other softening runs were performed by keeping pH at 5 with the aid of nitric acid addition (Figure 5.4).



Figure 5.4 PH–controlled kinetic test



Figure 5.5 Uptake of calcium (a) and magnesium (b)

As expected, the removal efficacy in pH–controlled conditions decreases for both calcium and magnesium (Figure 5.5).

To estimate the removal efficiency of calcium and magnesium, the maximum adsorption (RE) was calculated according to the following equation [31]:

$$\operatorname{RE} = \frac{C_i - C_f}{m} \cdot V$$

where $C_i [mg L^{-1}]$ is the initial concentration of cation in the tap water, $C_f [mg L^{-1}]$ the concentration of cation at the end of kinetic test, m [g] the sample mass and V [L] the volume of solution.

Collected data, shown in Table 5.1, confirms that the presence of zeolite increases the softening capacity of the samples. In fact, the higher removal of cations in uncontrolled pH conditions is due to the precipitation of calcium and magnesium at alkaline pH. Moreover, the ZEOP performances compare favorably with most of other materials investigated as softeners (data acquired from literature), suggesting that the geopolymer – zeolite composites can be proposed as a good alternative to natural and synthetic softener in the removal of calcium.

| SAMPLE | RE, mg g ⁻¹ | | REF | |
|-----------------------------------|------------------------|------------------|------------|--|
| | Ca ²⁺ | Mg ²⁺ | | |
| GEOP (UNCONTROLLED PH) | 43.38 | 4.52 | This study | |
| ZEOP (UNCONTROLLED PH) | 49.02 | 7.94 | This study | |
| ZEOP (PH=5) | 20.16 | 4.44 | This study | |
| COMMERCIAL ZEOLITE NA-A | 17 | - | [24] | |
| SYNTHESIZED ZEOLITE NA-A | 31 | - | [24] | |
| CLINOPTILOLITE | 11 | - | [32] | |
| SAND MATERIALS (NATURAL ZEOLITES) | 41.2 | - | [33] | |
| MODIFIED BENTONITE COATINGS | 14.63 | 14.63 | [34] | |
| NATURAL PUMICE STONES | 57.2 | 44.5 | [25] | |
| MODIFIED PUMICE STONES | 62.3 | 56.1 | [33] | |

Table 5.1 Removal efficiency of calcium and magnesium

To evaluate the kinetic mechanism controlling the softening process a pseudo-second-order kinetic model was used. This kinetic model assumes that the limiting step of the process is the ion exchange reaction, and that this reaction has a second order kinetic. Accordingly, kinetic data can be described by the following equation:

$$q_t = \frac{kq_e^2 t}{1 + kq_e t}$$

Where q_e is the amount of cation removed at equilibrium [mg L⁻¹], k [mg L⁻¹ min⁻¹] is the pseudo–second-order rate constant and t is the time [min].

Overall, all the kinetic curves were satisfactorily modelled with the pseudo–second order kinetic equation (see the coefficient of determination values in Table 5.2). Concerning the Ca²⁺ curve obtained under uncontrolled pH conditions, the model seems to underestimate the uptake at relatively short times (250 to 500 minutes, see Figure 5.6). On the contrary, the model overestimates the equilibrium uptake (see Table 5.2). This is likely due to the competiting contributes of precipitation and ion exchange phenomena on the overall uptake process, that the equation does not take into account. On the contrary, the pseudo–second order equation much better intepret the kinetic curves obtained at controlled pH (see

Figure 5.7), once again proving that in this case the cation exchange is the only operating process. Concerning the kinetic constants, both GEOP and ZEOP samples show a similar behaviour under uncontrolled pH conditions: the k constant for calcium uptake is about twice the magnesium one (Table 5.2). It means that both samples remove the Ca²⁺ ions faster than the the Mg²⁺ ions. Moreover, the k values obtained for ZEOP under uncontrolled pH are one order of magnitude higher than those obtained under controlled pH conditions: it shows that the ion exchange process is quite slower than the precipitation for both cations.

| | | GEOP | ZEOP | ZEOP |
|------------------|---|----------------------|----------------------|----------------------|
| | | (uncontrolled pH) | (uncontrolled pH) | (pH = 5) |
| Ca ²⁺ | q _e , mg g ⁻¹ | 54.4 (117.1%) | 55.9 (110.2%) | 22.5 (36.4%) |
| | k, mg g ⁻¹ min ⁻¹ | 7.51 e ⁻⁵ | 8.52 e ⁻⁵ | 4.58 e ⁻⁴ |
| | R ² | 0.975 | 0.978 | 0.985 |
| Mg ²⁺ | q _e , mg g⁻¹ | 5.9 (49.3%) | 9.7 (65.4%) | 5.1 (33.6%) |
| | k, mg g ⁻¹ min ⁻¹ | 4.15 e ⁻⁴ | 4.00 e ⁻⁴ | 1.60 e ⁻³ |
| | R ² | 0.976 | 0.988 | 0.963 |

Table 5.2 Kinetic pseudo-second order parameters for Ca²⁺ and Mg²⁺ removal on GEOP andZEOP samples

*Number in parentheses report the equilibrium uptake as the removed percentage of the initial cation concentration.



Figure 5.6 Modeling results for calcium (a) and magnesium (b) kinetic curves for GEOP and ZEOP samples under uncontrolled pH conditions



Figure 5.7 Modeling results for calcium (a) and magnesium (b) kinetic curves for ZEOP sample under controlled pH conditions (pH = 5)

Looking at an industrial scale application the regeneration and reusability of softener were investigated due to the increasing focus on the environment and the necessity to reduce the production of waste. Each saturated sample was put in contact with sodium chloride solution (1 M), at a solid–to–liquid ratio of 2.5 g L⁻¹ under continuous stirring for 24 h. By measuring the Ca²⁺ and Mg²⁺ concentration in the solution, at fixed time from 0 to 1440 minutes, the amount of cations removal was determined, that represents the percentage of regeneration of the adsorbent. The presence of the two zeolitic phases (Na–LTA and FAU–X) in the ZEOP

sample allows regenerating the softener. In fact, regeneration runs confirmed the complete reversibility of the softening process in controlled pH condition.

At the same time, the reusability of the softener was assessed monitoring its removal ability after subsequent softening cycles (S / L = 2.5 g L⁻¹ under continuous stirring for 4 h) without washing or regeneration. As shown in Figure 5.8, after the 1st cycle the ZEOP sample is able to remove after 4 hours about 60% of initial Ca²⁺ content and this efficiency remains almost the same after 8 cycles.



Figure 5.8 Consecutive runs of water softening test with ZEOP sample (n=number of cycles)

5.2 GAS ADSORPTION TESTS

Zeolites, in particular FAU–X zeolite, has been extensively used for long, either in standard industrial processes or in emerging fields, such as removal of hydrogen sulfide from biogas [36] and CO₂ capture [37] thanks to their generally high gas adsorption performance. FAU–X zeolite is industrially produced as a micronic powder, therefore shaping it represents a technological challenge. Again, geopolymer gel conversion represents an innovative method of structuring powdered zeolite without the use of a binder and, moreover, the presence of the geopolymer backbone ensures mechanical strength and porosity at the meso– scale. Therefore, the self-supporting FAU–X porous monolith obtained by two–steps method (see Chapter 4) is proposed as bulk type adsorbent in gaseous system of several molecules.

The adsorption tests were carried out using a plant operating under batch conditions in which a certain amount of gas was fed at different pressures. Figure 5.9 shows the schematic representation of the plant. This plant uses a gravimetric technique based on a McBain scale. The device is equipped with a quartz spring with a sensitivity of 5 mm mg⁻¹ and a springattached platinum sample pot that can hold 30 to 40 mg of the adsorbent sample. The amount of adsorbate is evaluated by measuring the elongation of the spring with the help of a cathetometer with a sensitivity of 0.05 mm. The gas pressure in the adsorption chamber is measured electronically using a capacitive pressure transducer (Edwards Datametrics 1500). A thermostating unit (FALC) allows to control the temperature of the gas in the adsorption chamber within a range of \pm 0.1 °K.

Before the measurement, the sample was subjected to an in-situ activation process carried out at 200 °C under high vacuum (P < 10^{-3} Pa) by means of an Edwards turbo-molecular pump for 2 hours. The degassing treatment dehumidifies the sample and removes the volatile compounds, making its surface available for adsorption. After activating the sample, adsorption experiment starts. The injection was carried out at room temperature (20 °C) and was repeated at a several increasing pressures injected every 30 min, to allow the sample to equilibrate with the gas. Prior to making each injection, the elongation of the spring was measured, and so the adsorbed amount was evaluated.



Figure 5.9 Schematic representation of adsorption plant

Two samples were tested for gas adsorption of some molecules, such as nitrogen (N_2), ethanol (EtOH), carbon dioxide (CO_2), water vapor (H_2O) and acetic acid (AcAc):

1. Geopolymeric sample obtained after 1 day of curing at 40 °C (GEOP)

water jacket

baffle valve

rotary pump

needle valve

diffusion pump

backing/roughing valve

pressure indicators pressure transducers

purge inlet valve

purge outlet valve

gas inlet

 FAU–X zeolite sample obtained by curing the previous with a post-treatment of 20 days at 60 °C (FAU–X)

The adsorption isotherms were modelled with Langmuir equation:

E1

F

G

G1

G2

Η

V2

V3

S1, S2, S3

T1, T2, T3 V1

$$q = q_{max} \cdot \frac{b \cdot p_{rel}}{1 + b \cdot p_{rel}}$$

where $q_{max} [mmolg^{-1}]$ is the maximum amount of adsorbed gas, *b* is the affinity and represents the compatibility between adsorbent and adsorbate molecules, and $p_{rel} = p_i / p_{sat}$ is relative pressure obtained by dividing the injection pressure, p_i , with saturation pressure, p_{sat} . After the adsorption run, a regeneration test was performed, activating the sample again under the same conditions and verifying that it reaches the pristine weight.

Both the selected samples did not adsorb nitrogen. The adsorption performances towards water vapor, ethanol and acetic acid, summarized in Figure 5.10, show that in all cases the presence of zeolite (FAU-X) significantly increases the adsorption properties of the monoliths both in terms of quantity adsorbed by the sample and affinity with the adsorbate molecule. In particular, regarding the CO₂ adsorption, the zeolite contained in the FAU–X sample, being selective towards CO₂, significantly increase both the affinity (by one order of magnitude) and the maximum adsorption, which is 4 times that of the GEOP sample. The same is true for water vapor adsorption, as the maximum adsorbed amount doubles and the affinity increases of one order of magnitude. The affinity increases especially in the case of the ethanol adsorption, reaching a value of approximately three orders of magnitude higher than that of GEOP sample. In the case of acetic acid, the behaviour differs considerably from that described by the Langmuir model, since in the FAU–X sample at prel above 0.5 the curve tends to rise. This evidence, combined with the fact that in this case the sample turned out to be notregenerable, confirms the hypothesis of a chemisorption phenomenon: most likely the sodium cations present in the sample react with acetic acid to produce sodium acetate. The same behaviour is also found in the GEOP sample: this adsorbs only acetic acid, while it is substantially inert towards the other molecules. In Table 5.3 are reported the values of q_{max}, b and of the coefficient of determination R² for all tests.

| Adsorbate molecules | Sample | q _{max} , mmol g ⁻¹ | b | R ² |
|---------------------|--------|---|----------|----------------|
| <u> </u> | GEOP | 0.798 | 31.559 | 0.960 |
| | FAU–X | 3.303 | 513.627 | 0.999 |
| H ₂ O | GEOP | 5.885 | 0.690 | 0.958 |
| | FAU–X | 11.089 | 42.532 | 0.980 |
| EtOH | GEOP | 0.653 | 4.145 | 0.911 |
| | FAU–X | 3.163 | 1804.885 | 0.986 |
| AcAc | GEOP | 8.741 | 1.118 | 0.097 |
| | FAU–X | 4.596 | 28.285 | 0.969 |





Figure 5.10 Adsorption tests on two selected sample with carbon dioxide, water vapor, ethanol and acetic acid

Many literature studies are available on CO₂ capture and storage technologies. Activated carbons [38], organic polymers [39], MOFs [40], zeolites [41], [42] geopolymers [43] and their composites [44] show high CO₂ adsorption capacity and therefore are proposed as bulk type adsorbent for CO₂ removal [45]. Table 5.4 reports the CO₂ adsorption capacity of different solid adsorbents in low-temperature systems. Collected data show that the FAU–X sample is a good candidate as bulk type adsorbent for CO₂ capture.

| Sorbent | Capacity, mmol g ⁻¹ | Temperature, °C | References |
|---|-----------------------------------|--------------------|------------|
| Activated Carbons | 0.57 | 25 | [46] |
| | 2.61 | | [47] |
| Spent coffee- derived Activated Carbons | 2.0 - 3.8 | 0 | [48] |
| Olive stones | 2.43 | 25 | [49] |
| Mesoporous Carbons | 1.50 | 25 | [50] |
| Zeolites | 0.32 - 6.3 | 0-40 | [51] |
| Binderless beads of FAU–X zeolite | 4.70 | 40 | [52] |
| FAU–X | 3.303 | 20 | This study |

Table 5.4 CO₂ adsorption capacity of several solid adsorbents

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CONCLUSIONS AND PRESPECTIVES

Collected data show that it is possible to obtain macroscopic objects characterized by a hierarchical porosity, containing macro–, meso– and micro–pores by a quite simple process named Geopolymer Gel Conversion (GGC) starting from a metakaolin based geopolymer. Macroporosity is obtained by the foaming promoted by silicon, mesoporosity is typical of the geopolymeric structure and microporosity is assured by the fact that zeolite crystals, grown after geopolymer setting by a low temperature hydrothermal treatment, cover the macropores walls.

The one-step method ensures zeolite crystallization inside the geopolymer matrix starting from a curing time of 3 days, leading to two distinct crystal phases, Na–LTA and FAU–X. The controlled co–crystallization of mixtures of Na–LTA and FAU–X, which is very interesting for detergent applications, can be obtained by tailoring the synthesis parameters. A positive correlation of both silicon content and relative humidity with the FAU–X growth was revealed, while, concerning the Na–LTA, an interdependent influence of both the process parameters was found. The nucleation and growth of both phases seems to be completed after 3 days of curing time. Beyond that period, no big alteration in the sample structure can be detected. The presence of a geopolymer backbone support and shape the zeolitic powder widening its technological application field.

Whereas the properties of geopolymer – zeolite composites depend on the quantities and on the type of zeolites that formed in the geopolymer matrix, a two–steps method was carried out for managing the crystallization of FAU–X zeolite alone. Therefore, the influence of post– treatment parameters, in terms of alkalinity, temperature and time, on zeolite crystallization was studied. A positive correlation of low alkalinity, long time and slightly higher temperature with the FAU–X growth was revealed.

Downstream of the characterization of the so obtained geopolymer – zeolite composites, in terms of chemical, physical and morphological analysis, the possibility of their application as bulk type adsorbent (both in aqueous and gaseous system) was investigated.

The study of water softening capacity of geopolymer – zeolite composites, obtained by one– step method, shows a high capacity to remove calcium and magnesium from tap water. These promising results, combined with regeneration and reusability of the samples, suggest the real possibility of using these ceramic foams in water softening process, and more generally as bulk type adsorbent, for example in the water purification from heavy metal.

At the same time, the gas adsorption capacity of FAU–X porous monoliths, obtained by two– steps procedure, was investigated. In particular, the adsorption isotherms of nitrogen, carbon dioxide, water vapor, ethanol and acetic acid were carried out. The zeolitic sample shows a high adsorption capacity with all the investigated molecules except for nitrogen. Therefore, these sample can easily be proposed as gas purification traps and their application with gaseous mixtures will be investigated.

In addition, to obtaining a controlled and homogeneous foaming process, an under vacuum curing process was performed by studying the effect of curing temperature and foaming agent (Silicon powder) content. A positive correlation of both silicon content and curing temperature with the Na–LTA zeolite growth was revealed by X–ray diffraction analysis. In fact, the slightly increase in temperature (60 °C instead of 40 °C) favours the crystallization of more Na–LTA zeolite, even in 1-day curing samples, which are generally amorphous. The absence of silicon powder decreases the Si / AI ratio which favours the crystallization of the Na–LTA zeolite. In fact, in the 3–day samples without silicon, cured both under normal conditions and under vacuum, more zeolite Na–LTA crystallizes instead of FAU–X. On the other hand, SEM analysis reveals that the under vacuum synthesis leads to the formation of larger crystals, and a significantly increase in physical properties was determined, in terms of water adsorption and open porosity. Collected data allow to conclude that the under vacuum synthesis actually stabilize the macroporosity obtained by silicon–promoted foaming.

At the same time the addition of a foaming stabilizer (vegetal surfactant) was evaluated. X– ray diffraction analysis confirms the presence of both zeolites (Na–LTA and FAU–X). Furthermore, a greater amount of crystalline phase was detected in all samples, by confirming that the addition of the surfactant stabilizes the macroporosity induced by the silicon– promoted foaming and consequently the zeolites have a more uniform surface on which to crystallize, and the better resolution of the peaks confirms the presence of larger crystals.

Finally, the use of a new foaming agent (Hydrogen Peroxide) was investigated. The presence of hydrogen peroxide (in several percentage) as pore agent does not affect zeolites crystallization. In fact, X–ray diffraction analysis confirms the presence of FAU–X and Na–LTA zeolites in all samples after 3 days of curing at 40 °C. Obviously, the absence of silicon powder as pore agent leads to the formation of a greater quantity of Na–LTA than FAU–X zeolite.

These promising results allow the possibility of continuing the research to optimize and functionalize the properties of geopolymer – zeolite composites, also in other application fields, such as catalysis, gas separation, biogas upgrading, heavy metal removal.

6. APPENDICE: ANALYSIS METHODS AND INSTRUMENTS

6.1 X–RAY DIFFRACTION ANALYSIS

X-ray diffraction is a common technique used for phase identification of a crystalline material; it is based on constructive interference between a monochromatic X-ray and a crystalline sample. The necessary condition for diffraction phenomena is that the wavelength of the radiation used is comparable with the distance between the atoms or the molecules to be analysed. The Bragg's law regulates the diffraction phenomenon (Figure A.1):

$$n \cdot \lambda = 2 d \sin \theta$$

where θ is the angle that the incident beam forms with the crystalline plane, λ is the wavelength of incoming radiation, d is the distance between two adjacent planes and n indicates the order of diffraction.



Figure A.1 Graphic representation of Bragg's law [1]

When a source emits a ray that hits the sample, it can be reflected both from the surface and from the underlying reticular plane. These two monochromatic rays have the same wavelength but cover different distances. From Bragg's law, note λ , the value of d is obtained for each value of $\sin \theta$, which corresponds to an intensity different from the background noise. From the XRD patterns it is possible to deduce qualitative and / or quantitative information

on the crystalline phases present in the sample and on the possible presence of an amorphous fraction (Figure A.2):



Figure A.2 Information from XRD pattern

6.2 SCANNING ELECTRON MICROSCOPY

Scanning Electron Microscopy does not exploit photons of light, like optical microscopy, but a beam of electrons that hits the sample (Figure A.3). There is an electro-optical column inside which the electron beam is formed under high vacuum ($P=10^{-4} / 10^{-5}$ mbar). The interaction between the sample and the electron beam takes place in a chamber, which is also kept under vacuum. Inside the column there is a sequence of diaphragms and lenses magnets which collimate the beam on the sample and a series of coils of scanning, to deflect the electron beam along equidistant parallel lines, to cover the scanning area. The primary electrons incident beam give rise to various effect such as secondary electrons, backscattered electrons and X-ray as shown in Figure A.4.



Figure A.3 Schematic diagram of scanning electron microscope [2]

The Volume of Generation is the minimum volume necessary for the emission of a detectable signal. The shape of the emission volume of backscattered electrons depends, for the same energy of the incident electrons, on the average atomic number of the sample. The signal produced by the sample is revealed by a scintillator, amplified by a photomultiplier and later elaborated, with the intervention of signal cleaning systems and elimination of aberration phenomena optics.



Figure A.4 Volume of Generation

6.3 INFRARED SPECTROSCOPY

Infrared spectroscopy or IR spectroscopy is a spectroscopic absorption technique, normally used in the field of characterization of materials for the study of chemical bonds. It is based on the absorption of infrared radiation (IR), with a wavelength between 0.78 and 100 microns [3]. When an infrared photon is absorbed by a molecule, the latter passes from its fundamental vibrational state to an excited vibrational state. The vibrations can be of two types: stretching of the chemical bond (stretching) and deformation of the binding angle (bending). In the IR spectrum two zones can be distinguished:

- zone of functional groups, which extends from 3800 to 1300 cm⁻¹ and includes bands due both to strains and to deformations of functional groups
- fingerprint area, from 1300 to 650 cm⁻¹, which owes its name to the presence of characteristic bands of each molecule because they originate from vibrations of the entire molecular skeleton [4].

6.4 ICP ATOMIC EMISSION SPECTROSCOPY

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for the detection of different metallic and non-metallic inorganic substances present in concentrations even of about one part per billion [5]. It is a type of emission spectroscopy that uses an inductively coupled plasma with a temperature in ranging from 6000 to 10000 °K to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. The ICP discharge is produced by the action of a radiofrequency excitation coil (solenoid), which surrounds a quartz tube through which flows an argon current. The radiofrequency field generates a variable magnetic field inside the coil, which induces currents in a conductive medium (in this case ionized argon). The result is a strong warming. Once ionized, the radiofrequency field can generate a plasma state on the sample to be analysed. The sample is brought into the spray chamber through a peristaltic pump; the use of the latter permits to analyze not only solution but also suspension and thick and viscous liquids. A schematic diagram of ICP-OES system is reported in Figure A.5.



Figure A.5 Schematic diagram of ICP-OES system[6]

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