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**TRABAJO FIN DE MASTER EN INGENIERÍA QUÍMICA**

# DEVELOPMENT OF STABLE GEOPOLYMERS TO WATER PURIFICATION APPLICATIONS.

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# ACKNOWLEDGEMENTS

*To my parents and my sister,*

*To my supervisors Anne Heponiemi, Hanna Runtti , Sari Tuomikoski and Mª Amparo Bes Pía,*

*To Rafa,*

*And my grandparents, wherever they are.*

# ABSTRACT

The rapid growth of society and industry has increased the demand of water, the amount of wastewater produced and the production of hazardous industrial by-products.

Hazardous waste refers to any waste which has in its composition toxic elements and heavy metals that cause or may cause danger to the environment or to human or animal health, either alone or in contact with other waste or substances.

Nowadays industrial hazardous waste includes fly ash, blast furnace slag and jarosite.

The fact that fly Ash and blast furnace slag have high amounts of aluminosilicates in their structure makes them suitable for study in the production of geopolymers in order to find a sustainable way to use them.

Geopolymers are inorganic materials obtained through a geopolymerization reaction in which a solid source of aluminosilicate is mixed with an alkaline activating solution, generating a material with excellent properties that can be used in many different applications e.g. adsorption.

Since wastewater contains a large amount of nitrogen and ammonia is one of the main parameters that can cause eutrophication, in this study, six geopolymers are synthesized using metakaolin (a clay material), fly ash and blast furnace slag as a solid source of aluminosilicates.

These materials are submited to several tests for checking their physical and chemical stability and then, they are subjected to batch adsorption experiments at different pH conditions in order to analyse their effectiveness in ammonium removal.

For those geopolymers that have been shown to be physically and chemically stable, another study is carried out where Jarosite is added as a raw material in the synthesis of geopolymers. This is performed at different compositions for each reagent and is checked their physical stability with the aim to analyse their stability.

**Keywords:** Hazardous waste, Hazardous by-product, Geopolymer, Geopolymerization reaction, Alkaline Activated Solution, Sodium Silicate, Aluminosilicates Metakaolin, Fly Ash, Blast Furnace Slag, Jarosite, Adsorption Experiments, Ammonium.

# RESUMEN

El rápido crecimiento de la sociedad y de la industria ha incrementado la demanda de agua, la cantidad de agua residual producida y la producción de subproductos industriales peligrosos.

Se entiende como residuo peligroso cualquier residuo que tenga en su composición elementos tóxicos y metales pesados que provoquen o puedan provocar un peligro para el medio ambiente, la salud humana o animal, ya sea solo o en contacto con otros residuos o sustancias.

Hoy en día, entre los residuos industriales se encuentran cenizas volantes, escorias de alto horno y Jarosita.

El hecho de que las cenizas volantes y las escorias de alto horno tengan altas cantidades de aluminosilicatos en su estructura, las hace aptas para ser estudiadas en la producción de geopolímeros, con el fin de encontrar una forma sostenible de utilizarlos.

Los geopolímeros son materiales inorgánicos obtenidos mediante una reacción de geopolimerización donde se mezcla una fuente sólida de aluminosilicato con una solución activadora alcalina, generando un material con excelentes propiedades, que puede ser utilizado en muchas aplicaciones diferentes, como la adsorción.

Dado que las aguas residuales contienen gran cantidad de nitrógeno y el amonio es uno de los principales parámetros que pueden causar eutrofización, en este estudio, se sintetizan seis geopolímeros utilizando metakaolin (un material arcilloso), cenizas volantes y escoria de alto horno como fuente sólida de aluminosilicatos.

Tras comprobar la estabilidad física y química de los mismos, estos se someten a experimentos de adsorción a diferentes condiciones de pH con el fin de analizar su eficacia en la eliminación de amonio.

Para los geopolímeros que han demostrado ser física y químicamente estables, se realiza otro estudio, donde se añade Jarosita como materia prima en la síntesis de geopolímeros. Esto se lleva a cabo a diferentes composiciones de cada reactivo y se comprueba su estabilidad.

**Palabras clave:** Residuos peligrosos, Subproducto peligroso, Geopolímero, Reacción de geopolimerización, Solución Activadora Alcalina, Silicato de sodio, Aluminosilicatos, Metakaolin, Cenizas volantes, Escoria de alto horno, Jarosita, Experimentos de adsorción, Amonio.

# RESUM

El ràpid creixement de la societat i de la indústria ha incrementat la demanda d'aigua, la quantitat d'aigua residual produïda, així com de subproductes industrials perillosos.

S'entén com a residu perillós qualsevol residu que tinga en la seua composició elements tòxics i metalls pesants que provoquen o puguen provocar un perill per al medi ambient, la salut humana o animal, ja siga sol o en contacte amb altres residus o substàncies.

Hui en dia, entre els residus industrials es troben cendres volants, escòries d'alt forn i Jarosita.

El fet que les cendres volants i les escòries d'alt forn tinguen altes quantitats d'aluminosilicats en la seua estructura, les fa aptes per a ser estudiades en la producció de geopolímers, a fi de trobar una forma sostenible d'utilitzar-los.

Els geopolímers són materials inorgànics obtinguts per mitjà d'una reacció de geopolimerització on es mescla una font sòlida d'aluminosilicat amb una solució activadora alcalina generant un material amb excel·lents propietats, que pot ser utilitzat en moltes aplicacions diferents, com l'adsorció.

Tenint en compte que les aigües residuals contenen gran quantitat de nitrogen i que l'amoni és un dels principals paràmetres que poden causar eutrofització, en este estudi, es sintetitzen sis geopolímers utilitzant Metakaolí (un material argilós) , cendres volants i escòria d'alt forn com a font sòlida d'aluminosilicats.

Després de comprovar l'estabilitat física i química d'aquests, es sotmeten a experiments d'adsorció a diferents condicions de pH, a fi d'analitzar la seua eficàcia en l'eliminació d'amoni.

Per als geopolímers que han demostrat ser física i químicament estables, es realitza un altre estudi, on s'afegeix Jarosita com a matèria primera en la síntesi de geopolímers. Açò es du a terme a diferents composicions de cada reactiu i es comprova la seua estabilitat.

**Paraules clau:** Residus perillosos, Subproducte perillós, Geopolímer, Reacció de geopolimerització, Solució Activadora Alcalina, Silicat de sodi, Aluminosilicats, Metakaolí, Cendres volants, Escòria d'alt forn, Jarosita, Experiments d'adsorció, Amoni.

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# DOCUMENT I:

# PROJECT MEMORY

# LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| RM | Raw Material |
| GP | Geopolymer |
| AAS | Alkali Activating Solution |
| OPC | Ordinary Portland Cement |
| MK | Metakaolin |
| FA | Fly Ash |
| BFS | Blast Furnace Slag |
| GBFS | Granulated Blast Furnace Slag |
| GGBFS | Ground Granulated Blast Furnace Slag |
| σ | Conductividad |
| w | Weight |
| g | Grams |
| h | Hour |

# 1.- Introduction

As it is known, the rapid growth of an industrial society has increased the demand of water and thus, the amount of wastewater produced, which has a negative impact on the environment [1]. Therefore, it has to be treated before discharge.

Among the parameters to be controlled in wastewater, there is nitrogen, which can exists in different compounds such as organic nitrogen, ammonium, nitrite and nitrate, being ammonium, one of the main parameters that can cause eutrophication [12,16]. Ammonium containing wastewaters exists e.g. in mining industry and in agriculture.

Therefore, the total content of ammonium in wastewater has to be reduced to the maximum discharge limit, which value usually depends on the rules set in different countries [12]. In Finland, the legal maximum limit for ammonium in wastewater treatment plants is usually 4 ppm, whether the water temperature is above 12ºC [12].

Nowadays, there are many techniques for nitrogen removal, where the most commonly used are nitrification-denitrification processes, ion exchange, air stripping of ammonia, reverse osmosis and adsorption [12].

However, the adsorption technique has become an interesting method due to its effectiveness is not influenced by temperature either by variations in wastewater quality [12,23]. In addition, its design is simple as well as the way to proceed and it is a cheap technique, as many industry by-products can be used to synthesize materials that can be used as adsorbents, replacing conventional adsorbent materials [1,14].

In the approach to replacing conventional adsorbents, geopolymers have recently gained interest for use in water and wastewater applications e.g. in the removal of metal ions, ammonium or dyes from wastewater [6,15,16].

The use of geopolymers in water purification applications is based on their attractive properties, as well as their porous and amorphous structure, their ion-exchange ability and the possibility of synthesizing these materials through industrial by-products, thus reducing pollution and contributing to the green technology [16,23].

The use of geopolymers is a new field of research and nowadays, the main solid materials used to synthesize them are metakaolin, fly ash and blast furnace slag where, the latter two, are industrial by-products produced in large quantities, and fly ash, was usually disposed of in landfills [26].

However, due to their environmental impact, they are being used by many researchers to try to find a suitable way to use them [26], contributing to the achievement of the Sustainable Development Goals set by the United Nations, thus it is necessary to keep investing in research.

# 2.- Research main goal

The aim of this research was to synthesize stable geopolymers using by-products from industry in order to study whether they can be used as adsorbents in the ammonium removal and also, to check if they can be still stable after introducing Jarosite in its structure.

# 3.- Geopolymers

Geopolymers are inorganic polymeric materials which were first developed by Joseph Davidovits in 1978 [1,2,5]. This type of material is characterized by its amorphous structure, as well as by its properties and by the wide range of possible applications in several industry sectors [3-7,12].

These materials are obtained through a geopolymerization reaction, where an aluminosilicate source is needed for the geopolymer synthesis [7,12]. The aluminosilicate source could be provided by natural materials, e.g. feldspar, kaolinite, sodalit and estibilie minerals, or by waste materials [5,8-10]. These, could be classified according to whether they have been suffer thermic treatment (calcination) or not [9]. Among the thermic treated materials, fly ash, blast furnace slag and metakaolin are the most widely raw materials used for the synthesis of geopolymers [8,11,12].

The thermic treatment produces a change in the structure of the starting material, so the microstructure and their properties will change and a high content of energy will be retained between the cavities of the particles (pores), as a result of the thermic treatment. It makes the material more reactive, losing some crystalline structure and getting a geopolymer with better properties [5,11].

The fact that geopolymers can be synthesized using industrial by-products make them more attractive to be investigated. Many researchers have focused on the use of these materials as a substitute for Ordinary Portland Cement (OPC) due to their good and rapid development of compressive strength, high thermal stability, excellent mechanical properties, large-scale availability and the possibility of obtaining cement that emits less amount of $CO_2$ through these materials [1-4,6,7,12,18].

However, geopolymers have other interesting properties which allow them to be used in many different applications, not only as a substitute of OPC [3]. In fact, its porous structure makes them suitable for use as catalysts and also, in drugs delivery applications [4].

On the other hand, water and wastewater are current issues that concern society. In this line, geopolymers have gained a great deal of interest in water and wastewater treatment applications due to their high physical and chemical stability, high durability, porous structure and ion-exchange properties [3,6,17]. In fact, the ion-exchange properties have allowed their use as adsorbent materials for the removal of dyes, as well as for the removal of metals or ammonium [3,12,13].

However, this is a relatively new area of research and these materials are being tested for this purpose by many researchers in synthetic water but then, in actual wastewater, many parameters can affect the adsorption removal efficiency of geopolymers [14].

For water purification applications geopolymers can be used as adsorbents, ion-exchangers, photocatalysts, membranes, filters and solidification/stabilization of residues among others [6]. Moreover, they can be also used in applications related to thermal insulation, fire- and corrosion resistant coatings filters, passive cooling systems, containment and immobilisation of toxic, hazardous and radioactive wastes, nuclear power industry among others. [3,5,7,12].

## 3.1 Geopolymerization

Geopolymers are formed through a geopolymerization reaction, in which an inorganic polymer is generated as a result of the reaction between a solid raw material source of aluminosilicate and an alkaline activating solution at temperatures below 100°C [1,20]. The alkaline activating solution is formed by a silicate and a hydroxide mixture which can be potassium hydroxide or sodium hydroxide where, the latter, is the most used in the synthesis of geopolymers [11].

Nowadays the exact geopolymerization mechanism is not known but it is supposed that the geopolymer synthesis is done as a consequence of putting in contact the aluminosilicate solid source with the alkaline activating solution [13]. As a result, the alkaline activating solution produces the formation of silicate and aluminate monomers. This is then followed by polymerization, generating a three dimensional (3D) structure composed of tetrahedral silicate and aluminate units [4]. These tetrahedrons are joined together by oxygen ions. Davidovits defined them as sialate units [19]. The sialate unit, the three dimensional structure of the geopolymer and the different types of geopolymer are shown in Figure 1.

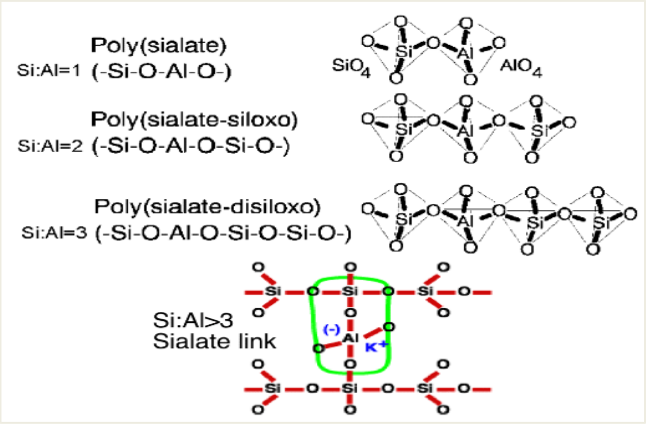

*Figure 1.* Types of geopolymer and sialate unit [19].

The $AlO_4$ groups which are forming the structural geopolymer network, have a negative charge due to the oxidation state three of the aluminium in the tetrahedron (coordination number 4). As a result, positive ions such as $Na^+$, $NH_4^+$, $K^+$, $Ca^{2+}$, $Li^+$, $Ba^{2+}$ or $H_3O^+$ can be associated with aluminium within the network cavities in order to stabilize loads [2,7].

According to Davidovits [19], the empirical formula of geopolymers is: $M_n[-(SiO_2)z\text{-}AlO_2]_nwH_2O$, where “M” refers to any of the cations that are mentioned above, “n” means the polymerization degree and “z” determines the resulting geopolymer type, which can be type 1, 2 or 3. If z=1, the network will be of the poly(sialate) type; if z = 2, the net shall be poly (sialate-siloxo) and, if z = 3, the net shall be poly(sialate-disiloxo)). The last parameter, “w”, refers the number of associated water molecules. The mechanism of geopolymerization reaction is explained in chapter 3.2 and it includes several steps.

## 3.2 Geopolymerization mechanism

As can be seen in Figure 2, the geopolymerization process starts when the solid aluminosilicate source is mixed with a highly alkaline solution. This mechanism is explained according to [11]. As a result of the presence of hydroxyl ions in the reacting medium, dissolution of the amorphous part of the solid aluminosilicate source material takes place, releasing to the reacting medium silicates, aluminates and aluminosilicates in oligomeric form.

At the beginning of this step, the amount of aluminate ions in the reacting medium is higher than that of silicates. This is because of the bond strength between aluminium and oxide ions is weaker than between silicon and oxide, therefore, the first ones are more susceptible to be dissolved by hydroxyl ions.

The dissolution of the amorphous part of the solid aluminosilicate source material is superficial, and non-reacted solid particles, as well as partially reacted or fully reacted particles, may remain in the solution. In this step of the geopolymerization mechanism, water is consumed, as it is shown in Figure 2.

The oligomers that are released in the reacting medium are regarded as the monomers of the reaction, thus they can react to each other and generate dimers, trimers, tetramers and so on. As a result, a saturated solution mainly composed of aluminosilicates is obained. The fact that the dissolution is saturated results in the condensation of oligomeric species, releasing the water consumed in the previous step (dissolution) to the reacting medium and generating a biphasic element composed of water and aluminosilicate oligomers (Gel 1 in Figure 2). This gel will occupy the empty space between the solid raw material particles that remain to react.

The formation of Gel 1 takes place due to the high content of $Al^{3+}$ ions that are in the reaction medium in the early stages of the process. As the reaction progresses, more Si-O groups of the initial solid aluminosilicate source are dissolved, increasing the concentration of silicon in the reacting medium and therefore, in the composition of the Gel 2.

Gel 2 is formed after being reorganized the elements that are in the reacting medium when Gel 1 is generated. The formation of the Gel 2 releases the consumed water in the medium, as shown in the Figure 2. Once the gel is formed, the system continues reorganizing and restructuring, increasing the bonds between the chains that compose it, generating a three-dimensional structure. This is an important process because it determines the distribution of pores in the structure of the material and therefore, its microstructure and properties.

The needed time for the gel formation depends on the raw materials used in geopolymerization process, as well as the concentration of the alkaline activating materials and the synthesis conditions. The geopolymerization mechanism ends with the polymerization and subsequent hardening step, where a final product with amorphous structure and good mechanical properties is obtained, the geopolymer. This can be seen schematically in Figure 2.

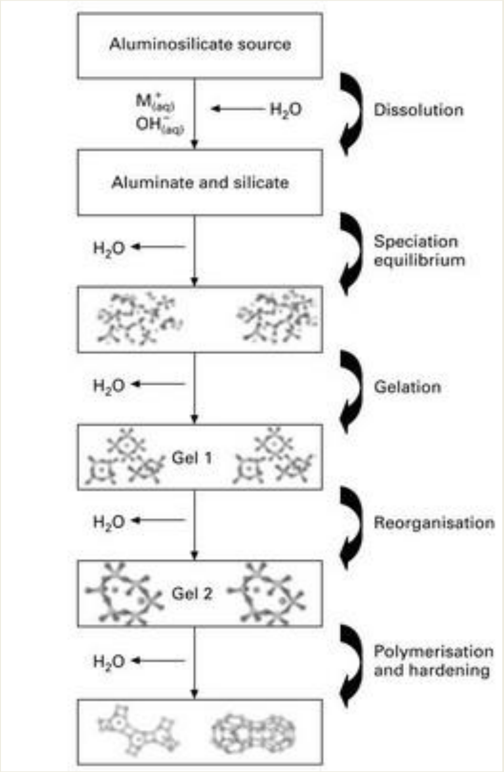

*Figure 2. Geopolymerization mechanism diagram [11].*

## 3.3 Variables in geopolymer synthesis

Microstructure and applications of the geopolymers are directly connected with the operating conditions in which geopolymers are synthesized. Among the main parameters that can affect the final geopolymer structure, includes the amount of water that is in the reacting medium; the alkaline activator type used in the geopolymer synthesis and its concentration in the solution.

Other parameter is the possibility of adding some reagent as a silicate source for preparing the alkaline activating solution. I addition, the relative quantities of silicon, aluminium and sodium also affects the microstructure and applications of the synthesized geopolymers. Other determining factors are temperature, curing time, the presence of other elements in the reacting medium and the type of raw material source of aluminosilicates used in the synthesis of geopolymers. All of this will be studied in chapters 3.3.1-3.3.5.

### 3.3.1 Raw material source of aluminosilicates

In order to synthesize geopolymers, a solid raw material which contain in its structure high amount of aluminium and silicon in the form of $Al_2O_3$ and $SiO_2$, is needed. As explained above, the source of aluminosilicate can be provided by natural or residual materials. The latter are usually by-products from industry, which are generated in processes subjected to temperature.

There is also the possibility of subjecting natural sources to heat treatment, i.e. a calcination process to convert the crystalline structure of the material into amorphous, in order to increase the reactivity of these materials in contact with the alkaline activating solution, thus obtaining geopolymers with better mechanical properties.

Therefore, one of the main parameters in geopolymer synthesis is the type of aluminosilicate source raw material used. Although it can come from different materials and, thus, can have different reactivity, the optimum is that the material has in its structure, high amount of aluminium and silicon in amorphous form. Raw materials source of aluminosilicates used in this project to synthesize geopolymers are explained in Section 3.4.

### 3.3.2 Water content

The water amount in the geopolymer synthesis, determines the solid/liquid starting materials portion that are used to generate the final geopolymer matrixes; being the solid content, the solid aluminosilicate source material. As it is previously mentioned, in chapter 3.2 referring to Geopolymerization mechanism, in the first step of the geopolymerization process, a certain amount of water is consumed.

This consumption decreases the amount of water that there is in the solution, increasing the content of hydroxide solution MOH, where M means alkaline or alkaline earth metal. Having high amounts of MOH in the solution makes faster the dissolution of the amorphous part of the aluminosilicate source solid material, promoting the early stages of the geopolymerization mechanism. As a result, more ions of aluminium and silicate are released into the reacting medium, improving the possibilities for the oligomers formation in a shorter time.

Moreover, that parameter also helps the final geopolymerization steps, making faster the oligomer's polycondensation and further hardness to the geopolymer system. According to this, all the geopolymerization steps are positively affected by the decrease of water content. However, if the water decrease is progressive in all the geopolymerization steps, it could decrease the solid particles moisture, hampering the workability and moulding of them in the solution, affecting, at the same time, the final geopolymer microstructure and thus, properties and applications.

To sum up, the water amount in the geopolymer synthesis is an important parameter that has to be regarded in this process because it would affect in the final geopolymer microstructure, properties and applications. Therefore, the worthy amount of water in the geopolymer synthesis should be such that the particles are enough wet, giving them the facility for working with them. According to several studies, the amount ratio between water and solid aluminosilicate source in the geopolymer synthesis should be among 0,3 and 0,5.

### 3.3.3 Alkaline activating solution

As discussed in chapter 3.2, the dissolution of the amorphous structure of the solid raw material source of aluminosilicate takes place in the first step of the geopolymerization mechanism [11].

This step is controlled by the ability of the alkaline activator to dissolve that structure and form reactive silicates and aluminates species.

The alkaline activating solution may consist of only one alkaline solution, but it is also possible to add an external source of alkaline activator to this solution.

The latter's role is to increase the dissolution of the amorphous structure in the solid aluminosilicate source material, favouring the geopolymerization process and the final obtaining of the product with the appropriate properties.

The alkaline activator can be either alkaline or alkaline earth.

The alkaline solution is usually composed of a concentrated dissolution of potassium hydroxide (KOH) or sodium hydroxide (NaOH). The last one is the most used in the synthesis of geopolymers [11].

The alkaline solution has to be highly concentrated because otherwise, the generated mass in the geopolymer synthesis is viscous rather than liquid, making the workability of the solution more difficult.

In addition, a high alkalinity of the solution is required because hydroxyl ions play an important role in dissolving the amorphous structure containing aluminium and silicon. Thus, the increase of hydroxyl ions in the solution increases the solubility of the aluminosilicate elements.

On the other hand, alkaline activators regulate the reaction kinetics and determine the final structure of the geopolymer network. These elements enter the cavities of the polysialate network and interact with the aluminium to compensate the loads.

As mentioned above, the alkaline activators typically used are potassium and sodium, although each interacts differently in the dissolution step of solid aluminosilicate as a result of the metallic cation effect.

The dissolution step of aluminosilicate is favoured by the presence of sodium as an alkaline activator in the hydroxide solution. The atomic radius of sodium is smaller than that of potassium, thus favouring the reaction of formation of smaller oligomers of silicates.

By contrast, the alkaline potassium activator favours the formation of larger silicate oligomers.

### 3.3.4 Curing temperature

Temperature is a another parameter that has to be regarded in the synthesis of geopolymer matrices, as it will determine the microstructure, properties and applications of the final product. Rising the curing temperature in the geopolymer synthesis, increases the dissolution of the active species that are in the solid raw material source of aluminosilicates.

The fact that in the solution there are high amount of active species achieving the final product with high mechanical properties. But it does not happen at all range of temperatures. In most part of research geopolymer projects, geopolymer synthesis has carried out at curing temperature below 100ºC.

There are studies where it is said that at curing temperatures among [30-90]ºC, it is possible to obtain geopolymers with better mechanical properties, particularly with better compression resistance. At curing temperature above 100ºC, water that is in the geopolymer structure, starts evaporating. This affects the material microstructure because it generates pores and microcracks, which could start to grow up inside the material structure, damaging the mechanical properties. Therefore, material can break up easier if a force is applied. However, curing temperature is a parameter that is also conditioned by the time curing; thus are dependent variables.

### 3.3.5 Curing time

Curing time determines available water amount that are in the geopolymer structure during the solid aluminosilicate source activating phase in the geopolymerization mechanism. The time that the geopolymers should be curing, also depends on if the geopolymers are submitted into a thermic curing temperature or if contrarily, they are curing at room temperatures. In terms of curing time for geopolymers that are thermic subjected, the optimum would be between 24 and 48 hours. Nevertheless if the geopolymer is cured at room temperature, it is required more curing time for obtaining a geopolymer with the necessary mechanical properties.

## 3.4 Raw material in geopolymer synthesis

Geopolymers are obtained through a geopolymerization reaction, where a source of aluminosilicate is required for the geopolymer synthesis. The source of aluminosilicate can be provided from both natural and waste materials [5,8-10]. These materials can be subjected to a heat treatment where a calcination of the material takes place [9].

As a consequence of this pre-treatment, modifications in the composition of the solid source material of aluminosilicate are generated and, therefore, changes in the structure of the material. The crystalline structure of the material becomes amorphous and a high content of energy is retained between the cavities of the particles (pores). As a result, the reactivity of the material when is in contact with the alkaline solution increase, obtaining a geopolymer with better mechanical properties [5,11].

Materials that are submitted to a thermic treatment have better compressive resistance in the early stages of the curing process. On the other hand, materials that have not been thermally treated have higher compressive strength in the final stages of the geopolymerization process. Among the natural aluminosilicate source for the geopolymer synthesis kaolinite, sodalit and estibilie minerals can be used, meanwhile the most widely waste materials used in geopolymer synthesis are fly ash and blast furnace slag [8,11].

Kaolinite stands out for being a clayey material that is mostly found in the earth's crust [7,11]. It is not directly used in the synthesis of GP, but rather a conditioning treatment of the aluminosilicate source must first be carried out. This consists of submitting Kaolinite into a thermic process where the material is exposed to temperature for a certain period of time, obtaining as a result, metakaolin.

Depending on how long the material is exposed to a certain temperature, different types of metakaolin can be obtained. metakaolin obtained when kaolinite is thermally treated at 750ºC for 24 hours is typically used as a raw material in geopolymer synthesis.

In this project several geopolymers are synthesized using metakaolin, fly ash and blast furnace slag (granulated and fine) as raw material source of aluminosilicates. In addition, other study is carried out where Jarosite is used as a raw material in order to analyse how it works in geopolymerization process.

These materials are explained in Sections 3.4.1, 3.4.2, 3.4.3 and 3.4.4 as well as how to obtain them. The composition of the materials used to synthesize the geopolymers is shown in the section 4.1.

### 3.4.1 Metakaolin

Metakaolin is a material that can be directly used in geopolymer synthesis and comes from the calcination of Kaolinite at temperatures ranging from 500-800ºC (being metakaolin the dehydroxylated form of kaolinite) [7,11,13].

As a result of the thermic treatment, there is a decrease in the crystalline part of the material and therefore, an increase in the amorphous part. Moreover, the specific surface area of the material increases, making it more reactive in contact with the alkaline activating solution and thus, obtaining a final product with better mechanical properties [11]. This makes the use of metakaolin preferable instead of Kaolinite in geopolymer synthesis.

Metakaolin geopolymers have been studied as adsorbent materials in the removal of $Cd^{2+}$, $Pb^{2+}$, $Cs^{+}$, $Cr^{3+}$ and $NH_4^+$ cations from aqueous solutions [14], since the geopolymerization process improves the removal efficiency and adsorption capacity of the raw materials [12]. Thus, metakaolin raw material without being subjected to a geopolymerization process has a poor $NH_4^+$ removal efficiency, whereas the geopolymerization process of this aluminosilicate material increases the $NH_4^+$ removal capacity [12].

Moreover, many researches have used metakaolin in the synthesis of geopolymers due to its high reactivity and purity in comparison with other clays [15] and also, because it is easy to obtain and regenerate, as well as for its low temperature dependence as an ion exchanger [16].

However, in the calcination process carried out to obtain metakaolin, high temperature as well as long time is required. As a result, high amounts of carbon dioxide, the greenhouse gas, is released. Moreover, it needs high amount of water for being mixed with other materials [5].The reaction conditions of the calcination process make the use of metakaolin not an optimal option for large-scale production of some materials.

### 3.4.2 Fly ash

As it is mentioned before, fly ash is one of the main raw materials used for the synthesis of geopolymers.

The first European standard for building materials (EN450) defines fly ash as dust grains which are mainly composed of glass particles, produced during the combustion of coal. During combustion and gasification processes of coal, the non-combustible matter of coal is obtained as a by-product, which is known as fly Ash. [2,21]

This glass particles can be spherical or rounded, but fly ash can also contain irregular shaped particles which come from the coal mineral because of the combustion of coal does not have an 100% of performance, so there could be non-burned particles in the fly ash composition. In case fly ash particles are submitted to a thermic treatment, the reactivity of the amorphous material structure in the geopolymerization process would increase [5].

Besides, the glass particles granulometry is tiny and the composition of them is quite similar to the coal's mineral composition before the combustion. So, the main components in their chemical composition are $SiO_2$, $Al_2O_3$, CaO and $Fe_2O_3$, which therefore contain the essential elements required for the geopolymer synthesis [7,24,26].

According to the coal combustion process, the produced dust grains could be different, with different chemical composition and therefore, different properties [24]. Thus, fly ash could be classified into two groups: Class C fly ash and Class F fly ash [25]. Class C fly ash is characterized due to their cementitious and pozzolanic properties and for having a high content of silica and alumina in its composition, but less amount as the Class F fly ash, which also contains these elements in its composition, but higher percentage. This type of fly ash is obtained through the combustion of lignites and subbituminous coal [24].

On the other hand, Class F fly ash comes from the combustion of anthracites and bituminous coal, providing pozzolanic properties to these particles [24]. Figure 3 shows the amount of each element that fly ash has to contain for being classified as a Class C or Class F fly ash.

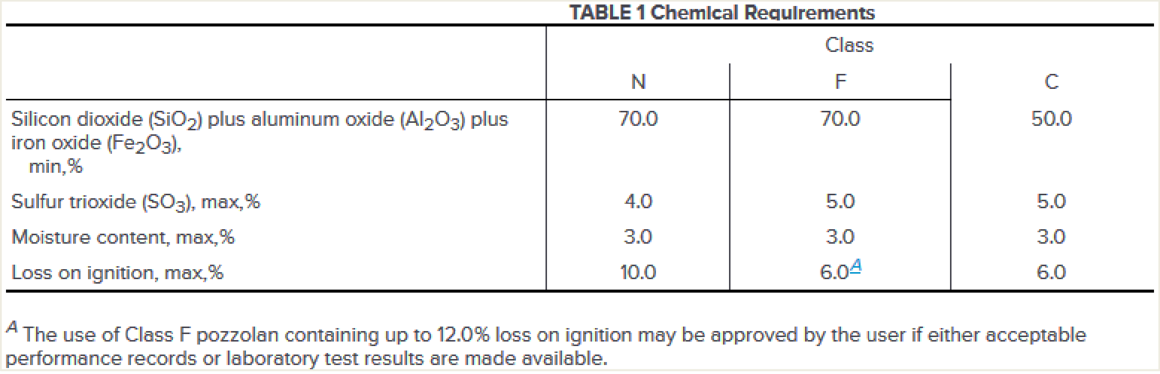

**TABLE 1 Chemical Requirements**

| | Class | | |
|---|---|---|---|
| | N | F | C |
| Silicon dioxide ($SiO_2$) plus aluminum oxide ($Al_2O_3$) plus iron oxide ($Fe_2O_3$), min,% | 70.0 | 70.0 | 50.0 |
| Sulfur trioxide ($SO_3$), max,% | 4.0 | 5.0 | 5.0 |
| Moisture content, max,% | 3.0 | 3.0 | 3.0 |
| Loss on ignition, max,% | 10.0 | 6.0[A] | 6.0 |

[A] The use of Class F pozzolan containing up to 12.0% loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.

*Figure 3. Amount of components for the Class C and Class F fly ash [25].*

In Finland, between 600 and $700 \cdot 10^3$ tons of fly ash are produced annually by power industries [21] and are usually disposed in landfills [26]; only a small percentage of them are reused (20-30%) [22]. In order to find a solution to the environmental problem that fly ash concerns, these materials have been applied as an additive to generate new, less polluting cements [19,22,26]. On the other hand, they have been used to remove and immobilize toxic and heavy metals and organic compounds from aqueous solutions such as copper ions [5,18,26], as well as a cheap resource for synthesizing zeolite [26].

This material has high reactivity [5] and it is available worldwide. However, its use is limited; thus, geopolymerization can be an effective method for the use of this material, in order to decrease the pollution and provide an alternative solution to this environmental problem, since this material has a high content of aluminosilicate [7].

### 3.4.3 Blast furnace slag

Blast furnace slag is one of the main raw materials used for the synthesis of geopolymers. This is a non-metallic co-product of iron production, which is mainly applied in civil engineering applications and is primarily composed of silicates, aluminosilicates and calcium-alumina-silicates [27].

This material is produced as a residue of smelting iron in a blast furnace and its composition and its particle size depend on the cooling system used, as well as the type of furnace and ores used to obtain iron [7,13,27].

If water is used to cool the material quickly and then, a grinding process is applied, a highly reactive, glassy granular material is produced. This material is called granulated blast furnace slag (GBFS) and consists of $SiO_2$, CaO, $Al_2O_3$ and MgO [7].

The production of slag has increased from the 20th century with the development of industry and, through the centuries, has been used mainly in construction purposes, as an alternative material for cement production, both for its good properties and for its abundance and easy availability [7,13,27].

On the other hand, GBFS has been used as an additive in the geopolymerization process to obtain fly ash geopolymers, in order to improve the reactivity of fly ash and therefore, the performance of geopolymers [7,24].

In addition, blast furnace slag geopolymer could serve as a feasible metal and metalloid sorbent with a specific utilization prospect in the mining industry [14]. All these characteristics make them a suitable material for the production of geopolymers.

### 3.4.4 Jarosite

Jarosite is a hazardous industrial by-product from zinc manufacturing industry obtained during the extraction of zinc from its sulphide ore through a hydrometallurgical process [30,31]. Zinc is a metallic material wildly used in the prevention of corrosion applications which is not found in abundance in the earth's crust; thus it is obtained mainly through the Roast-Leach-Electrowin (RLE) process [28]. In fact, this process represents 85% of the world's zinc production [28,32].

This technique consists of three main stages: roasting, leaching and purification, and electrolysis process [30], where Jarosite is obtained in the second stage as a suitable way to eliminate iron oxide, copper, lead, sulphur, cadmium and chromium from the hydrometallurgical processes [30,31].

Jarosite can be expressed by $MFe_3(SO_4)_2(OH)_6$ formula, where M means a metal cation such Na, K, Pb or ammonium among others, is an [29,32].

Hydrometallurgical by-products are dangerous for the environment and for the health of humans and animals due to the elements in their composition, being an issue of concern. Hydrometallurgical processes leads large amount of hazardous waste, including Jarosite, since for each tonne of zinc metal produces by RLE technique, 0,5 tonne of this hazardous waste, with high content of iron oxide, Cd, As and Pb is generated [28].

This material has been disposed to hazardous landfills or trailing dams [28]. However, a sustainable alternative is needed to use them safely and effectively.

# 4.- Materials and Methods

As it is previously mentioned, the research main goal is to synthesize stable geopolymers, using by-products from industry, in order to check whether geopolymers can be used as adsorbents in ammonium removal, and also prove whether they can be still stable after introducing Jarosite (a by-product from hydrometallurgical processes) in their structure.

In this section, the industry by-products used to synthetize the geopolymers will be studied, as well as the steps carried out in the laboratory for synthesizing geopolymers, for doing the stability test of them and also, for the geopolymer adsorption experiments. Moreover, several experiments will be carried out in order to study the behaviour of Jarosite in geopolymer matrices. All of that will be explained thereupon.

## 4.1 Materials

In this project, metakaolin (MK), fly ash (FA) and blast furnace slag (BFS) and jarosite were used as raw materials for the geopolymer synthesis. The chemical composition of each by-product and the origin of them are shown in the following sections:

### 4.1.1 Metakaolin

Table 1 shows the chemical composition of metakaolin raw material used in this study, which was provided by a Finnish company. Composition was determined via X-Ray Fluorescence (XRF).

*Table 1. Chemical composition of the metakaolin raw material, expressed in (%).*

| CaO | $SiO_2$ | MgO | $Al_2O_3$ | $SO_3$ | $Na_2O$ | $K_2O$ | $Fe_2O_3$ | Mn | $TiO_2$ | L.O.I. |
|---|---|---|---|---|---|---|---|---|---|---|
| 0,06 | 53,10 | - | 40,30 | - | - | 2,72 | 1,89 | - | 0,12 | 3,60 |

### 4.1.2 Fly ash

Fly ash raw material used in this project was provided by a Finnish supplier. Its composition, determined by X-Ray Fluorescence (XRF), is shown in the following table:

*Table 2. Chemical composition of the fly ash raw material expressed in (%).*

| $Al_2O_3$ | $SiO_2$ | $K_2O$ | $Fe_2O_3$ | $Na_2O$ | MgO | CaO | Others |
|---|---|---|---|---|---|---|---|
| 21,71 | 48,59 | 2,11 | 8,03 | 1,06 | 2,40 | 7,32 | 8,78 |

### 4.1.3 Blast furnace slag

As the other raw materials, blast furnace slag's composition was determined by X-Ray Fluorescence (XRF) and it is shown in the Table 3. This material was provided by a Finnish company.

*Table 3. Chemical composition of the blast furnace slag raw material expressed in (%).*

| CaO | $SiO_2$ | MgO | $Al_2O_3$ | $SO_3$ | $Na_2O$ | Ba | Others | L.O.I | Sum |
|---|---|---|---|---|---|---|---|---|---|
| 38,5 | 27,2 | 9,4 | 8,4 | 3,8 | 0,3 | 0,0 | 2,9 | 0,5 | 91,0 |

As it can be seen from Tables 1, 2 and 3, the main components of the raw materials used in this project, are aluminum oxide ($Al_2O_3$) and silica ($SiO_2$). Therefore, these materials could be regarded as aluminosilicates source materials, satisfying one of the requirements for the geopolymer synthesis.

### 4.1.4 Jarosite

The chemical composition of Jarosite was provided by a Finnish supplier, a company that produce this material as a byproduct of the hydrometallurgical processes for obtaining Zinc (Zn).

*Table 4. Chemical composition of Jarosite.*

| | |
|---|---|
| **Al** | 0,020078 |
| **As** | 0,200683 |
| **Ca** | 0,002391 |
| **Cd** | 0,001736 |
| **Co** | 0,014233 |
| **Cr** | 0,003565 |
| **Cu** | 0,345542 |
| **Fe** | 31,5642 |
| **$H_2O$** | 13,9544 |
| **K** | 0,039505 |
| **Mg** | 0,000353 |
| **Mn** | 0 |
| **Na** | 2,51465 |
| **Ni** | 0,657129 |
| **P** | 0 |
| **Pb** | 0,023847 |
| **S** | 16,2729 |
| **Se** | 0,003853 |
| **Si** | 0,016015 |
| **Zn** | 0,001881 |
| **Mo** | 0 |
| **Ti** | 0,001016 |
| **U** | 0 |

## 4.2 Methods

In this section the steps that were followed in the laboratory for the geopolymer synthesis, the geopolymer stability test, the adsorption experiments and the Jarosite study will be explained.

### 4.2.1 Synthesis of geopolymers

For the geopolymer synthesis, is necessary an aluminosilicate source and an alkaline activating solution. In this case, the aluminosilicate source is provided by the raw materials used in the geopolymerization, which are: metakaolin, fly ash and blast furnace slag.

On the other hand, the alkaline activating solution will be composed by a solution of 10M NaOH and $Na_2SiO_3$ solution in a weight ratio of 1 (w/w=1). The sodium silicate solution used was an extra pure solution, which was available in the laboratory. Thus, for obtaining the alkaline activating solution, first of all, the 10M NaOH solution has to be prepared.

#### 4.*2.1.1 Preparation of NaOH 10 M solution*

In order to prepare one liter of 10M NaOH solution, first of all, 400 g of solid sodium hydroxide has to be weight and introduce into a 1 liter volumetric flask. The sodium hydroxide used in this step was provided by Merck KGaA Company and supplied in the form of pellets with a molecular weight of 40 g/mol.

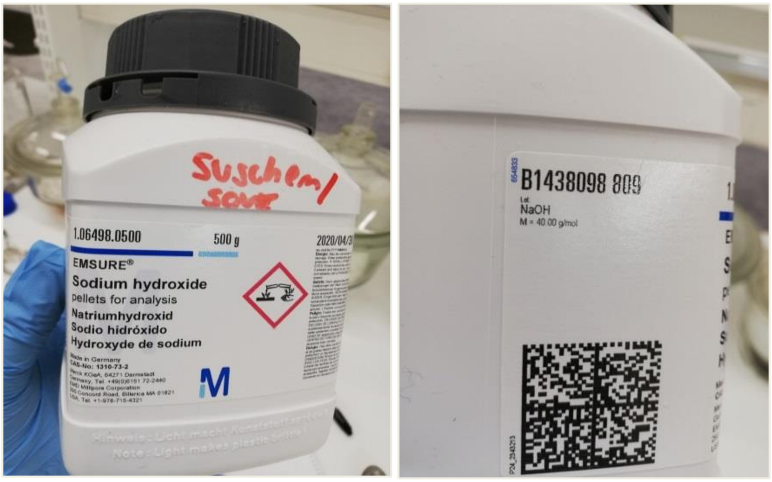

*Figure 4. Sodium Hydroxide used for preparing 10 M NaOH solution.*

Once the pellets are in the volumetric flask, deionized water is added until achieve the mark of 1 L. In that moment, a decrease of the volume of the dissolution is produced as a consequence of an exothermic reaction. This can be seen in Figure 5:

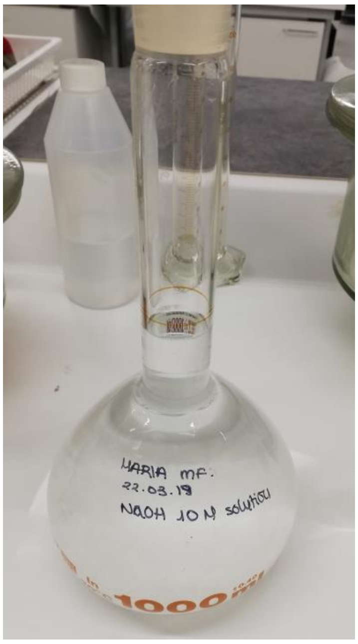

*Figure 5. Volume decrease of the solution because of an exothermic reaction.*

Finally, when the solution achieves room temperature, deionized water is added up to the 1L mark. That solution is characterized for being highly corrosive. Therefore, the room temperature 10 M NaOH solution should be introduced into a plastic recipient for avoiding the precipitation of silicate and the decrease of hydroxyl ions in the solution, which would cause a decrease in the molarity of the dissolution.

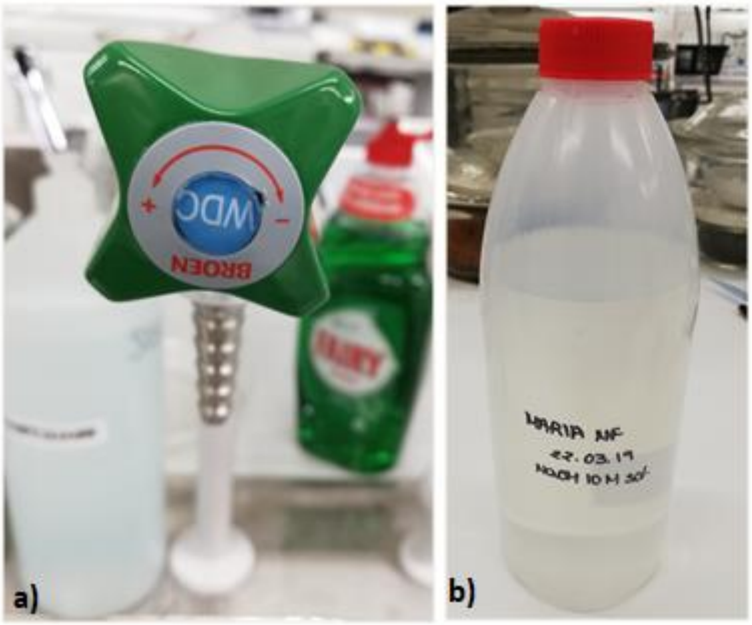

*Figure 6. a) Deionized water used in the laboratory. b) 10 M NaOH  solution in a plastic bottle.*

### 4.2.1.2 Preparation of Alkaline Activating Solution

For preparing the alkaline activating solution that is going to be used in the geopolymer synthesis, 10M NaOH solution and technical grade of sodium silicate solution are mixed in a weight ratio of 1. In this case, 60,01 g of the solution was prepared using 30,06 g of 10M NaOH solution and 29,95 g of technical grade of sodium silicate solution. The technical grade sodium silicate solution was also supplied by Merck KGaA Company and the alkaline activating solution was allowed to stand during 24 h before use.

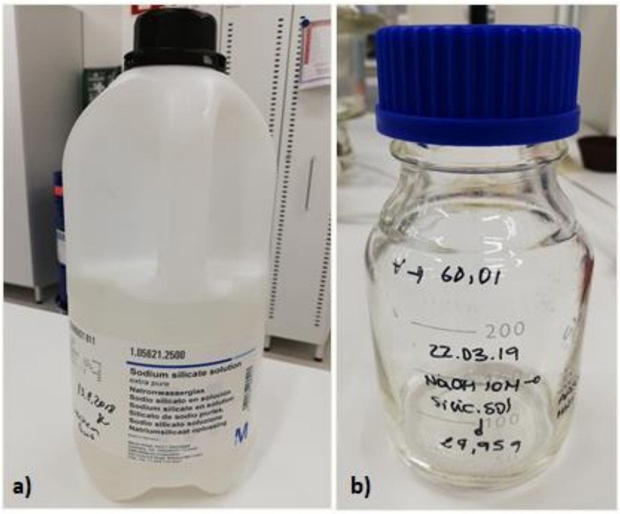

*Figure 7. a) Technical grade sodium silicate solution used in the preparation of the AAS. b) Alkaline Activating Solution.*

### 4.2.1.3 Mixture

After waiting 24 h allowing the alkaline activating solution to stand, geopolymers are prepared using metakaolin, fly ash and blast furnace slag as raw materials. Those will be mixed with the alkaline activating solution which was previously prepared in a weight ratio of $w_{RM}/w_{AAS}$=1,3:1.

According to this weight ratio and regarding that it is wanted to be prepared geopolymers composed only by each raw material, and also, geopolymers as a result of the combination of two of the mentioned raw materials, the amount of each raw material that has to be used for prepare 20 g of geopolymer is 11,70 g and 9 g of AAS – alkaline activating solution.

In case the geopolymers are composed by two of the raw materials, the total amount of each one should be 5,85 g, keeping constant the amount of AAS. The mixing procedure was carried out in a beaker, introducing the reagents in the appropriate quantity and mixing them during 15 minutes with a mixer (BOSH ErgoMixx 450W; third speed position).

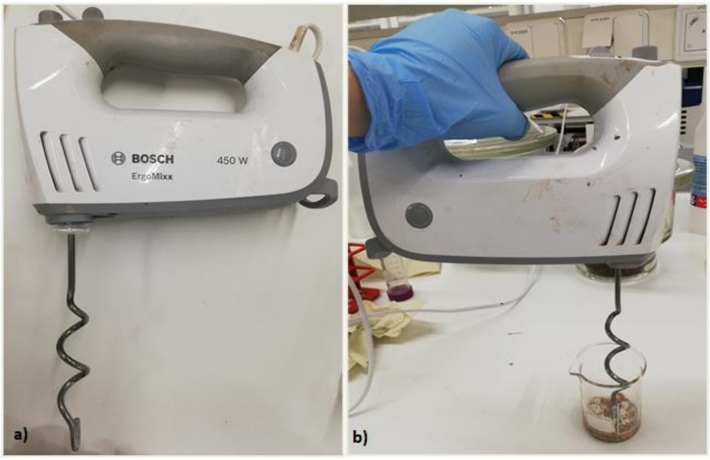

*Figure 8. a) Mixer (BOSH ErgoMixx 450W). b) Mixing process in geopolymer synthesis.*

Table 5 demonstrates the theoretical amount of each reagent for the geopolymer synthesis.

*Table 5. Theoretical amount of each reagent in geopolymer synthesis.*

| | | $w_{RM}$ (g) | | $w_{AAS}$ (g) |
|---|---|---|---|---|
| **GP1** | **MK** | 11,7 | | 9 |
| **GP2** | **FA** | 11,7 | | 9 |
| **GP3** | **BFS** | 11,7 | | 9 |
| **GP4** | **MK + FA** | **MK** | **FA** | 9 |
| | | 5,85 | 5,85 | |
| **GP5** | **MK + BFS** | **MK** | **BFS** | 9 |
| | | 5,85 | 5,85 | |
| **GP6** | **BFS + FA** | **BFS** | **FA** | 9 |
| | | 5,85 | 5,85 | |

#### *4.2.1.4 Casting and curing*

The mass that is generated in the previous step is introduced into a mould and it is manually shocked for 10 seconds for release the possible air bubbles that could be inside the mass. After that, the moulds are allow to stand for consolidate inside a laboratory fume cupboard during 7 days.

#### *4.2.1.5 Crushing, sieving, washing and drying*

After one week, the formed geopolymers has to be removed from the moulds, crushed, sieved (to separate the geopolymer particles according to a specific particle size), washed and dried. After that, the geopolymers will be ready for testing its chemical stability and its ammonium removal adsorption capacity.

- Crushing:

In the crushing step, first, the mechanical stability of the synthesized geopolymers is tested in order to check if they can be broken using hand strength. Those geopolymers that can be broken in this way would not be mechanically stable and, therefore, would not have the properties that characterize geopolymers. Then, the synthesized geopolymers are broken into smaller parts with a laboratory hammer and these parts are introduced one by one into a laboratory crusher to obtain smaller geopolymer particles.

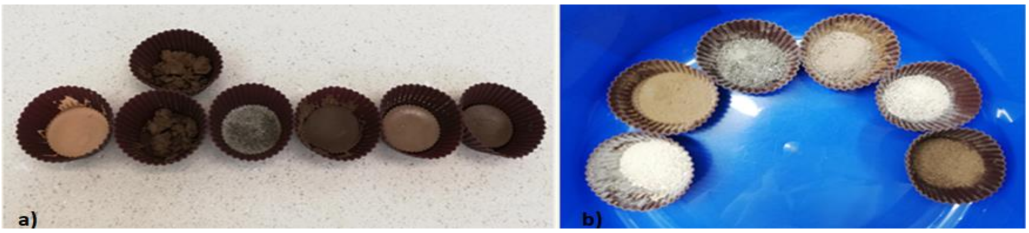

*Figure 9. From left to right, from GP1 to GP6 a) Before and b) After crushing.*

- Sieving:

Once the geopolymers are crushed, geopolymer is put into a mesh sieve which ranges from 1 mm to 250 micrometers and is sieved manually. This procedure is performed for each synthesized geopolymer and between each sieving process the sieves are washed with deionized water during 10 minutes in an ultrasonic machine (without heating) and are dried at room temperature.

*Figure 10. Mesh sieves from 1mm to 250 µm.*

Once the geopolymer samples and the raw materials are sieved, particles which particle sizes are between 1 mm and 250 µm, are introduced in a falcon tube previously weighted. Afterwards, the falcon tube with the sample content is also weighted. These are the samples used in this project to perform all the experiments. The same procedure is carried out for particles with a particle size lower than 250 µm, as well as for those with a particle size upper than 1 mm.

- Washing:

The total amount of geopolymer obtained with a particle size between 1 mm and 250 micrometres is placed in a falcon tub and mQ-water is added up to the mark of 45 mm. Then, the falcon tubes are introduced into the laboratory shaker and are shacked at 300 rpm for 10 minutes. Afterwards, the samples are submitted to a centrifuge process at 3000rpm during 3 minutes. After that, pH of mQ-water is measured with a pH-meter and the mQ-water that is in the falcon tube is changed for new one using a laboratory pipette.

This procedure was repeated 19 times to decrease the pH of the solution. For the pH test, the pH-meter has to be calibrated and for that, are used three prepared solutions, one at pH 4, another one at pH 7 and the last one at pH 10.

- Drying:

After the washing step, the maximum possible of mQ-water is removed from the falcon tubes using a laboratory pipette. The remaining mQ-water with the solid geopolymer particles are putted into a ceramic mortar, which eventually is introduced into a laboratory oven for being dried at 105ºC for 24h.

*Figure 11. From left to right, from GP1 to GP6 in a ceramic mortars before being dried.*

*Figure 12. Drying laboratory oven at 105ºC.*

The sieving, washing and drying process is also carried out for the raw material used in the synthesis of the geopolymers, in order to compare and analyse the results obtained for geopolymers and raw materials after the stability test and also in the adsorption experiments.

### 4.2.2 Stability test

Once the geopolymer has been synthesized, it must be verified that the synthesized geopolymers are chemically stable. To this end, a stability test will be carried out to determine the electrical conductivity of the geopolymer in solution with mQ-water after 2, 6 and 24 hours.

The conductivity test determines the ability of a solution to conduct electric current. In this analysis, a conductivity result is obtained and its value depends on the total amount of dissolved ions that are in the solution. Therefore, if the obtained value has changed considerably between two consecutive measurements, it means that the geopolymer is not chemically stable, neither its structure, thus chemical reactions are happening in the solution which makes increasing the total amount of dissolved ions in the solution and also the conductivity value result.

For the stability test, first, one gram of the geopolymer sample has to be introduced into a falcon tube. This step was carefully carried out because the geopolymer suffers electrostatic effect when it is going to be introduced into the falcon tube. To avoid losing GP, a paper filter was used during the weighting step of GP.

Afterwards, 25 mL of mQ-water are introduced into the falcon tube. The mQ-water used for that was 10/05/19 mQ-water. Then, the falcon tubes which contain the geopolymer and mQ-water are put into a shaker at 300 rpm during 24h. After 2, 6 and 24 hours, the falcon tubes has to be removed from the shaker, submitted to a centrifuge process (3 min; 3000rpm) and a measurement of the conductivity of the solution.

The centrifuge process is done to separate the solid particles of the geopolymer from the mQ-water and having a clear measure of the solution conductivity. In this step, the falcon tube has to be introduced into the centrifuge machine symmetrically, using a balance falcon tube in case that the number of samples to be inserted is not an even number. For the conductivity test, first, the conductivity meter has to be calibrated using a prepared solution of KCl 0,1 M.

Figure 13. Shaking Machine.

Figure 14. Centrifuge.

### 4.2.3 Adsorption experiments

In this case, the geopolymers synthesized in section 4.2.1 are submitted to adsorption experiments in order to check whether they are able to remove ammonium ions from a 500 ppm solution of $NH_4^+$ and therefore whether they can be used as adsorbents in ammonium removal applications.

In order to carry out these experiments, first of all, the ammonium solution has to be prepared and then, the sorption experiments will be performed at different pH conditions with the aim of analyze how does the pH affects in the ammonium adsorption capacity of the synthesized geopolymers. The steps for the preparation of the ammonium solution, the experimental adsorption conditions, as well as the procedure for adsorption experiments are explained below.

#### *4.2.3.1 Preparation of the $NH4^+$ 500 ppm solution*

In order to prepare two litters of $NH_4^+$ 500 ppm solution, first of all, 2,965 g of solid ammonium chloride has to be weight and introduce into a 2 liter volumetric flask. Once the solid particles are in the volumetric flask, deionized water is added until the mark of 2 L was achieved. The ammonium chloride used in this step was provided by Merck KGaA company and its molecular weight was 53,49 g/mole.

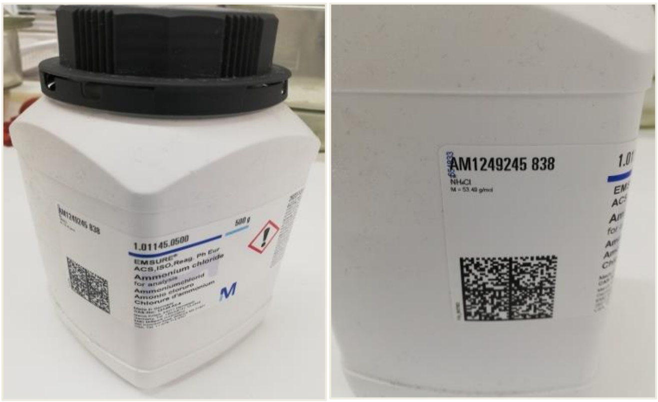

*Figure 15. Ammonium Chloride used for preparing NH4+ 500ppm solution.*

#### *4.2.3.2 Preparation of the LiCl 3M solution*

In order to measure the amount of ammonium ions with ion-selective electrode which are in the solution after sorption experiments, 500 µL of LiCl 3M solution are used to adjust the amount of ions in the solution. Section 4.2.3.4 explains when this solution has to be used.

For preparing 100 mL of LiCl 3M solution, first of all, 12,717 g of solid lithium chloride has to be weight and introduce into a 100 mL volumetric flask. Once the solid particles are in the volumetric flask, deionized water is added until achieve the 100 mL mark. In that moment, a decrease of the volume of the dissolution is produced as a consequence of an exothermic reaction. When the solution achieves room temperature, deionized water is added up to the 100 mL mark.

The lithium chloride used in this step was provided by VWR Chemicals company and its molecular weight was 42,39 g/mol.

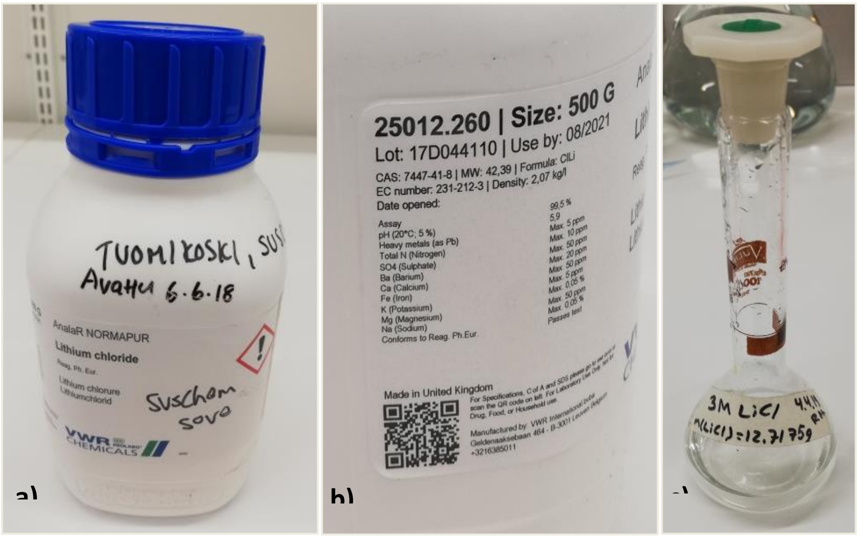

*Figure 16. a), b) Lithium Chloride used for preparing LiCl 3M solution. c) 100 mL of the LiCl 3M solution.*

### *4.2.3.3 Conditions of adsorption experiments*

Batch adsorption experiments are carried out at different pH conditions, for each synthesized geopolymer, in order to analyze its ability to adsorb ammonium ions from the 500 ppm $NH_4^+$ solution. The same procedure is also carried out for the solid raw materials used in the synthesis of the geopolymers but, these materials, without being subjected to a geopolymerization process, in order to check how the geopolymerization process can affect in the ammonium removal performance of these materials. That is, these batch adsorption experiments are carried out for metakaolin, fly ash and blast furnace slag raw materials.

On the other hand, the adsorption experiments are also performed without adsorbent dose as a zero sample, thus a total of 40 experiments are carried out according to the experimental sorption conditions that are shown in the Table 6:

*Table 6. Conditions of adsorption experiments.*

| Initial Solution pH$^a$ | Initial $NH_4^+$ (mg/L) | Adsorbent Dose (g/L) | Temp. (ºC) | Contact Time (h) |
|---|---|---|---|---|
| 2, 4, 6, 8 | 500 | 5 | 25 | 4 |

$^a$ Adjusted with 0,1 M NaOH or 0,1 M HCl.

### *4.2.3.4 Procedure for Adsorption experiments*

For adsorption experiments, the pH-meter must first be calibrated using the standard solutions at pH 4, 7 and 10.

After that, an aliquot of 400 mL from the 500 ppm $NH_4^+$ solution is taken and introduced into a beaker. The pH of the solution is checked and adjusted to the required pH by adding drops of 0,1M NaOH or 0,1M HCl. On the other hand, 0,2 g of each geopolymer and raw material that is going to be tested is weighted and introduced into beakers. There are 9 different sorbents (6 GP and 3 RM) and therefore, 9 beakers are needed.

From the adjusted solution, an aliquot of 40 mL is taken and introduced into a beaker. This is performed 13 times. One for each synthesized geopolymer (6 in total), one for each raw material used in the geopolymer synthesis (3 in total), and one for each pH condition to be studied (4 in total). Nine of the thirteen beakers contain 0,2 g of the adsorbent previously weighted inside. The remaining ones only contain $NH_4^+$ solution adjusted to the pH of the study.

This is carried out in order to compare the results obtained in adsorption experiments with and without adsorbent, to analyze whether the synthesized geopolymers or the solid raw materials have adsorbed ammonium.

Once the sorbent material is in dissolution and in agitation with the $NH_4^+$ solution, the pH of the solution is adjusted by adding drops of 0,1M NaOH or 0,1M HCl for 4 hours. This is also performed for the $NH_4^+$ solution at four different pHs without being in contact with any adsorbent material. The experimental set-up for adsorption experiments is shown in the following image:

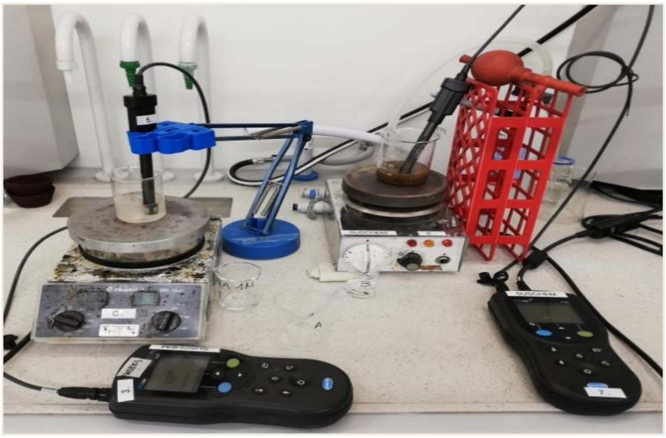

Figure 17. Experimental set-up for adsorption experiments.

After 4 hours, an aliquot of 25 mL is taken from the beaker that does not contain adsorbent and is introduced in another beaker, where 500µL of 3M LiCl solution were previously added. Afterwards, the ammonium concentration in the solution is measured with an ammonium electrode (which has to be previously calibrated).

The same procedure is carried out for each beaker containing geopolymer or raw material as an adsorbent (9 times), and also, for the solutions without sorbent dosage, at different pH conditions. After that, the tested solutions are trough into a big beaker with the aim to recover the lithium to the waste bottle.

### 4.2.4 Jarosite study

Jarosite is a waste material from the hydrometallurgical industry and is characterized as a carcinogenic material, which is toxic to the person in contact with the product, as well as to aquatic organisms, with long-lasting harmful effects. There is not much research on the behaviour of Jarosite in the synthesis of geopolymers. Therefore, in this research, new geopolymers are synthesized using Jarosite as a raw material.

The addition of Jarosite as a raw material for the synthesis of new geopolymers is performed for those geopolymers that have been shown to be both physically and chemically stable in the previous research of Synthesis of Geopolymers (Section 4.2.1). In this case, the Jarosite study is divided into three different studies, where new geopolymers are synthesized using different compositions of Jarosite, as well as different experimental reaction conditions. These modifications are done in order to analyse how the Jarosite does works in the geopolymerization process, and also to know if there is any possibility to contribute to the green technology, using industry by-products for generating other useful materials, thus decreasing the pollution.

The following sections explain the synthesis conditions of the Jarosite geopolymers in each study. Respiratory protection measures (mask) must to be taken in all of them, since Jarosite is a toxic material. The waste particles of this material, must to be placed in a laboratory plastic bag.

#### *4.2.4.1 Jarosite Study 1*

As it is not known how Jarosite affects the synthesis of geopolymers, in Jarosite Study 1, for each geopolymer that has been shown to be chemically and physically stable, three samples of the new geopolymer are carried out. In each sample, the weight ratio of the solid raw materials used in the synthesis is modified, keeping constant the weight ratio between the solid aluminosilicate source raw material and the alkaline activating solution. The latter, is the same as in the first study carried out, i.e. (1,3:1).

In this case, is not necessary to prepare the alkaline activating solution; it was prepared in the first study (Synthesis of Geopolymers; section 4.2.1). Thus, the theoretical amounts of solid raw materials in the synthesis of new geopolymers range from the same portion in weight for each, to 1/3 and 1/6 of Jarosite with respect to the raw material source of aluminosilicates. Procedure for synthesizing geopolymers is the same as the explained in the first study (Synthesis of geopolymers).

After allowing samples to consolidate, they are tested in order to check if they are physically and chemically stable. Chemical stability is only carried out for new geopolymer samples that have proven to be physically stable. Table 7 shows the recipe with the theoretical quantities of each reagent for the synthesis of the jarosite geopolymers (Jarosite Study 1).

*Table 7. Recipe for the Jarosite geopolymer synthesis (Jarosite Study 1).*

| JAROSITE GEOPOLYMER RECIPE – STUDY 1 | | | | | |
|---|---|---|---|---|---|
| | **ALKALINE ACTIVATED SOLUTION** | | **RM + ALKALINE ACTIVATED SOLUTION + JAROSITE** | | **w/w** |
| | **REAGENTS** | **w/w** | **REAGENTS** | **$w_{REAGENT}$ (g)** | |
| 1 | NaOH 10M ; $Na_2SiO_3$ | 1:1 | RAW MATERIAL | 7,80 | $w_{RM}/w_{Asol}$ = 1,3:1<br>$w_{RM}/w_{Jarosite}$ = 1:1 |
| | | | AA SOLUTION | 6,00 | |
| | | | JAROSITE | 7,80 | |
| 2 | NaOH 10M ; $Na_2SiO_3$ | 1:1 | RAW MATERIAL | 9,10 | $w_{RM}/w_{Asol}$ = 1,3:1<br>$w_{RM}/w_{Jarosite}$ = 3,033:1 |
| | | | AA SOLUTION | 7,00 | |
| | | | JAROSITE | 3,90 | |
| 3 | NaOH 10M ; $Na_2SiO_3$ | 1:1 | RAW MATERIAL | 10,40 | $w_{RM}/w_{Asol}$ = 1,3:1<br>$w_{RM}/w_{Jarosite}$ = 6,5:1 |
| | | | AA SOLUTION | 8,00 | |
| | | | JAROSITE | 1,60 | |

#### *4.2.4.2 Jarosite Study 2*

In the second study of the synthesis of geopolymers using Jarosite as raw material, some modifications in the synthesis conditions of Jarosite geopolymers are carried out with respect to the first study done (Jarosite study 1). Among them, the size of the Jarosite solid particles used in the synthesis, as well as the type of alkaline activating solution used.

In this case, solid particles of Jarosite are used whose particle size is less than 63 $\mu$m and the alkaline activating solution is a solution of NaOH 10 M (in the second study, there is no sodium silicate solution added as a component of AAS). As far as this dissolution is concerned, it is not necessary to prepare it, as it has already been prepared for the geopolymer synthesis procedure.

In order to obtain solid particles of Jarosite of this diameter, a sieving process is carried out with sieves of 63 micrometers mesh. On the other hand, the total quantity of each raw material to be added for the geopolymer synthesis in Study 2 is the same as in the previous case and thus the weight ratio among them.

Procedure for synthesizing geopolymers is the same as the explained in the first study (Geopolymer Synthesis; Section 4.2.1). After allowing samples to consolidate, they are tested in order to check if they are physically and chemically stable.

The following table shows the recipe with the theoretical quantities of each reagent for the synthesis of the Jarosite geopolymers (Jarosite Study 2). The recipe changes with respect to Jarosite Study 1 are highlighted in blue.

*Table 8. Recipe for the Jarosite geopolymer synthesis (Jarosite Study 2).*

| | **JAROSITE GEOPOLYMER RECIPE – STUDY 2** | | | |
|---|---|---|---|---|
| | **ALKALINE SOLUTION** | **RM + ALKALINE SOLUTION + JAROSITE** | | **w/w** |
| | **REAGENTS** | **REAGENTS** | **$w_{REAGENT}$ (g)** | |
| 1 | NaOH 10M | RAW MATERIAL | 7,80 | $w_{RM}/w_{Asol}$ = 1,3:1<br>$w_{RM}/w_{Jarosite}$ = 1:1 |
| | | ALKALINE SOLUTION | 6,00 | |
| | | JAROSITE | 7,80 | |
| 2 | NaOH 10M | RAW MATERIAL | 9,10 | $w_{RM}/w_{Asol}$ = 1,3:1<br>$w_{RM}/w_{Jarosite}$ = 3,033:1 |
| | | ALKALINE SOLUTION | 7,00 | |
| | | JAROSITE | 3,90 | |
| 3 | NaOH 10M | RAW MATERIAL | 10,40 | $w_{RM}/w_{Asol}$ = 1,3:1<br>$w_{RM}/w_{Jarosite}$ = 6,5:1 |
| | | ALKALINE SOLUTION | 8,00 | |
| | | JAROSITE | 1,60 | |

### *4.2.4.3 Jarosite Study 3*

In this study, geopolymers are synthesized using jarosite and alkaline activating solution as main reagents in the synthesis. In this case, no solid raw material source of aluminosilicate is added.

The aim of this study is to test whether it is possible to obtain a final product with the characteristics and properties of geopolymers, without using metakaolin, fly ash or blast furnace slag as raw material in the synthesis of geopolymers.

Jarosite Study 3 is divided into three different parts where, in each of them, the composition of the raw materials used in the synthesis is different. This is shown in the following sections.

- Study 3-1

After Study 1 and 2 of Jarosite Geopolymer synthesis, Study 3-1 is carried out, where the reagents used for synthesis are jarosite, NaOH and $Na_2SiO_3$ solution, in the chemical composition shown in the Table 9, where the last two reagents are in alkaline activating solution form, in a weight ratio of 1:1.

*Table 9. Composition of the raw materials in the Study 3-1 of Jarosite geopolymers synthesis.*

| Raw Materials | Chemical Composition (%) |
|---|---|
| Jarosite | 82 |
| NaOH 8M | 9 |
| $Na_2SiO_3$ solution | 9 |

The way to prepare one liter of NaOH 8 M solution is the same as that explained for the 10 M NaOH solution (section 1.1 of the Geopolymer Synthesis). However, in this case, the amount of NaOH (s) to be added is less due to the molarity of the solution. Specifically, 320,04 g of NaOH (s) were added to prepare one liter of NaOH 8 M solution. These were introduced into a volumetric flask and deionized water was added to reach the 1L mark.

As explained above, an exothermic reaction occurs, decreasing the volume of the sodium hydroxide solution; once the solution reaches room temperature, deionized water up to the 1L mark is added and the solution is moved from the volumetric flask to a plastic bottle due to its corrosive character. In this case, to prepare 100,22 g of alkaline activating solution, 50,11 g of NaOH 8 M and 50,11 g of $Na_2SiO_3$ solution (weight ratio of 1) were mixed and allowed to stand for 24 h before used in geopolymer synthesis.

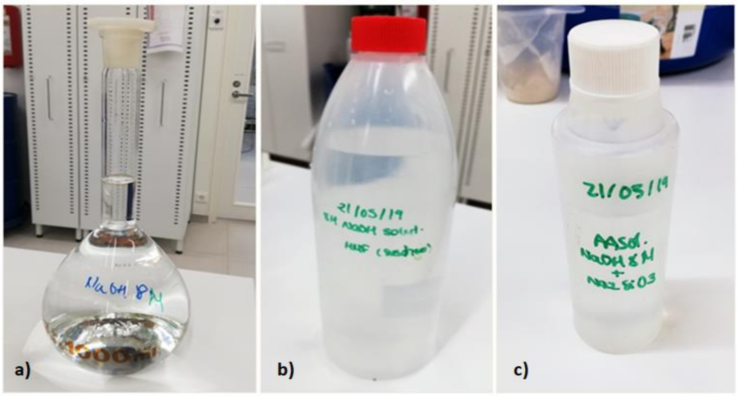

*Figure 18. a) 10 M NaOH solution in volumetric flask. b) NaOH 8 M solution in a plastic recipient. c) Study 3.1 AASolution.*

The synthesis procedure to be followed is the same as that explained in the Synthesis of geopolymers section. Specifically, points 1.3 and 1.4 refer to "Mixture" and "Casting and curing" respectively.

In order to analyze how the presence of sodium silicate solution as an alkaline activator affects the geopolymer synthesis, the explained study (Study 3-1) is carried out without $Na_2SiO_3$ as a component in the alkaline activating solution. Therefore, in this case, the AAS is composed only of NaOH 8 M. The composition of each reagent in the geopolymer synthesis is shown in the following table:

*Table 10. Composition of Study 3-1 without $Na_2SiO_3$.*

| Raw Materials | Chemical Composition (%) |
|---|---|
| Jarosite | 82 |
| NaOH 8M | 18 |

- Study 3-2

The chemical composition of the raw materials used in the synthesis of Jarosite geopolymer is shown in the following table:

*Table 11. Composition of the raw materials in the Study 3-2 of Jarosite geopolymers synthesis.*

| Raw Materials | Chemical Composition (%) |
|---|---|
| Jarosite | 61,95 |
| AAS | 24,78 |
| Distilled $H_2O$ | 13,27 |

In this case, the weight ratio of Jarosite raw material in the synthesis is decreased 20,05% meanwhile the one concerning to the AAS is increased 6,78%. Besides distilled water is added as a reagent in the geopolymer synthesis in a L/S weight ratio of 0,4, according to the specifications explained in the Water Content section (3.3.2). Where "L" refers to distilled water and "S" to Jarosite.

This study is carried out twice. The first one, using alkaline activating solution composed only of NaOH 8 M solution and, the other one, with alkaline activating solution composed of NaOH 8 M and sodium silicate solution (technical grade) in a weight ratio of 1. Thus, in the second case, NaOH 8 M and $Na_2SiO_3$ are in a proportion of 12,39% each.

- Study 3-3

The chemical composition of the raw materials used in the synthesis of Jarosite geopolymer is shown in the Table 12.

*Table 12. Composition of the raw materials in the Study 3-3 of Jarosite geopolymers synthesis.*

| Raw Materials | Chemical Composition (%) |
|---|---|
| Jarosite | 46,10 |
| AAS | 35,46 |
| Distilled $H_2O$ | 18,44 |

In this case, the portion between distilled water and jarosite remains constant, i.e. 0,4 L/S ratio. The weight ratio between Jarosite and AAS is 1,3:1. This weight ratio between solid raw material and AAS was previously established in Jarosite Study 1 and 2. In Study 3-3 the weight ratio of Jarosite raw material in synthesis is reduced by 35,90% with respect to Study 3-1, while that of AAS is increased by 17,45%.

As the previous Jarosite geopolymer studies, this study is performed twice. The first one, using alkaline activating solution composed only of NaOH 8 M solution and, the other one, with alkaline activating solution composed of NaOH 8 M and sodium silicate solution (technical grade) in a weight ratio of 1. Thus, in the second case, NaOH 8 M and $Na_2SiO_3$ are in a proportion of 17,73% each.

# 5.- Experimental results

In the following sections, the experimental results obtained in the synthesis of geopolymers, the stability test of them, the adsorption experiments, as well as in the jarosite study are shown. In order to synthesize geopolymers, a bibliographic research was first carried out which can be seen in Tables 2, 3 and 4 of the Appendixes.

## 5.1 Synthesis of geopolymers

In order to synthesize the geopolymers, first of all, a 10 M NaOH solution was prepared. The experimental amounts used to prepare the solution are shown in Table 5 (Appendixes).

On the other hand, according to Table 5 (Section 4.2.1.3), in order to synthesize a geopolymer, 9 g of the alkaline activating solution is needed. As six geopolymers were wanted to be synthesized, the required amount of alkaline activating solution was 54 g. Nevertheless, 60,01 g of alkaline activating solution was prepared, mixing 10 M NaOH solution and sodium silicate solution (technical grade), according to the experimental amounts that are shown in Table 6 (Appendixes).

Once the alkaline activating solution was prepared and allowed to stand for 24 h, the geopolymers were prepared following the theoretical amounts exposed in Table 5 (Section 4.2.1.3). However, it is difficult to obtain the exact weight of each reagent experimentally. Therefore, Table 7 (Appendixes) shows the experimental amount used to synthesize each geopolymer.

In addition, Table 8 (Appendixes) shows the mass composition of the raw materials used in the synthesis. It was calculated according to the real amount of each reagent. However, during the geopolymerization process, there could be a loss of some reagents; this would be the ideal composition of the geopolymers. The aspect of the geopolymers once they were synthesized is shown in the Figure 19 where can be seen that all synthesized geopolymers, except GP2, have more or less the same aspect.

*Figure 19. From left to right, from GP1 to GP6 the first day that they were synthesized.*

Some are more solid than others because by the time the photo was taken, all the geopolymers were synthesized and therefore, the curing step had already started. Nevertheless, in appendixes, some pictures of the geopolymers after the mixture step; in liquid state, are shown (Figure 1).

The GP2 was synthesized twice, because some experimental error was thought to have been made due to the appearance of the GP2. However, after the second synthesis of this geopolymer, the result remained the same. Instead of obtaining a liquid geopolymer mass after the geopolymerization process, the mass of the geopolymer turned out to be very solid.

Its mechanical properties were high, as the geopolymer properties, but its structure was not in accordance with the structure that the geopolymer must have once synthesized. In particular, for this sample, the mixing stage of the geopolymerization process was easy at the beginning. However, once the solid fly ash particles had adsorbed the alkaline solution in the mixing stage, workability with the geopolymer mass was difficult, as it became more solid.

This may be due to the fact that there was not enough solid-liquid ratio in the reaction medium. Therefore, the fly ash solid particles did not have enough moisture; in this case, the mixing process was harder once the solid particles had absorbed the alkaline activating solution from the reaction medium.

As explained in section 3.3, among the main parameters that can affect the final result of the geopolymer is the amount of water that is in the reaction medium. As seen in section 3.3.2, all the geopolymerization steps are positively affected by the decrease of the water. If that decrease remains constant in all the geopolymerization steps, the moisturizing between solid particles can decrease, hampering the workability and moulding of them in the solution, and thus, affecting the final geopolymer microstructure, properties and applications. Therefore, the amount of water in the geopolymer synthesis should be such that the particles are enough wet, giving them the facility for working with them.

In this research, the geopolymers were synthesized without adding an external water source, only the one that makes up the alkaline activating solution. However, that was not enough for the GP2 synthesis.

In order to obtain a GP2 with the appropriate microstructure, shape and properties, another GP2 was synthesized, following the same procedure and the same theoretical amount of solid raw material and alkaline activating solution as in the other two GP2 synthesized samples. But, in this case, 15 mL of deionized water was also added.

Water was added in order to increase the humidity of the solid aluminosilicate particles, making easier the workability of the generated mass during the geopolymerization process, and therefore, favoring the obtaining of a liquid mass as a result of the mixing process.

In this case, another alkaline activating solution had to be prepared because the first one was finished. The experimental quantity of each reagent used to prepare the solution is shown in the appendixes, Table 9. Similarly, the experimental amount of fly ash, alkaline activating solution and deionized water used to synthesize the new sample of GP2 is shown in the appendixes, Table 7.

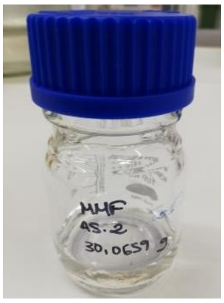

Figure 20. AAS-2 for preparing another sample of GP2.

The geopolymer mass obtained in the mixing stage of the geopolymerization process, after adding water as a reagent in the geopolymer synthesis, is shown in the Figure 21. There, the geopolymer mass is compared with the shape of the first two GP2 samples obtained.

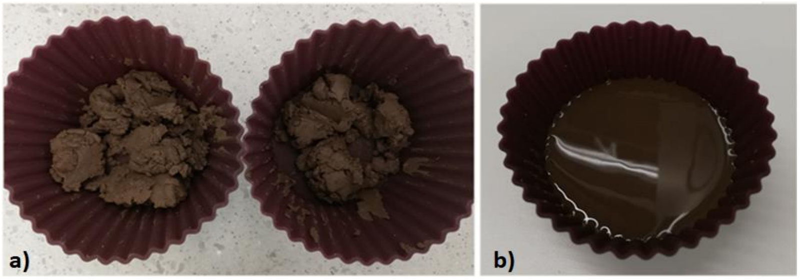

Figure 21. Aspect of GP2 samples: a) synthesized without water. b) Synthesized adding water.

As can be seen in Figure 21 b) and Figure 22, the new GP2 sample does not look like the first two synthesized samples (Figure 21 a)). In this case, the sample is not as solid as the first ones, it is liquid, and therefore, the workability with this sample was easier, obtaining a final geopolymer mass typical of a geopolymer synthesis process.

In the following image the aspect of the synthesized geopolymers in their third curing day can be seen. For the new GP2 sample, that was the aspect after being synthesized.

Figure 22. Aspect of the geopolymers, from left to right, from GP1 to GP6, the third curing day. GP2 repeated (Day 1).

As a result of the curing process, the geopolymer samples are more solid in their third curing day, rather than in the first one. As more time the geopolymers are submitted to a curing process, they become harder and with better mechanical properties.

In this case, the geopolymers were allowed to stand for consolidate inside a laboratory fume cupboard during 7 days and afterwards they were crushed, sieved, washed and dried according to the procedure described in section 4.2.1.5.

All the geopolymers were physically stable, a laboratory hammer was needed to crush them, it was not possible to crush them with the force of the hand. In the crushing step, almost all the GP5 was crushed without the metal box being placed in the discharge area of the crushed material. Therefore, the sample was contaminated. By the time it was noticed, almost the entire GP5 sample was consumed and the rest was crushed normally (with the metal box). However, the total amount of pure GP5 sample obtained after crushing was not enough; a new GP5 was synthesized according to the reagent amounts that are in Table 10 (Appendixes).

The total amount of each geopolymer sample after sieving is shown in Table 11 (Appendixes). After sieving metakaolin raw material, the amount of this was so high; it was divided into two parts (RM 1.1 and RM 1.2), for washing them separately, in order to increase the washing performance of this material. However, only RM 1.1 was used in the experiments carried out in this project.

The geopolymer samples were washed using mQ-water to reduce the pH of the solution composed of mQ-water and the solid geopolymer particles. It was wanted to wash them until achieve a constant pH of 7 for all of them. However, it takes a long time to reach that pH, so finally geopolymer samples were washed 19 times. The solid raw materials were washed 5 times.

The variation in pH of the geopolymer samples as they were washed is shown in Table 12 (Appendixes). This table shows that the pH of the solid raw materials used in the synthesis the first time that they were washed was high, almost pH 10 for metakaolin raw material and pH above 11 for fly ash and blast furnace slag raw materials.

As expected, the pH of the synthesized geopolymers was higher, because they were synthesized using a raw materials that had a high initial pH with mQ-water and also, they were synthesized through a geopolymerization process, in a highly alkaline medium. Even though they were subjected to a washing stage, pH of the samples was still high.

After the washing stage, samples were dried. The amounts obtained from each geopolymer synthesized after drying, as well as from each raw material used in the geopolymerization process, are shown in Table 13 (Appendixes).

## 5.2 Stability Test

Once the geopolymers were synthesized, a stability test of them was carried out in order to analyze whether they were chemically stable. The same study was also performed for the raw material used in the synthesis of the geopolymers in order to analyze whether there is any difference between them.

These raw materials were also subjected to the same treatments that were applied for the geopolymers once synthesized, i.e. the raw materials were sieved, washed and dried before the stability study and the stability test was carried out according to the procedure set out in paragraph 4.2.2.

In this study, three conductivity values were obtained for each raw material used and each geopolymer synthesized. These values were obtained after 2, 6 and 24 hours of geopolymer contact and agitation with mQ-water. The conductivity results in the stability test for each sample are shown in Table 13.

*Table 13. Conductivity results for the raw materials used in the geopolymerization and for the synthesized geopolymers.*

| | **RM1** | **RM2** | **RM3** | **GP1** | **GP2** | **GP3** | **GP4** | **GP5** | **GP6** |
|---|---|---|---|---|---|---|---|---|---|
| **w GP (g)** | 1,0001 | 1,0002 | 1,0001 | 1,0004 | 1,0000 | 1,0004 | 1,0001 | 1,0004 | 1,0003 |
| **$\sigma_{2\,h}$ (µS/cm)** | 28,0 | 1147 | 48,5 | 332,0 | 186,2 | 129,7 | 413,0 | 587,0 | 171,1 |
| **$\sigma_{6\,h}$ (µS/cm)** | 36,8 | 1161 | 55,5 | 429,0 | 195,1 | 150,3 | 470,0 | 716,0 | 178,5 |
| **$\sigma_{24\,h}$ (µS/cm)** | 47,5 | 1197 | 77,1 | 652,0 | 208,5 | 185,9 | 562,0 | 962,0 | 193,3 |

The chemical stability of synthesized geopolymers is analysed through the conductivity measurements shown in Table 13.

As explained in section 4.2.2, the conductivity value depends on the total amount of dissolved ions in the solution. Thus, if between two consecutive measurements, the obtained conductivity value has increased considerably, the synthesized geopolymer is chemically unstable. As a result, it tends to decompose into different substances, increasing the total amount of dissolved ions in the solution and therefore, the conductivity measurement of the solution.

According to Table 13, the conductivity value after each measurement has increased for all analysed samples in different ways. Conductivity measurements for RM2 (fly ash raw material) are high. To ensure that these values are correct, the fly ash raw material stability test was carried out twice and the values obtained remained high and around the values shown in Table 13.

The following table shows the increase in conductivity between the value obtained after 2 hours and after 6 hours, as well as between the measurement after 2 hours and 24 hours of the geopolymer being in contact and agitated with mQ-water. In addition, the percentage deviation among these values is also calculated and shown below.

*Table 14. Difference and percentage deviation between conductivity results after 2 and 24 h for each sample.*

| | RM1 | RM2 | RM3 | GP1 | GP2 | GP3 | GP4 | GP5 | GP6 |
|---|---|---|---|---|---|---|---|---|---|
| **σ [6h - 2h] (μS/cm)** | 8,80 | 14,00 | 7,00 | 97,00 | 8,90 | 20,60 | 57,00 | 129,00 | 7,40 |
| **σ [24h - 2h] (μS/cm)** | 19,50 | 50,00 | 28,60 | 320,00 | 22,30 | 56,20 | 149,00 | 375,00 | 22,20 |
| **Deviation $_{6-2}$ (%)** | 31,43 | 1,22 | 14,43 | 29,22 | 4,78 | 15,88 | 13,80 | 21,98 | 4,32 |
| **Deviation $_{24-2}$ (%)** | 69,64 | 4,36 | 58,97 | 96,39 | 11,98 | 43,33 | 36,08 | 63,88 | 12,97 |

According to Table 14, among the raw materials used in the synthesis of geopolymers, RM2 (fly ash raw material) is the most chemically stable because the increase in conductivity between the value obtained after 2 hours and after 24 hours is only 4,36%, while for the RM1 and the RM3, this increase is 69,64% and 58,97% respectively.

On the other hand, GP2 and GP6 are the most stable synthesized geopolymers, with an increase in conductivity with respect to the first measure of 11,98% and 12,97% respectively. Although there is an increase in conductivity of these materials after each measurement, this is not so high. In addition, it is not possible to obtain as a result of the stability test, a conductivity value such as mQ-water; there is always an increase.

GP2 was synthesized using RM2 as raw material for the synthesis. This raw material has proven to be the most chemically stable solid aluminosilicate source material, so it could be one of the reasons why GP2 has turned out to be the most chemically stable synthesized geopolymer.

On the other hand, GP6 was synthesized using RM2 and RM3. As seen above, RM3 is less stable than RM2 due to its percentage increase in conductivity. However, synthesized GP6 is chemically stable.

For the geopolymers GP3 and GP4, the conductivity of the solution after 24 h increased by 43,33% and 36,08% respectively with respect to the conductivity value obtained after 2h. This means that these geopolymers are less chemically stables than GP2 and GP6. With respect to GP1 and GP5, both are not chemically stable, as their conductivity value after 24 h are so high, increasing by 96,39% and 63,88% respectively with respect to the conductivity value obtained after 2h.

GP 1 was synthesized using RM1 as the solid raw material for the synthesis. As seen above, this raw material has been shown to have a 69,74% increase in conductivity. It could be a reason why the synthesized geopolymer has turned out a chemically unstable material. Similarly, GP5 was synthesized by mixing RM1 and RM3, the least chemically stable solid raw materials and it also turned out to a chemically unstable material.

For those geopolymers that are physically and chemically stables, a Jarosite study will be carried out. In this case, GP2 and GP6 are the most chemically stable geopolymers. On the other hand, GP3 and GP4 have an increase in the conductivity results superior to the former. However, these will be regarded as chemically stable geopolymers in this study. In contrast, GP1 and GP5 can be regarded as chemically unstable geopolymers. This will be explained in section 5.4.

## 5.3 Adsorption Experiments

Once the geopolymers had been synthesized and their physical and chemical stability analyzed, batch adsorption experiments at different pH conditions were carried out according to the procedure explained in section 4.2.3, where the aim of this study is to analyze how the pH condition and the geopolymerization process can affect the removal efficiency of $NH_4^+$ from the adsorbent material.

For the adsorption experiments, a 500 ppm ammonium solution was prepared with the experimental amounts of deionized water and $NH_4Cl$ (s) shown in Table 16 (Appendixes). The adsorbent dosage used in each batch adsorption experiment, as well as the ammonium concentration in the solution with and without adsorbent after four hours for each sample analyzed, is shown in section 6.4 (Appendixes).In addition, the removal efficiency and adsorption capacity of each sample, measured after 4 hours, are also presented in this section, whose values are calculated using the expressions (4) and (5).

According to literature, it is assumed that at low pH, there is a competition between $H^+$ ions and cationic adsorbates ($NH_4^+$), hampering the adsorption of the cationic element to be removed [12]. On the other hand at high pH, $NH_4^+$ deprotonates to $NH_3$ (g), that leaves the reacting medium [12]. Thus, this pH condition is not favorable for ammonium removal by the adsorption method. However, in this case, the maximum removal efficiency and adsorption capacity of the analyzed samples has been achieved at low pH and high pH, i.e. pH 2 and pH8 respectively.

In this study, GP1 has experienced the highest removal efficiency of all synthesized geopolymers, which was 27,12% at pH 2. At pH 6 and pH8, its removal efficiency was 19,85% and 18,89% respectively (still higher than the other removal efficiency obtained in the other materials). On the other hand, the high removal efficiency for GP2 was 14,53% at pH 8 followed by 14,24% at pH 2. At pH 6 the removal efficiency was about 6,4%.

For GP3 it could be said that there is almost no adsorption, as the maximum efficiency was 2,37% at pH 2 and the same could be said for GP4, which is the only geopolymer that present the highest removal efficiency of all synthesized geopolymers, at pH 6. This value was 8,42% (not high).

Moreover, GP5 starts with no ammonium removal at pH 2 and then, the removal efficiency is increasing with the pH, having the maximum removal efficiency at pH 8 of 16,10%. On the other hand, for the GP6 there is only ammonium adsorption at pH 8 with a removal efficiency of 6,30% (not high).

In this study, it has been demonstrated that the geopolymerization process increase the removal efficiency by adsorption of these materials that have been synthesized through this technique. This can be seen in Graphs 1, 2 and 3 of the Appendixes, where geopolymers have better removal efficiency than the raw materials used in the synthesis (without being subjected to a geopolymerization process). However, the removal efficiency obtained is not enough. In addition, all samples analyzed did not experience adsorption removal at pH 4, the values obtained are below 0 which means that there were no adsorption of $NH_4^+$.

## 5.4 Jarosite Study

In this section, the experimental results obtained in Jarosite Study are shown. In the Jarosite Study, new geopolymers were synthesized using the same reagents as in the first synthesized geopolymers (MK, FA, BFS, AAS), and also, Jarosite.

The synthesis of the new geopolymers was carried out for those geopolymers which were synthesized in section 4.2.1 (Synthesis of Geopolymers), that have been shown to be both physically and chemically stable.

As explained in section 5.2 (Stability Test), of all the synthesized geopolymers (GP1 to GP6), GP2 and GP6 are the geopolymers that have proven to be the most chemically and physically stable.

On the other hand, GP3 and GP4 are also physically stable, but the conductivity of the solution after 24 hours has increased 43,33% and 36,08% respectively with respect to the conductivity value obtained after 2 hours.

This means that these are less chemically stables, but, for the Jarosite Study, both are regarded more or less chemically stables, in order to synthesize new geopolymers using also BFS as raw material in the synthesis of Jarosite geopolymers.

However, GP1 and GP5 have proved to be physically stable, with high mechanical resistance but not chemically stable, as their conductivity value after 24 hours has increased by 96,39% and 63,88% respectively with respect to the conductivity value obtained after 2 hours. Therefore, these geopolymers are not taken as a reference to synthesize new geopolymers by adding Jarosite as raw material in their structure.

In both cases (GP1 and GP5), metakaolin was used to synthesize them and both were chemically unstable. It is not known whether this raw material is the reason why the geopolymers are not stable but, in this case, metakaolin was also used to synthesize all samples of Jarosite GP4. The synthesized GPs are analysed below to see if metakaolin had a negative effect on the geopolymerization of Jarosite geopolymers.

On the other hand, two different types of blast furnace slag were used in the jarosite studies: ground granulated blast furnace slag and fine blast furnace slag; where the difference between the two materials lies in the size of the particles that compose it, which depends on the cooling treatment applied to obtain this material (processes for obtaining iron).

The two materials were used in order to compare how the particle size of this material affects the synthesis of the geopolymer. The first one, granulated BFS, is characterized by being composed of larger solid particles, meanwhile the particles of the second one, are smaller.

In addition, in some experiments, a certain amount of distilled water was added to give the geopolymer mass the fluidity that it needs to work with it. Otherwise, the result may be the same as that obtained in the first two fly ash geopolymer samples (GP2) synthesized in the first study (Synthesis of Geopolymers), i.e. obtaining a solid product that looks like a rock. It can be appreciate in Figure 21 a).

The amount of water added in each case is not the same and was added according to the shape of the geopolymer mass during the geopolymerization process. The exact amounts of water added to each synthesized geopolymer, as well as the added quantity of other reagents, and the final aspect of each synthesized geopolymer are shown in the Appendixes, for each Jarosite study carried out.

### 5.4.1 Jarosite Study 1

The Jarosite geopolymers synthesis was performed according to the theoretical amounts for each reagent shown in Table 7 (section 4.2.4.1). However, it is difficult to obtain the exact weight of each product experimentally. Therefore, Table 29 (Appendixes) shows the experimental amount used for synthesizing each geopolymer.

For the Jarosite study, a new alkaline activating solution was prepared. Table 28 (Appendixes) shows the amount of each reagent used to prepare the solution.

As can be seen in Table 29, the amount of water added in the geopolymerization process was higher in those geopolymers that contain a high percentage of solid raw materials in their structure, i.e. samples 1 and 2 of each synthesized geopolymer.

Section 7.1 of Appendixes shows the aspect of the samples from Jarosite Study 1 at different curing times, and also, the aspect of these samples after testing their physical stability, i.e., after being subjected to a bending and compressive forces applied by the hands.

Even though all the samples pictures are in the Appendixes, in this section, some of them are shown in order to make easier the comprehension of the analysis of the geopolymer shown below.

- *GP2:*

For the synthesized samples of GP2, in the section 7.1 of Appendixes is shown the aspect of the samples once they were synthesized and also, after 3, 6, 12, 14, 18, 35, 40 and 42 curing days. In addition, samples are also shown after the physical stability test, where the samples were subjected to hand applied compressive and bending forces. This test was carried out in the 42nd curing day.

In this case, Figure 23, 24 and 25 shows the samples once synthesized, as well as on the 3rd curing day, and on the 42nd curing day respectively.

*Figure 23. From left to right, aspect of the samples 1, 2 and 3 of the GP2 once they were synthesized.*

*Figure 24. From left to right, aspect of the samples 1, 2 and 3 of the GP2 (3rd curing day).*

*Figure 25. From left to right, aspect of the samples 1, 2 and 3 of the GP2 after crushing (physical stability test; 42th curing day).*

As is shown in Figure 23, the geopolymer mass obtained in the geopolymerization process is fluid, according to what it should look like. Samples 1 and 2 of GP2 are more fluid than the third, as the amount of water added in the geopolymer synthesis of these two samples is greater than in the last sample.

After three curing days, the samples were submitted to a compressive strength in order to check their compressive resistance and compare it with the samples synthesized in the first study (without using Jarosite as a reagent in the synthesis).

In this case, after three curing days, the samples were solid, but these were broken after applying a compressive stress with the hands. For the geopolymer samples that were synthesized without using Jarosite, on their 3$^{rd}$ curing day, they were more solid and physically stable, as they did not break after applying a compressive stress.

On the other hand, the geopolymer matrix of the first two samples is less consistent than that of the third sample. Figure 24 shows, for these two samples, the existence of loose solid particles in the mold walls and also, around the solid geopolymer matrix, which means that the bonds between the particles that make up the geopolymer matrix are weak and therefore, the mechanical strength of these samples is not high.

In addition, for samples 1 and 2 of GP2, there is a white lay on the top of the matrix as a result of the high presence of sodium. Moreover, Figure 25 shows the result of the physical stability test. In this case, when the first two samples were subjected to compressive stress, they went from having a solid structure to breaking down into loose solid particles, like sand. Therefore, these samples are not physically stable.

The sample 3 of GP2 has a consistent structure. However, it broke when a compressive stress was applied. The applied stress had to be stronger, so it is not as easy to break as samples 1 and 2. In addition, it breaks into smaller, solid and consistent pieces, without releasing loose solid particles. Therefore, this sample is regarded as a good one, although it breaks when a force is applied.

It may need more curing time for became as strong as the geopolymers, and also, the fact that it was subjected to a compressive force on its third curing day could have affected its microstructure and therefore, its properties. In this way, some cracks could be in the microstructure of the material as a result of the applied stress, generating preferential pathways for the breakage of the material and, therefore, making easier the breakage of the sample.

- *GP3-Granulated:*

For the synthesized samples of GP3-Granulated, in the section 7.1 of Appendixes is shown the aspect of the samples once they were synthesized and also, after 1, 2, 6, 8, 12, 29, 34 and 36 curing days. In addition, samples are also shown after the physical stability test, where the samples were subjected to hand applied compressive and bending forces. This test was carried out in the 36th curing day.

In this case, Figure 26, 27 and 28 shows the samples once synthesized, as well as on the 29th curing day, and on the 36th curing day respectively.

*Figure 26. From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated. For the sample 1 and 2, aspect after being synthesized. For sample 3, aspect after 20 h of synthesis.*

*Figure 27. From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated (29th curing day).*

*Figure 28. From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated after crushing (physical stability test; 36th curing day).*

As is shown in Figure 26, the geopolymer mass obtained in the geopolymerization process is fluid. However, they were not as fluid as the GP2 samples, as the GGBFS particles are larger. The sample 3 once synthesized is less fluid, since no water was added in the synthesis of the geopolymer (Figure 14 Appendixes).

On the other hand, Figure 24 (Appendixes) shows that sample 1 of GP3-Granulated is not homogeneous; the geopolymer matrix is composed of several layers, each with different color, which means that the components of each layer are different, as well as the microstructure and properties.

Thus, at the bottom of the geopolymer matrix, a grey and rough layer can be appreciated (Figure 24; Appendixes). This means that there are more GGBFS particles. It makes sense due to these particles are larger and then, heavier, so they tend to be at the bottom of the geopolymer matrix.

Above this layer, there is a brown layer mainly composed of Jarosite and, at the top of the matrix, there is a layer of a lighter colour as a result of the sodium presence. This material tends to disintegrates easily into smaller particles when a compressive stress is applied (Figure 28), so it is not physically stable.

Moreover, sample 2 of GP3-Granulated has also a white layer at the top of the matrix and loose solid particles surround the matrix. This sample is not physically stable; as it braked easily, turning into loose solid particles when a weak compressive stress was applied. In fact, its behaviour is like sand.

GP3-Granulated sample 3 has less sodium presence (no white layer on top, only a few dots). The particle size makes the sample heterogeneous at some points, where there is a greater presence of GGBFS solid particles. This sample was broken into smaller and consistent pieces, without releasing solid particles, when a compressive stress was applied. The applied stress was stronger to achieve sample breakage.

In addition, this sample was thin, so the total volume of the sample that receives the applied stress is smaller, increasing the possibility to achieve a stress equal than the plastic deformation stress of the material and therefore, increasing the possibility to achieve the breakage point of the sample (more than if the sample were thick).

In this case, of all GP3-Granulated samples, the third sample has better properties and strong structure. It may need smaller particles of blast furnace slag to obtain a matrix with properties according to properties of the geopolymers. It will be studied below.

- *GP3-Fine:*

For the synthesized samples of GP3-Granulated, in the section 7.1 of Appendixes is shown the aspect of the samples once they were synthesized and also, after 1, 2, 6, 8, 12, 29, 34 and 36 curing days. In addition, samples are also shown after the physical stability test, where the samples were subjected to hand applied compressive and bending forces. This test was carried out in the 36th curing day.

In this case, Figure 29, 30 and 31 shows the samples once synthesized, as well as on the 12th curing day, and on the 36th curing day respectively. For the third sample synthesized, no water was added in the synthesis, so it becomes more solid.

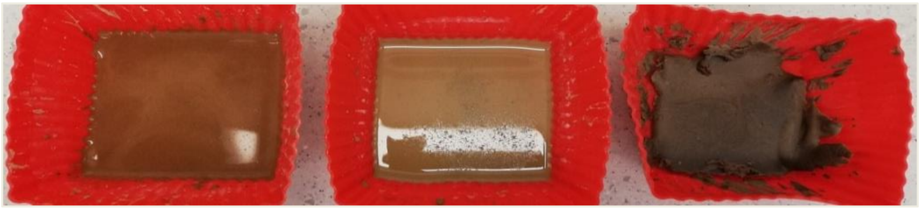

*Figure 29. From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine. For the sample 1 and 2, aspect after being synthesized. For sample 3, aspect after 2 h of synthesis.*

*Figure 30. From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine (12th curing day).*

*Figure 31. From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine after crushing (physical stability test; 36th curing day).*

As can be seen in Figure 30 the sample 1 of GP3-Fine has a solid structure on its 12th curing day, with a lighter colored surface layer due to the high presence of sodium. As a result of the physical stability test where a compressive force is applied, the solid geopolymer matrix turns into smaller solid pieces as well as smaller particles which look like sand (Figure 31). This sample is not physically stable due to it is easy to break but, in this case, it is more stable than the geopolymer sample synthesized with GGBFS.

On the other hand, as shown in Figure 30, the second sample of GP3-Fine has a surface layer of different colors (from lighter to darker) which separates from the geopolymer matrix. This sample is not physically stable, as it breaks and disintegrates easily after applying a compressive stress. However, it is more stable than the sample synthesized using GGBFS.

Moreover, the third sample of GP3-Fine was synthesized without adding an external water source. This sample was more solid and homogeneous, without a light colored layer reflecting the presence of sodium. In this case, a material of high consistency and resistance was obtained, with high mechanical properties, since it was difficult to break and the breakage took place where there were defects in the net (pores, as a result of some air bubbles being trapped in the material net). This can be seen in Figure 37 (Appendixes). On the other hand, the width of the sample was thin, which facilitated the breakage of the sample, but it was still hard; this sample is regarded physically stable and which look like ceramic.

In this case, the role of the particle size of a blast furnace slag has been analyzed and the geopolymers that have been synthesized with blast furnace slag of smaller particle size are more homogeneous, with better mechanical properties and, therefore, more physically stable.

- *GP4:*

For the synthesized samples of GP3-Granulated, in the section 7.1 of Appendixes is shown the aspect of the samples once they were synthesized and also, after 1, 5, 7, 11, 28, 33 and 35 curing days. In addition, samples are also shown after the physical stability test, where the samples were subjected to hand applied compressive and bending forces. This test was carried out in the 35th curing day.

In this case, Figure 32, 33 and 34 shows the samples once synthesized, as well as on the 7th curing day, and on the 35th curing day respectively.

*Figure 32. From left to right, aspect of the samples 1, 2 and 3 of the GP4 once they were synthesized.*

*Figure 33. From left to right, aspect of the samples 1, 2 and 3 of the GP4 (7th curing day).*

*Figure 34. From left to right, aspect of the samples 1, 2, 3 of the GP4 after crushing (physical stability test; 35th curing day.*

As can be seen in Figure 33 the sample 1 of GP4 has a lighter colored surface layer at the top of the material, with high amount of disintegrated solid particles. The bottom of the geopolymer material is more solid and consistent. However, once a compressive force is applied, the material breaks releasing solid pieces as well as smaller particles which looks like sand; this is not physically stable.

On the other hand, the sample 2 of GP4 does not have a white layer that breaks away from the geopolymer matrix; this material is more solid. However, this sample is not homogeneous as it does not have a single colour, which means that the composition is not the same in the whole sample. As a result of the material being subjected to compressive stress and bending, it breaks releasing solid pieces as well as smaller particles into the air. The strength required to break the material higher than in the first synthesized sample but it is still low; this is not physically stable.

Moreover, the third sample of GP4 has different colours in its structure; it is not uniform. In addition, it has a layer with cracks at the top of the geopolymer which has separated from the solid material. Its colour is brown, thus it might contain high amount of jarosite or fly ash particles.

This material breaks easily when a compressive strength is applied; it is not physically stable. All synthesized samples of GP4 are physically unstable. One of the reasons could be the use of metakaolin as a raw material source of aluminosilicates in the synthesis, since it has been demonstrated that the geopolymer samples synthesized with this material (GP1 and GP5) are also not chemically stables.

- *GP6-Granulated:*

For the synthesized samples of GP6-Granulated, in the section 7.1 of Appendixes is shown the aspect of the samples once they were synthesized and also, after 1, 5, 7, 11, 28, 33 and 35 curing days. In addition, samples are also shown after the physical stability test, where the samples were subjected to hand applied compressive and bending forces. This test was carried out in the 35th curing day.

In this case, Figure 35, 36 and 37 shows the samples once synthesized, as well as on the 28th curing day, and on the 35th curing day respectively.

*Figure 35. From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 after synthesis. Sample 3 after 1 curing day.*

*Figure 36. From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 on the 27th curing day. Sample 3 on the 28th curing day.*

*Figure 37. From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated after crushing (physical stability test). Samples 1 and 2 on the 34th curing day. Sample 3 on the 35th curing day.*

As can be seen in Figure 36 the sample 1 of GP6-Granulated has a lighter colored surface layer due to the presence of sodium. This layer has separated from the solid geopolymer matrix and there are small solid particles at the top of the material. This material break whether a compressive stress is applied (Figure 37), thus it is not physically stable. However, it breaks into smaller and consistence solid pieces instead of smaller particles like sand, which makes it more stable but it is not enough.

Sample 2 of GP6-Granulate does not have a white layer that breaks away from the solid geopolymer matrix. However, this sample is not homogeneous as it does not have a single colour, which means that the composition is not the same in the whole sample. This can be seen in Figure 59 (Appendixes), where at the bottom of the sample, the structure of the material is rougher due to the presence of GGBFS particles.

As explained above, the particles of this material are heavier and tend to be at the bottom of the geopolymer matrix. If a frictional force is applied at the bottom of the sample, these particles tend to release from the geopolymer matrix. If frictional stress is applied to the top of the material, no particles are released because it is more solid, is not porous and is mainly composed of Jarosite particles and sialates.

If a compressive force is applied, the material is easily broken into smaller solid pieces releasing smaller particles into the air. The same behavior was experimented with the third sample of GP6-Granulated after applying a compressive force (Figure 37). Therefore, these two samples are not physically stable. On the other hand, the sample 3 of GP6-Granulated has a layer that separates from the solid geopolymer matrix and there, is presence of silicate as it is white (Figure 36).

All synthesized samples of GP6-Granulated were physically unstable, probably because of the size of the particles. The results of the synthesized geopolymers with BFS-Fine (with smaller particle size) are analyzed below.

- *GP6-Fine:*

For the synthesized samples of GP6-Granulated, in the section 7.1 of Appendixes is shown the aspect of the samples once they were synthesized and also, after 1, 2, 4, 5, 6, 7, 8, 27, 28, 33 and 35 curing days. In addition, samples are also shown after the physical stability test, where the samples were subjected to hand applied compressive and bending forces. This test was carried out in the 35th curing day.

In this case, Figure 38, 39 and 40 shows the samples once synthesized, as well as on the 7th-8th curing day, and on the 35th curing day respectively.

*Figure 38. From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 and 2 after 1 h of the synthesis. Sample 3 after one day curing.*

*Figure 39. From left to right, aspect of the sample 1, 2, 2' and 3 of GP6-Fine. Sample 1, 2 and 2' on the 7th curing day. Sample 3 on the 8th curing day.*

*Figure 40. From left to right, aspect of the sample 1, 2, 2' and 3 of GP6-Fine after crushing (physical stability test). Sample 1 and 2 on the 33th curing day. Sample 3 on the 35th curing day.*

As can be seen in Figure 39 the sample 1 of GP6-Fine has a white layer at the top of the solid geopolymer matrix as a result of the presence of sodium and also, there are fine loose particles, which have not been consolidated into a solid matrix.

This sample is not physically stable, since it breaks releasing smaller particles into the air when a compressive and bending strength is applied. The same happens for the sample 2 of GP6-Fine. In addition, it also has a layer that is separated from the solid matrix. This layer is not as white as in the first sample, but it has different colours at the top of the surface.

On the other hand, the 2' sample of GP6-Fine does not have a layer at the top of the matrix. In fact, this material is uniform and looks like ceramic, it has high mechanical properties and a high strength is needed to break this material. One of the reasons that could favour sample breakage is the fact that it is not very wide; the applied stress is spread over a small volume of the material. It is considered a really good and physically stable sample.

The third sample of the GP6-Fine does not have a layer at the top of the matrix but the top surface colour is darker. In addition, a high strength is needed to break this material so it has high mechanical properties; the sample is physically stable.

In this case, BFS particle size has been shown to play an important role in the synthesis of stable geopolymer matrices, since in BFS-Fine geopolymer samples there are samples that are physically stable, whereas in BFS-Granulated geopolymer samples all are physically unstable.

- *Conclusions for Jarosite Study 1 samples:*

In this study, many samples had a layer at the top of the geopolymer matrix which is separated from the solid material. These types of samples were usually physically unstable. On the other hand, the role of the BFS particle size was analysed, resulting the BFS-Fine more suitable in the synthesis of the geopolymers, since the materials obtained were more consistent, with better mechanical properties and more physically stable.

In this case, only the following samples were stable: GP2-3, GP3-3 (Granulated and Fine), GP6-2' Granulated and GP6-3 (Granulated and Fine). Thus, any of the GP4 samples were physically stable, either all the first samples synthesized in each GP.

### 5.4.2 Jarosite Study 2

The Jarosite geopolymers synthesis in the Jarosite Study 2 was performed according to the theoretical amounts for each reagent that are shown in Table 8 (section 4.2.4.2). However, it is difficult to obtain the exact weight of each product experimentally. Therefore, Table 30 (Appendixes) shows the experimental amount used for synthesizing each geopolymer. In addition, for the geopolymers GP2, GP3 (Granulated and Fine) and GP4 some more samples were synthesized.

In contrast to Study 1, the alkaline activating solution used in the synthesis was the solution of 10 M NaOH instead of a solution composed of a mixture of 10 M NaOH solution and $Na_2SiO_3$ solution in a weight ratio of 1. In addition, for the synthesis process, solid Jarosite particles with a particle size lower than 63 µm were used.

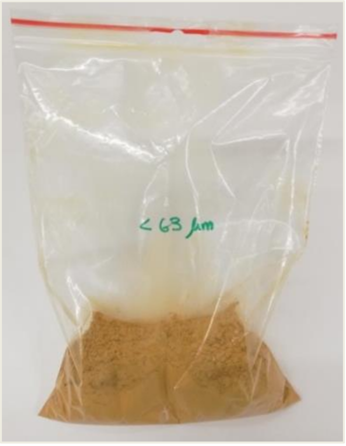

*Figure 41. Solid Jarosite particles with particle size less than 63 µm.*

Section 7.2 of Appendixes shows the aspect of the samples from Jarosite Study 2 at different curing times, and also, the aspect of these samples after testing their physical stability, i.e., after being subjected to a bending and compressive forces applied by the hands.

Even though all the samples pictures are in the Appendixes, in this section, some of them are shown in order to make easier the comprehension of the analysis of the geopolymer shown below.

- *GP2:*

The aspect of the samples of GP2 once synthesized, as well as after 1, 3, 22, 24, 27, 29 and 31 curing days is shown in section 7.2 of Appendixes. On the 31th curing day, the stability test was carried out.

In this case, Figure 42, 43 and 44 shows the samples after one day curing, as well as on the 7th-8th curing day, and on the 35th curing day respectively.

*Figure 42. From left to right, aspect of the sample 1, 2, 3 and 4 of GP2. Sample 1, 2 and 4 after one curing day. Sample 3 on the 3rd curing day (Study 2).*

*Figure 43. From left to right, aspect of the sample 1, 2, 3 and 4 of GP2. Sample 1, 2 and 4 on the 22th curing day. Sample 3 on the 24th curing day (Study 2).*

*Figure 44. Aspect of the sample 1, 2, 3 and 4 of GP2 after crushing (physical stability test). Sample 1, 2 and 4 on the 29th curing day. Sample 3 on the 31th curing day (Study 2).*

In this case, sodium is presence in the samples 1, 2 and 4 of the GP2, being greater in the first sample, whose upper surface of the geopolymer is completely white, with solid loose particles around.

These samples are not physically stable, since a compressive strength is applied; they all break and turn into smaller particles which look like sand.

For the first and fourth samples, the force applied to break the material samples was greater than in the second. In this case, only the third synthesized sample is physically stable. There is no white layer as a result of the high presence of sodium. The sample is strong, solid and with high mechanical properties and high stability, since is needed a really high strength for the breakage of the material. Figure 78 (Appendixes) shows that there are some parts in the structure of the material that are darker. However, this is a really good sample.

- *GP3-Granulated:*

The aspect of the samples of GP3-Granulated once synthesized, as well as after 21, 26 and 28 curing days is shown in section 7.2 of Appendixes. The stability test of the samples was carried out on the 31st curing day.

In this case, Figure 45, 46 and 47 shows the samples after one day curing, as well as on the 21st curing day, and on the 31st curing day respectively.

Figure 45. From left to right, aspect of the sample 1, 2, 3, 4 and 5 of GP3-Granulated once synthesized (Study 2).

Figure 46. From left to right, aspect of the sample 1, 2, 3, 4 and 5 of GP3-Granulated (21th curing day). (Study 2).

Figure 47. From left to right, aspect of the sample 1, 2, 3, 4 and 5 of GP3-Granulated after crushing (28th curing day). (Study 2).

In this case, the presence of sodium appears in the first synthesized sample, with a white layer at the top of the geopolymer surface. However, this layer does not separate from the geopolymer matrix as occurred in the samples synthesized in Jarosite Study 1.

This sample had a porous structure which was easier to break applying a weak compressive strength; this is not physically stable.

Samples 2 and 3 of GP3-Granulated were hard and it was difficult to break them applying a compressive stress. However, when a friction force was applied, the structure of the material disintegrated, releasing solid BFS particles. Therefore, these samples are not physically stable. As explained in the previous study, it may be due to the size and weight of the particles of GGBFS.

The behaviour of sample 4 of the GP3-Granulated is similar to that of samples 2 and 3. The obtained matrix was hard, like a rock and it was less porous as the other synthesized geopolymers. However, in the corner of the material, there is a disintegration of the material structure when a friction force is applied. In this case, the released particles are smaller.

The upper surface of the last synthesized sample was composed of small, shiny crystals. This material also breaks down releasing small particles. (It can be easier to see in the Appendix photos). In this case, all the GP3-Granulated samples are physically unstable.

- *GP3-Fine:*

The aspect of the samples of GP3-Fine once synthesized, as well as after 3, 24, 27, 29, 31, 32 and 34 curing days is shown in section 7.2 of Appendixes. The stability test of the samples was carried out on the 31$^{st}$ curing day.

All the synthesized GP3-Fine samples at different curing times are shown below.

Figure 48. From left to right, aspect of the sample 1, 2, 3 and 4 of GP3-Fine once synthesized. Sample 3 on the 3rd curing day (Study 2).

Figure 49. From left to right, aspect of the sample 1, 2, 3 and 4 of GP3-Fine. Sample 1, 2 and 4 on the 24th curing day; sample 3 on the 27th curing day (Study 2).

Figure 50. From left to right, aspect of the sample 1, 2, 3 and 4 of GP3-Fine after crushing (physical stability test). Sample 1, 2 and 4 on the 31th curing day; sample 3 on the 34th curing day (Study 2).

In this case, the presence of sodium appears in the first synthesized sample, with a white layer at the top of the geopolymer surface. However, this layer does not separate from the geopolymer matrix as occurred in the samples synthesized in Jarosite Study 1. There is also sodium presence in the second and the fourth sample but, to a lesser extent.

The first sample had a porous structure which was easier to break applying a weak compressive strength; this is not physically stable and it turns into small particles that looked like sand. The second synthesized sample is interesting, since its structure has two different colours, mainly white and brown, where the white part had the typical shape of dendrites, as if the sample had experience a dendritic cooling. This can be seen in more detail in Figure 91 (Appendixes).

The geopolymer obtained was a hard, non-porous material. It was difficult to break as the compressive strength applied for that purpose was high. So, it is regarded as physically stable material.

On the other hand, GP3-Fine sample 3 has a black spot on the top surface of the geopolymer. There is no white layer or loose particles around the material.

The texture was fine, not rough, pleasant to the touch and similar to that of the tiles or porcelain. It looks like a ceramic material, with a high mechanical strength as it was not possible to break it with the hand. It is a really good material, with high physical stability.

Sample 4 of GP3-Fine is also an interesting material; it looks like porcelain, with more or less good mechanical properties. However, after applying a force, the sample experienced a clean, consistent break, without releasing particles into the air (without disintegrating). The breakage was easier because the material had cracks in its structure, so it is easier to break in this case. These cracks could have formed as a result of applying compressive forces, at lower curing times, in order to check the hardness of the material. In this case, this material is regarded as a physically stable material.

- *GP4:*

The aspect of the samples of GP4 once synthesized, as well as after 3, 24, 27, 29, 31 and 33 curing days is shown in section 7.2 of Appendixes. The stability test of the samples was carried out on the 31-33th curing day.

In this case, Figure 51, 52 and 53 shows the samples after one day curing, as well as after 3, 24-27 and 31-33 curing day respectively.

*Figure 51. From left to right, aspect of the sample 1, 2, 3 and 4 of GP4 once synthesized. Sample 3 on the 3rd curing day (Study 2).*

*Figure 52. From left to right, aspect of the sample 1, 2, 3 and 4 of GP4. Sample 1, 2 and 4 on the 24th curing day; sample 3 on the 27th curing day (Study 2).*

*Figure 53. From left to right, aspect of the sample 1, 2, 3 and 4 of GP4 after crushing (physical stability test). Sample 1, 2 and 4 on the 31th curing day; sample 3 on the 33th curing day (Study 2).*

In this case, the silicate presence is noticed in samples 1, 2 and 4 of GP4.

Sample 1 has a porous structure, with a white layer at the top of the material that separates from the solid structure. This material is not physically stable; it becomes small particles such as sand, when a compressive strength is applied. The same behaviour is also experienced in the second and the fourth synthesized samples, but the stress applied to break the samples was a little higher. Thus, these materials are not physically stable. On the other hand, sample 3 of GP4 is physically stable, since it does not break after applying a hand compressive force. It has good mechanical properties, with high compressive resistance.

In addition, the texture of this sample was also fine, not rough, pleasant to the touch and similar to that of the tiles or porcelain. In Figure 102 of Appendixes it can be observed that this sample has experienced a dendritic cooling in some points of its structure.

- *GP6-Granulated:*

The aspect of the samples of GP6-Granulated once synthesized, as well as after 1, 22, 27 and 29 curing days is shown in section 7.2 of Appendixes. The stability test of the samples was carried out on the 29th curing day.

In this case, Figure 54, 55 and 56 shows the samples after 1, 22 and 29 curing days respectively.

*Figure 54. From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated once synthesized (Study 2).*

*Figure 55. From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated on the 22th curing day (Study 2).*

*Figure 56. From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated after crushing (physical stability test) on the 29th curing day (Study 2).*

In this case, the sodium presence is noted in samples 1 and 2 (a little).

The first GP6-Granulated synthesized sample is not physically stable; it breaks down and becomes small particles, like sand, when a compressive stress is applied. GP6-Granulate sample 2 has a lighter and brighter top surface. This sample seems that needs more curing time to be completely dry, as it behaves like mud (Figure 109-Appendixes show it in more detail). In this case, it is difficult to analyse its physical stability, it must be done later.

On the other hand, sample 3 of GP6-Granulated also seems to need more time to dry completely. However, it has high mechanical strength, as it did not break when a compressive force was applied; is physically stable.

In Figure 110 of Appendixes it can be observed that this sample has experienced a dendritic cooling in certain points of its structure.

- *GP6-Fine:*

The aspect of the samples of GP6-Fine once synthesized, as well as after 3, 6, 21, 24, 27, 29, 31, 32, 34, 35 and 37 curing days is shown in section 7.2 of Appendixes. The stability test of the samples was carried out on the 31-34-37th curing day.

All the synthesized GP3-Fine samples at different curing times are shown below.

*Figure 57. From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 once synthesize; sample 2 on the 3rd curing day; sample 3 on the 6th curing day (Study 2).*

*Figure 58. From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 on the 21th curing day; sample 2 on the 24th curing day; sample 3 on the 27th curing day (Study 2).*

*Figure 59. From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine after crushing (physical stability test). Sample 1 on the 31th curing day; sample 2 on the 34th curing day; sample 3 on the 37th curing day (Study 2).*

In this case, the sodium presence is noted in sample 1 of GP6-Fine.

The first GP6-Granulated synthesized sample is not physically stable; it breaks down and becomes small particles, like sand, when a compressive stress is applied.

GP6-Granulate sample 2 is physically stable, with good mechanical properties. High compressive and flexural strength was needed to break the sample. This sample also looks like a ceramic material.

On the other hand, sample 3 of GP6-Fine also has high mechanical strength. It was possible to break the sample due to it is not very wide and was broken after three curing days, facilitating the breakage of the sample. However, the stress applied for breaking the sample was high and it is regarded a physically stable material.

- *Conclusions for Jarosite Study 2 samples:*

In this study, there also was a presence of sodium in many samples, but not as much as in the previous Jarosite study carried out. In fact, in this case, this white layer does not tend to be separated from the solid geopolymer matrix.

As in the previous study, none of the Samples 1 of each synthesized geopolymer is physically stable. These samples are characterized by having in its structure the same amount of Jarosite and raw material source of aluminosilicates and less amount of alkaline activating solution.

In this case, some of the Sample 2 of each synthesized geopolymer are physically stables, being the third samples, the most physically stable. (The same was experienced in the previous study). Specifically, the samples that were stable in this study are: GP2-3, GP3-2,3,4 (Fine), GP4-3, GP6-3 (Granulated) and GP6-2-3 (Fine).

The role of the BFS size particle was also analysed in this study, where the samples synthesized using the BFS material with smaller particles, were more consistent, with better mechanical properties and more physically stable.

### 5.4.3 Jarosite Study 3

This section shows the experimental results of the Jarosite Study 3.

This study is characterized by using Jarosite and alkaline activating material in the synthesis of the geopolymers (without adding an aluminosilicate solid source). The experimental amounts used to synthesize each geopolymer sample are shown in the Appendixes, section 7.3. In this section, there are many photos of the samples at different curing times, as well as after tested their physical stability, where compressive and compressive force was applied by the hands.

Even though all the samples pictures are in the Appendixes, in this section, some of them are shown in order to make easier the comprehension of the analysis of the geopolymer shown below.

- Study 3-1:

The aspect of the samples of Study 3-1 once synthesized, as well as after 4, 8, 21, 26 and 28 curing days is shown in section 7.3 of Appendixes.

In this case, the stability test was carried out on the 28th curing day.

The aspect of the samples on their 4th curing day, as well as when the stability test was performed are shown below.

*Figure 60. Aspect of the Jarosite Study 3-1 geopolymer on the 4th curing day.*

*Figure 61. Aspect of the Jarosite Study 3-1 geopolymer on the 28th curing day after crushing (physical stability test).*

In this case, there also appears a white layer at the top of the geopolymer matrix that separates from the solid structure of the material. This layer appears for the sample which was synthesized using as alkaline activating solution, a solution of NaOH 8M.

In both cases, the samples are physically unstable, as they break more easily when applying a force than the samples synthesized in the other two studies.

On the other hand, the particles of the second sample looks like smaller pellets.

- Study 3-2:

The aspect of the samples of Study 3-1 once synthesized, as well as after 13, 18, and 20 curing days is shown in section 7.3 of Appendixes. In this case, the stability test was carried out on the 20th curing day. The aspect of the samples on their 13th curing day, as well as when the stability test was performed are shown below.

*Figure 62. Aspect of the Jarosite Study 3-2 geopolymer on the 13th curing day.*

*Figure 63. Aspect of the Jarosite Study 3-2 geopolymer on the 20th curing day after crushing (physical stability test).*

In this case, the presence of sodium is noted in both samples. However, the white layer is more noticeable in the first sample, which was synthesized using an 8M NaOH solution as an alkaline activator solution.

In both cases, the samples are physically unstable, as they break more easily, behaving like sand, when applying a force than the samples synthesized in the other two studies (Jarosite Study 1 and 2).

- Study 3-3:

The aspect of the samples of Study 3-1 once synthesized, as well as after 13, 18, and 20 curing days is shown in section 7.3 of Appendixes. In this case, the stability test was carried out on the 20th curing day. The aspect of the samples on their 13th curing day, as well as when the stability test was performed are shown below.

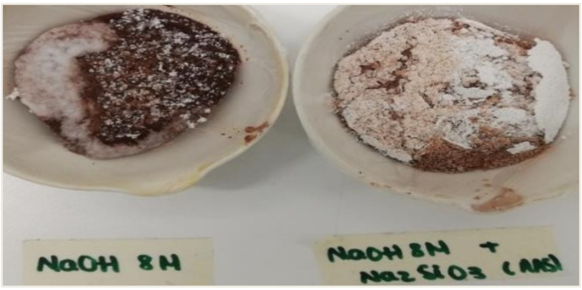

*Figure 64. Aspect of the Jarosite Study 3-3 geopolymer on the 13th curing day.*

*Figure 65. Aspect of the Jarosite Study 3-3 geopolymer on the 20th curing day after crushing (physical stability test).*

In this case, the presence of sodium is most noticeable in the second sample (NaOH 8M + $Na_2SiO_3$), with a white layer at the top of the surface that separates from the geopolymer material. It seems that the second sample has not been consolidated neither turned into a solid structure, since the mold is full of small loose solid particles. Therefore, it is physically unstable and it breaks easily when a stress is applied.

On the other hand, the sample synthesized using an 8M NaOH solution as an alkaline activator solution has a few white particles at the top of the surface. Unlike the other sample, this sample has been consolidated and a solid and consistent material is obtained. Nevertheless, this sample is a bit wet, it is like mud. Therefore, it needs more curing time to test its physical stability but, of all the samples that were synthesized in the study 3, this one is the most stable.

- *Conclusions for Jarosite Study 3 samples:*

The aim of this study was to test whether it is possible to obtain a final product with the characteristics and properties of geopolymers, without using metakaolin, fly ash or blast furnace slag as raw material in the synthesis of geopolymers.

On the other hand, different samples were prepared for each study, changing the composition of the alkaline activating solution, in order to analyze how the presence of sodium silicate solution as an alkaline activator affects the geopolymer synthesis.

This study demonstrates that a solid source material of aluminosilicate is needed to obtain a final product with properties such as geopolymers. However, of all the synthesized samples, the sample of the Study 3-3 which was synthesized using an 8M NaOH solution as an alkaline activator solution is the best one, since it becomes solid, without loose particles around. But it is not possible to analyze its physically stability; it needs more curing time to be completely dry.

Moreover, the presence of sodium is noted in all samples, regardless of the type of AAS used in the synthesis.

# 6.- Conclusions

As explained above, society and industrial development have increased the production of wastewater and hazardous industrial by-products that must be treated and reused in a sustainable way, with geopolymers being one of the possible options.

In this study, six geopolymers were synthesized using metakaolin, fly ash and blast furnace slag.

In the geopolymerization process was observed that fly Ash geopolymer required an external water source in the synthesis, as it became solid like rocks the first two times it was synthesized. In addition, it was corroborated that the longer geopolymers are subjected to a curing process, they become harder and with better mechanical properties.

In this case, all synthesized geopolymers were physically stable, but not all were chemically stable, as the conductivity value after each measurement increased for all samples analysed in different ways.

The most stable geopolymers were GP2 and GP6, with an 11,98% and 12,97% increase in conductivity with respect to the first measure, respectively. For GP3 and GP4, this increase was 43,33% and 36,08%, and for GP1 and GP5 was 96,39% and 63,88% respectively. That means that GP3 and GP4 were less stable than GP2 and GP6, and GP1 and GP5 were chemically unstable.

Adsorption experiments were carried out for the synthesized geopolymers as well as for the solid raw materials and was noticed that the geopolymerization process increases the ammonium removal efficiency and adsorption capacity of the raw materials.

The maximum removal efficiency and adsorption capacity of the samples analyzed has been achieved at low pH and high pH, i.e. pH 2 and pH 8 respectively.

GP1 has experienced the highest removal efficiency of all synthesized geopolymers, which was 27,12% at pH 2. At pH 6 and pH8, its removal efficiency was 19,85% and 18,89% respectively (still higher than the other removal efficiency obtained in the other materials). For GP2, GP3, GP5 and GP6 the highest removal efficiency at pH 8 was 14,53%, 2,37% 16,10% and 6,30% respectively. For GP4 the highest value was 8,42% at pH .

In Jarosite study it has been verified that the particle size of BFS has an important effect in the microstructure and properties of the geopolymer obtained; with BFS-Fine more physically stable geopolymers are obtained, hard and with good mechanical properties.

On the other hand, some of the samples have at the top of the solid material a white layer, as a result of the sodium presence, which tends to separate from the geopolymer matrix.

Of all synthesized samples, none of the Samples 1 of each synthesized geopolymer is physically stable. Samples which are more stable are Samples 3 and some of the Samples 2, thus the optimum recipe to obtain Jarosite stable geopolymers would be between these two compositions of reagents.

Even though some of the synthesized geopolymers have experienced ammonium adsorption and the performance of adsorption removal is not enough, so it is necessary to continue investing in research to find the optimal formulations for ammonium removal and also, to find a viable option for Jarosite.

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# APPENDIXES

## 1. Notation

The raw materials used in this research for the synthesis of geopolymers are expressed throughout the study by the acronyms RM 1, RM 2 and RM 3. Similarly, synthesized geopolymers are expressed as GP followed by a number, which refers to the sample of synthesized geopolymer. The raw materials used under these acronyms as well as the raw materials used to synthesize each geopolymer are shown in the following table.

*Table 1.* Notation for this study.

| **RM 1** | **RM 2** | **RM 3** | **GP1** | **GP2** | **GP3** | **GP4** | **GP5** | **GP6** |
|---|---|---|---|---|---|---|---|---|
| MK | FA | BFS | MK | FA | BFS | MK + FA | MK + BFS | BFS + FA |

## 2. Bibliographic Research for the Recipe

For the synthesis of geopolymers, first of all, a bibliographic research was carried out to get an idea of the order of magnitude of the composition used to obtain stable geopolymer matrices. The bibliographic research for each raw material source of aluminosilicates is shown below.

*Table 2. Bibliographic research for synthesize Metakaolin geopolymer.*

|  | **METAKAOLIN GEOPOLYMER** |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | **ALKALINE SOLUTION** |  | **RM + ALKALINE SOLUTION** |  | **OTHER CONDITIONS** | **REF[a].** |
|  | **REAGENTS** | **w/w** | **REAGENTS** | **w/w** |  |  |
| 1 | NaOH 10 M | 1:1 | MK | 1,3:1 | 15' Mix, 2' Vibrated, 25ºC, 3d | [13] |
|  | $Na_2SiO_3$ |  | AAS |  |  |  |
| 2 | NaOH 10 M | 1:1 | MK | 1,3:1 | 15' Mix, 2' Vibrated, 25ºC, 3d | [14] |
|  | $Na_2SiO_3$ |  | AAS |  |  |  |
| 3 | NaOH (s) | $Na_2O\cdot1{,}34SiO_2\cdot10{,}5H_2O$ | MK | 1,4:1 | 10' Mix; 800 rpm, 3% Photocatalitic element, 5' 1000 rpm | [33] |
|  | $Na_2SiO_3$ |  | AAS |  |  |  |
| 4 | NaOH 10 M | 1:1 | MK | 1,3:1 | 15' Mix, 2' Vibrated, 22ºC, 3d | [12] |
|  | $Na_2SiO_3$ |  | AAS |  |  |  |

[a] Ref. are shown in section 7 (References of Project Memory Document).

*Table 3. Bibliographic research for synthesize Fly Ash geopolymer.*

|  | **FLY ASH GEOPOLYMER** |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | **ALKALINE SOLUTION** |  | **RM + ALKALINE SOLUTION** |  | **OTHER CONDITIONS** | **REF[a].** |
|  | **REAGENTS** | **w/w** | **REAGENTS** | **w/w** |  |  |
| 1 | NaOH (s) | Na2O·0,7SiO2·10,5H20 | FA | 0,66:1 | 10'Mix, 800rpm, Elem. Fotocatal. 3% pes, 5' 1000rpm | [33] |
|  | Na2SiO3 |  | ALKALINE SOLUTION |  |  |  |

[a] Ref. are shown in section 7 (References of Project Memory Document).

*Table 4. Bibliographic research for synthesize Blast Furnace Slag geopolymer.*

| | BFS GEOPOLYMER | | | | | |
|---|---|---|---|---|---|---|
| | **ALKALINE SOLUTION** | | **RM + ALKALINE SOLUTION** | | **OTHER CONDITIONS** | **REF[a].** |
| | **REAGENTS** | **w/w** | **REAGENTS** | **w/w** | | |
| 1 | NaOH 10M<br>Na2SiO3 | 1:1 | BFS<br>ALKALINE SOLUTION | 3:2 | 15'Mix, 2'Vibrated, 25ºC, 3d | [13] |
| 2 | NaOH 10M<br>Na2SiO3 | 1:1 | BFS<br>ALKALINE SOLUTION | 3:2 | 15'Mix, 2'Vibrated, 25ºC, 3d | [14] |

[a] Ref. are shown in section 7 (References of Project Memory Document).

## 3. Preliminary Calculations

Several solutions for geopolymer synthesis and sorption experiments were prepared in the present research. Below are the mathematical operations that were carried out to know the theoretical quantity of each reagent that should be used to prepare the solutions. However, the experimental quantity used is not always is the same as the theoretical quantity. Thus, in the following sections, the real quantities used in each case are shown.

### 1- *Preparing NaOH 10 M solution:*

The operations carried out for calculating the amount of NaOH (s) that has to be added are:

$$[NaOH] = 10\frac{mole}{L}$$

$$n = \frac{m}{MW} \tag{1}$$

Where n=10 mol and MW is the NaOH Molecular Weight, which is 40,00 g·mole$^{-1}$. So, the amount of NaOH that has to be weight is:

$$\boxed{m_{NaOH} = 10\,mole \cdot 40{,}00\frac{g}{mole} = 400g}$$

### 2- *Preparing 500 ppm $NH_4^+$ solution:*

For preparing a 500 ppm $NH_4^+$ solution, it is needed the following amount of $NH_4Cl$:

The concentration of the solution is expressed in ppm, which means:

$$ppm = \frac{mg}{L}$$

$$[Sol] = 500ppm \rightarrow 0{,}5\,\frac{g}{L}$$

Mass concentration can be expressed as:

$$C = \frac{m}{V} \tag{2}$$

For adsorption experiments 40 mL are required for samples containing adsorbent doses (6 for GP and 3 for RM) and 25 mL for the non-absorbent; and the same, four times, for each pH condition studied. Therefore, a total of 1540 mL is required. However, 2L of the solution is going to be prepared for having enough solution in case needed.

Thus:

$$V_{sol} = 2L$$

$$m_{NH4} = C_{Sol} \cdot V_{Sol} = 1g$$

Using (1) and knowing that [$NH_4$] and [$NH_4Cl$] is 18,03846 g·mole$^{-1}$ and 53,4915 g·mole$^{-1}$ respectively, moles of $NH_4$ are:

$$n_{NH4} = \frac{m_{NH4}}{MW_{NH4}} = 0{,}055\ mole$$

According to the following expression, the theoretical amount of NH4Cl is:

$$n_{NH4} = n_{NH4Cl} \tag{3}$$

$$\boxed{m_{NH4Cl} = n_{NH4Cl} \cdot MW_{NH4Cl} = 2{,}965g}$$

3- *Preparing NaOH 8 M solution:*

In this case, the procedure is the same as for preparing NaOH 10 M solution. As the molarity of the 8M solution is lower, the amount of NaOH (s) to be used will be lower.

The operations carried out for calculating the amount of NaOH (s) that has to be added are:

$$[NaOH] = 8\frac{mole}{L}$$

$$n = \frac{m}{MW}$$

Where n=8 mole and M is the NaOH Molecular Weight, which is 40,00 g·mole$^{-1}$. So, the amount of NaOH that has to be weight is:

$$\boxed{m_{NaOH} = 8\ mole \cdot 40{,}00\frac{g}{mole} = 320g}$$

### 4- *Preparing LiCl 3 M solution:*

For preparing 100 mL of 3M LiCl solution, it is needed the following amount of LiCl (s):

$$3M = \frac{n_{LiCl}}{0{,}1L} \rightarrow n_{LiCl} = 0{,}3\, mole$$

$$m_{LiCl} = n_{LiCl} \cdot MW_{LiCl}$$

Where, the molecular weight for the LiCl is 42,39 g·mole$^{-1}$. So, the amount of LiCl that has to be weight is:

$$\boxed{m_{LiCl} = 0{,}3\, mole \cdot 42{,}39 \frac{g}{mole} = 12{,}717g}$$

## 4. Synthesis of Geopolymers

In this section, the experimental reagents amounts for preparing the solutions as well as the experimental results obtained are shown.

### *4.1 Preparing NaOH 10 M solution*

*Table 5.* Experimental amounts of each reagent to prepare NaOH 10M solution.

| | |
|---|---|
| **$V_{dis}$ (mL)** | 1000 |
| **$w_{NaOH}$ (g)** | 400 |

### *4.2 Preparing Alkaline Activating Solution*

*Table 6.* Experimental amount of each reagent used to prepare the alkaline activating solution.

| | |
|---|---|
| **$w_{NaOH\ 10\ M}$ (g)** | 30,06 |
| **$w_{Na2SiO3}$ (g)** | 29,95 |

### *4.3 Mixture*

Experimental amounts used in the synthesis of geopolymers:

*Table 7.* Experimental amount of each reagent in the synthesis of geopolymers.

| | $w_{RM}$ (g) | | $w_{AAS}$ (g) | $V_{H_2O}$ (mL) | $w_{MOLD}$ (g) | $w_{GP + MOLD}$ (g) | $w_{GP}$ (g) |
|---|---|---|---|---|---|---|---|
| **GP1** | 11,7030 | | 9,0055 | - | 10,5280 | 25,4438 | 14,9158 |
| **GP2[a]** | 11,7001 | | 9,0599 | 15 | 10,7498 | 44,5352 | 12,8693 |
| **GP2.1 (FAIL)** | 11,7100 | | 9,0096 | - | 11,1935 | 30,2684 | 19,0749 |
| **GP2.2 (FAIL)** | 7,6709 | | 5,8967 | - | 10,9226 | 23,7919 | 12,8693 |
| **GP3** | 11,7085 | | 9,0091 | - | 10,6638 | 30,0889 | 19,4251 |
| **GP4** | MK | FA | 9,0383 | - | 10,8699 | 29,5968 | 18,7269 |
| | 5,8612 | 5,8570 | | | | | |
| **GP5** | MK | BFS | 9,0009 | - | 10,9555 | 30,1321 | 19,1766 |
| | 5,8687 | 5,8528 | | | | | |
| **GP6** | BFS | FA | 9,0525 | - | 11,0779 | 29,7424 | 18,6645 |
| | 5,8603 | 5,8606 | | | | | |

[a] This is the GP2 sample. GP2.1 and GP2.2 are synthesized samples which did not have a geopolymer structure.

- *Composition:*

*Table 8.* Composition and weight ratio for each synthesized geopolymer.

| | % RM | | % AAS | w/w | |
|---|---|---|---|---|---|
| **GP1** | 56,5130 | | 43,4870 | 1,2995 | |
| **GP2[a]** | 32,7184 | | 25,3353 | 1,2914 | |
| **GP2.1 (FAIL)** | 56,5165 | | 43,4835 | 1,2997 | |
| **GP2.2 (FAIL)** | 56,5384 | | 43,4616 | 1,3009 | |
| **GP3** | 56,5148 | | 43,4852 | 1,2996 | |
| **GP4** | MK | FA | 43,5444 | $w_{RM}/w_{AAS}$ | $w_{MK}/w_{FA}$ |
| | 28,2379 | 28,2177 | | 1,2965 | 1,0007 |
| **GP5** | MK | BFS | 43,4356 | $w_{RM}/w_{AAS}$ | $w_{MK}/w_{BFS}$ |
| | 28,3206 | 28,2438 | | 1,3023 | 1,0027 |
| **GP6** | BFS | FA | 43,5774 | $w_{RM}/w_{AAS}$ | $w_{BFS}/w_{FA}$ |
| | 28,2106 | 28,2120 | | 1,2948 | 0,9999 |

[a] This is the GP2 sample. GP2.1 and GP2.2 are synthesized samples which did not have a geopolymer structure.

- *Alkaline Activating Solution 2:*

*Table 9.* Experimental amount of each reagent used to prepare the alkaline activating solution 2.

| | |
|---|---|
| $w_{NaOH\ 10\ M}$ (g) | 15,0305 |
| $w_{Na2SiO3}$ (g) | 15,0354 |

## 4.4 Casting and Curing

*Figure 1.* Aspect of a) GP4, b) GP5 New and c) GP6 once after mixing stage.

## 4.5 Crushing, Sieving, Washing and Drying

- ***Crushing:***

*Table 10.* Experimental amount of each reagent in the synthesis of GP5 New.

| | $w_{RM}$ (g) | | $w_{AAS}$ (g) | $w_{MOLD}$ (g) | $w_{GP + MOLD}$ (g) | $w_{GP}$ (g) |
|---|---|---|---|---|---|---|
| | MK | BFS | | | | |
| **GP5 New** | 5,8500 | 5,8505 | 9,0287 | 45,1813 | 58,6051 | 13,4238 |

- ***Sieving:***

*Table 11.* Total amount of geopolymer samples after sieving.

| | | **GP1** | **GP2** | **GP3** | **GP4** | **GP5 pure** | **GP5 imp** | **GP6** |
|---|---|---|---|---|---|---|---|---|
| **< 0,25 µm** | EMPTY TUBE | - | 11,6523 | 11,5307 | 11,5287 | 11,6668 | 11,6668 | 11,5712 |
| | TUBE + RM | - | 20,6435 | 12,4899 | 15,7029 | 13,8912 | 13,8912 | 15,9704 |
| | RM | - | 8,9912 | 0,9592 | 4,1742 | 2,2244 | 2,2244 | 4,3992 |
| **[0,25 µm - 1mm]** | EMPTY TUBE | 11,6403 | 11,5446 | 11,5748 | 11,5896 | 11,5743 | 11,5907 | 11,6609 |
| | TUBE + RM | 17,7126 | 16,0463 | 16,5989 | 17,3630 | 12,9516 | 18,4612 | 18,9621 |
| | RM | 6,0723 | 4,5017 | 5,0241 | 5,7734 | 1,3773 | 6,8705 | 7,3012 |
| **> 1 mm** | EMPTY TUBE | - | 11,5427 | 11,5596 | 11,5632 | 11,6668 | 11,6668 | 11,5851 |
| | TUBE + RM | - | 13,7052 | 19,8306 | 15,9260 | 13,8912 | 13,8912 | 13,3572 |
| | RM | - | 2,1625 | 8,2710 | 4,3628 | 2,2244 | 2,2244 | 1,7721 |

- *Washing:*

The variation of the pH samples as they were washed is shown below. The pH was not checked in all the washing times.

*Table 12.* Variation of the pH of the samples after washing.

| | | RM 1.1 | RM 1.2 | RM 2 | RM 3 | GP1 | GP2 | GP3 | GP4 | GP5 pure | GP5 imp | GP5 New | GP6 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **pH (time washed)** | **pH (1)** | 9,52 | 9,83 | 11,59 | 11,02 | 12,06 | 12,34 | 12,66 | 11,57 | 11,74 | 12,15 | 12,56 | 12,25 |
| | **pH (2)** | 9,10 | 9,33 | 10,46 | 10,56 | - | - | - | - | - | - | 12,52 | - |
| | **pH (3)** | 9,21 | 9,23 | 10,89 | 10,40 | 11,98 | 12,09 | 11,86 | 11,99 | 11,05 | 11,94 | 12,45 | 11,94 |
| | **pH (4)** | 10,00 | 10,14 | 11,34 | 11,29 | - | - | - | - | - | - | - | - |
| | **pH (5)** | 9,89 | 10,03 | 10,78 | 11,14 | - | - | - | - | - | - | - | - |
| | **pH (6)** | - | - | - | - | 11,69 | 11,68 | 11,57 | 11,74 | 11,27 | 11,64 | 12,29 | 11,55 |
| | **pH (9)** | - | - | - | - | 11,38 | 11,28 | 11,15 | 11,58 | 10,70 | 11,46 | 11,89 | 11,39 |
| | **pH (10)** | - | - | - | - | 11,58 | - | - | 11,73 | 11,58 | - | 11,85 | - |
| | **pH (15)** | - | - | - | - | 11,16 | 10,58 | 11,62 | 11,68 | 10,92 | 11,48 | 11,71 | 11,50 |
| | **pH (19)** | - | - | - | - | 11,42 | 11,34 | 11,61 | 11,57 | 10,46 | 11,32 | 11,63 | 11,47 |

- *Drying:*

*Table 13.* Amount of raw material and geopolymer samples after drying, expressed in grams (g).

| | RM 1.1 | RM 1.2 | RM 2 | RM 3 | GP1 | GP2 | GP3 | GP4 | GP5 pur | GP5 imp | GP6 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $w_{MOLD}$ | 65,2954 | 42,6608 | 65,5010 | 36,6013 | 42,9138 | 69,9852 | 70,6342 | 56,5190 | 17,3998 | 38,9260 | 78,7976 |
| $w_{WET}$ | 76,6948 | 52,9920 | 74,8203 | 59,7464 | 54,4446 | 79,1600 | 78,3933 | 54,4115 | 17,4498 | 49,7147 | 89,3345 |
| $w_{DRY}$ | 71,6234 | 48,1884 | 70,2168 | 52,2548 | 49,4758 | 73,0742 | 74,6932 | 50,0369 | 16,3026 | 45,0809 | 85,0525 |
| $w_{GP}$ | 6,3280 | 5,5276 | 4,7158 | 15,6535 | 6,5620 | 3,0890 | 4,059 | 6,4821 | 1,0972 | 6,1549 | 6,2549 |

*Figure 2.* Raw materials after dried.

## 5. Stability Test

*Table 14.* Conductivity results for the Raw Materials used in the geopolymerization and for the synthesized geopolymers.

| | **RM1** | **RM2** | **RM3** | **GP1** | **GP2** | **GP3** | **GP4** | **GP5** | **GP6** |
|---|---|---|---|---|---|---|---|---|---|
| **w GP (g)** | 1,0001 | 1,0002 | 1,0001 | 1,0004 | 1,0000 | 1,0004 | 1,0001 | 1,0004 | 1,0003 |
| **$\sigma_{2\,h}$ (µS/cm)** | 28,0 | 1147 | 48,5 | 332,0 | 186,2 | 129,7 | 413,0 | 587,0 | 171,1 |
| **$\sigma_{6\,h}$ (µS/cm)** | 36,8 | 1161 | 55,5 | 429,0 | 195,1 | 150,3 | 470,0 | 716,0 | 178,5 |
| **$\sigma_{24\,h}$ (µS/cm)** | 47,5 | 1197 | 77,1 | 652,0 | 208,5 | 185,9 | 562,0 | 962,0 | 193,3 |
| **$\sigma_{[2h-6h]}$ (µS/cm)** | 8,8 | 14 | 7 | 97 | 8,9 | 20,6 | 57 | 129 | 7,4 |
| **$\sigma_{[24h-2h]}$ (µS/cm)** | 19,5 | 50 | 28,6 | 320 | 22,3 | 56,2 | 149 | 375 | 22,2 |

As shown Table 14, the conductivity value for each sample has increased from the first measurement (after 2h) to the second measurement (after 6h) and to the last one (after 24 h) in:

*Table 15.* Percentage deviation between conductivity results after 2 and 24 h for each sample.

| | **RM1** | **RM2** | **RM3** | **GP1** | **GP2** | **GP3** | **GP4** | **GP5** | **GP6** |
|---|---|---|---|---|---|---|---|---|---|
| **Deviation 6-2 (%)** | 31,43 | 1,22 | 14,43 | 29,22 | 4,78 | 15,88 | 13,80 | 21,98 | 4,32 |
| **Deviation 24-2 (%)** | 69,64 | 4,36 | 58,97 | 96,39 | 11,98 | 43,33 | 36,08 | 63,88 | 12,97 |

## 6. Adsorption Experiments

### *6.1 Preparing 500 ppm $NH_4^+$ solution*

*Table 16.* Experimental amount for preparing 500 ppm of $NH_4^+$ solution.

| | |
|---|---|
| **$V_{dis}$ (mL)** | 2000 |
| **$w_{NH_4Cl}$ (g)** | 2,9679 |

### *6.2 Bibliographic Research for Adsorption Experiments*

*Table 17.* Bibliographic research for Adsorption experiments.

| | **Initial Solution pH[a]** | **Initial $NH_4^+$ (mg/L)** | **Adsorbent Dose (g/L)** | **Temp. (ºC)** | **Contact Time (h)** | **Particle size (micro m)** | **REF.** |
|---|---|---|---|---|---|---|---|
| 1 | 2, 3, 4, 5 | | 0,1 | 25 | 24 | | [1] |
| 2 | 4, 6, 8 | 50 | 5 | 22 | 24 | 63-125 | [12] |
| 3 | 4, 6, 8, 10 | | 5 | 20-23 | 24 | | [14] |

[a] Adjusted with 0,1 M NaOH or 0,1 M HCl.

### *6.3 Actual conditions in Adsorption Experiments*

*Table 18.* Conditions of adsorption experiments in this project.

| **Initial Solution pH[a]** | **Initial $NH_4^+$ (mg/L)** | **Adsorbent Dose (g/L)** | **Temp. (ºC)** | **Contact Time (h)** |
|---|---|---|---|---|
| 2, 4, 6, 8 | 500 | 5 | 25 | 4 |

### *6.4 Experimental Results*

In this section, the experimental results in the adsorption experiment for each raw material and each synthesized geopolymer are shown. The removal efficiency (RE) and adsorption capacity (q) were calculated using the following expressions:

$$RE(\%) = \frac{C_0 - C_t}{C_0} \cdot 100 \tag{4}$$

Where, "$C_0$" (mg·L$^{-1}$) is the initial concentration and "$C_t$" (mg·L$^{-1}$) is the concentration at time "t" (hours). Adsorption capacity at time t, "$q_t$" (mg·g$^{-1}$) was determined using Eq. (5):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \tag{5}$$

Where, "V"(L) is the volume of the studied solution and "m" (g) is the mass of the adsorbent.

In this case, the volume of the studied solution was 0,04L (constant value).

- *RM1:*

*Table 19.* Adsorption results for RM1.

| | WITHOUT ADSORBENT | | WITH ADSORBENT | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{RM1}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 295 | 0,2002 | 2,00 | 254 | 13,90 | 8,19 |
| **pH 4** | 4,00 | 293 | 0,2001 | 4,00 | 336 | -14,68 | -8,60 |
| **pH 6** | 6,01 | 275 | 0,2002 | 6,02 | 297 | -8,00 | -4,40 |
| **pH 8** | 8,00 | 413 | 0,2006 | 8,00 | 392 | 5,08 | 4,19 |

- *RM2:*

*Table 20.* Adsorption results for RM2.

| | WITHOUT ADSORBENT | | WITH ADSORBENT | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{RM2}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 295 | 0,2000 | 2,00 | 294 | 0,34 | 0,20 |
| **pH 4** | 4,00 | 293 | 0,2000 | 4,00 | 314 | -7,17 | -4,20 |
| **pH 6** | 6,01 | 393 | 0,2000 | 6,00 | 352 | 10,43 | 8,20 |
| **pH 8** | 8,00 | 413 | 0,2000 | 8,00 | 382 | 7,51 | 6,20 |

- *RM3:*

*Table 21*. Adsorption results for RM3.

| | **WITHOUT ADSORBENT** | | **WITH ADSORBENT** | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{RM3}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 295 | 0,2000 | 2,00 | 276 | 6,44 | 3,80 |
| **pH 4** | 4,00 | 293 | 0,2002 | 4,00 | 306 | -4,44 | -2,60 |
| **pH 6** | 6,00 | 285 | 0,2004 | 6,00 | 271 | 4,91 | 2,79 |
| **pH 8** | 8,00 | 270 | 0,2002 | 8,00 | 295 | -9,26 | -5,00 |

- *GP1:*

*Table 22*. Adsorption results for GP1.

| | **WITHOUT ADSORBENT** | | **WITH ADSORBENT** | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{GP1}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 295 | 0,2003 | 2,00 | 215 | 27,12 | 15,98 |
| **pH 4** | 4,02 | 296 | 0,2000 | 4,01 | 311 | -5,07 | 0,40 |
| **pH 6** | 6,03 | 393 | 0,2003 | 6,03 | 315 | 19,85 | 15,58 |
| **pH 8** | 8,00 | 413 | 0,2000 | 8,00 | 335 | 18,89 | 15,60 |

- *GP2:*

*Table 23*. Adsorption results for GP2.

| | **WITHOUT ADSORBENT** | | **WITH ADSORBENT** | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{GP2}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 295 | 0,2000 | 2,00 | 253 | 14,24 | 8,40 |
| **pH 4** | 4,01 | 296 | 0,2005 | 4,01 | 330 | -11,49 | -3,39 |
| **pH 6** | 6,01 | 393 | 0,2004 | 6,02 | 368 | 6,36 | 4,99 |
| **pH 8** | 8,00 | 413 | 0,2004 | 8,00 | 353 | 14,53 | 11,98 |

- *GP3:*

*Table 24*. Adsorption results for GP3.

| | **WITHOUT ADSORBENT** | | **WITH ADSORBENT** | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{GP3}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 295 | 0,2001 | 2,00 | 288 | 2,37 | 1,40 |
| **pH 4** | 4,01 | 296 | 0,2005 | 4,01 | 296 | 0,00 | 3,39 |
| **pH 6** | 6,01 | 393 | 0,2005 | 6,03 | 413 | -5,09 | -3,99 |
| **pH 8** | 8,00 | 270 | 0,2000 | 8,00 | 274 | -1,48 | -0,80 |

- *GP4:*

*Table 25*. Adsorption results for GP4.

| | WITHOUT ADSORBENT | | WITH ADSORBENT | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{GP4}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 295 | 0,2000 | 2,00 | 280 | 5,08 | 3,00 |
| **pH 4** | 4,01 | 296 | 0,2004 | 4,04 | 371 | -25,34 | -11,58 |
| **pH 6** | 6,00 | 285 | 0,2002 | 6,00 | 261 | 8,42 | 4,80 |
| **pH 8** | 8,00 | 270 | 0,2003 | 8,00 | 273 | -1,11 | -0,60 |

- *GP5:*

*Table 26.* Adsorption results for GP5.

| | WITHOUT ADSORBENT | | WITH ADSORBENT | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{GP5}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 304 | 0,2001 | 2,00 | 315 | -3,62 | -2,20 |
| **pH 4** | 4,01 | 359 | 0,2002 | 4,02 | 351 | 2,23 | 1,60 |
| **pH 6** | 6,01 | 321 | 0,2003 | 6,01 | 309 | 3,74 | 2,40 |
| **pH 8** | 8,01 | 292 | 0,2000 | 8,01 | 245 | 16,10 | 9,40 |

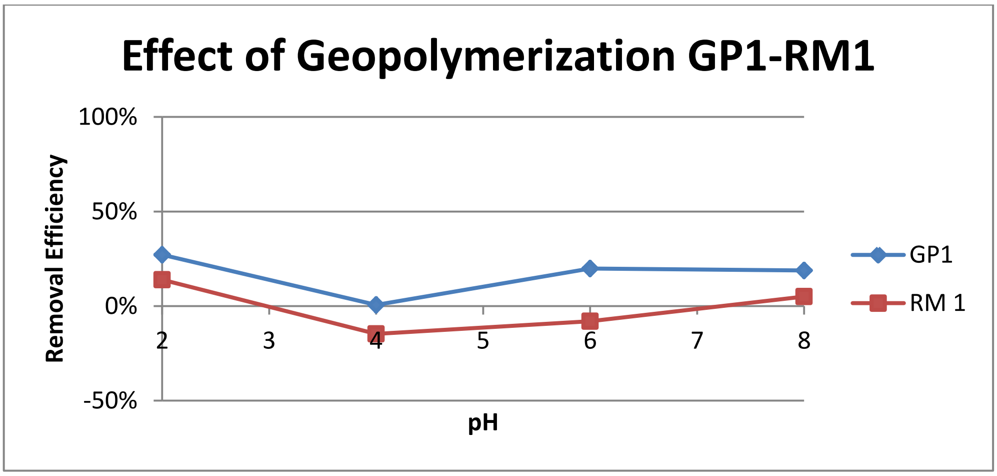
- *GP6:*

*Table 27.* Adsorption results for GP6.

| | WITHOUT ADSORBENT | | WITH ADSORBENT | | | | |
|---|---|---|---|---|---|---|---|
| | **pH** | **$[NH_4^+]$** | **$w_{GP6}$** | **pH** | **$[NH_4^+]$** | **RE (%)** | **$q_t$ (mg·L$^{-1}$)** |
| **pH 2** | 2,00 | 295 | 0,2000 | 2,00 | 305 | -3,39 | -2,00 |
| **pH 4** | 4,01 | 296 | 0,2003 | 4,01 | 343 | -15,88 | -5,99 |
| **pH 6** | 6,00 | 285 | 0,2002 | 6,00 | 294 | -3,16 | -1,80 |
| **pH 8** | 8,00 | 270 | 0,2000 | 8,00 | 253 | 6,30 | 3,40 |

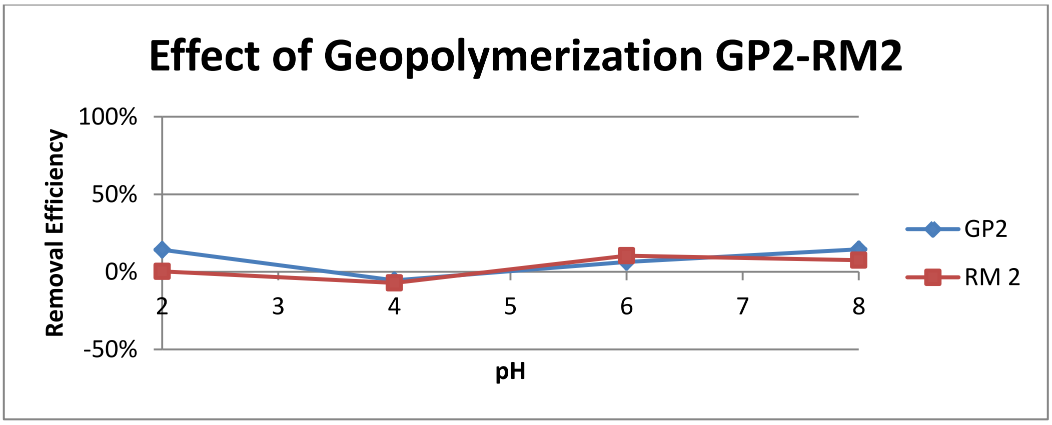
In the following graph, is compared the adsorption results in terms of removal efficiency at different pH conditions, for the Metakaolin raw material without being subjected to a geopolymerization process (RM1; red colour) with the geopolymer synthesized using Metakaolin as a solid aluminosilicate source in the synthesis (GP1; blue colour). It is also carried out for fly ash raw material (RM2) with GP2 and BFS raw material (RM3) with GP3, Graphs 2 and 3 respectively.

- *RM1 vs GP1:*



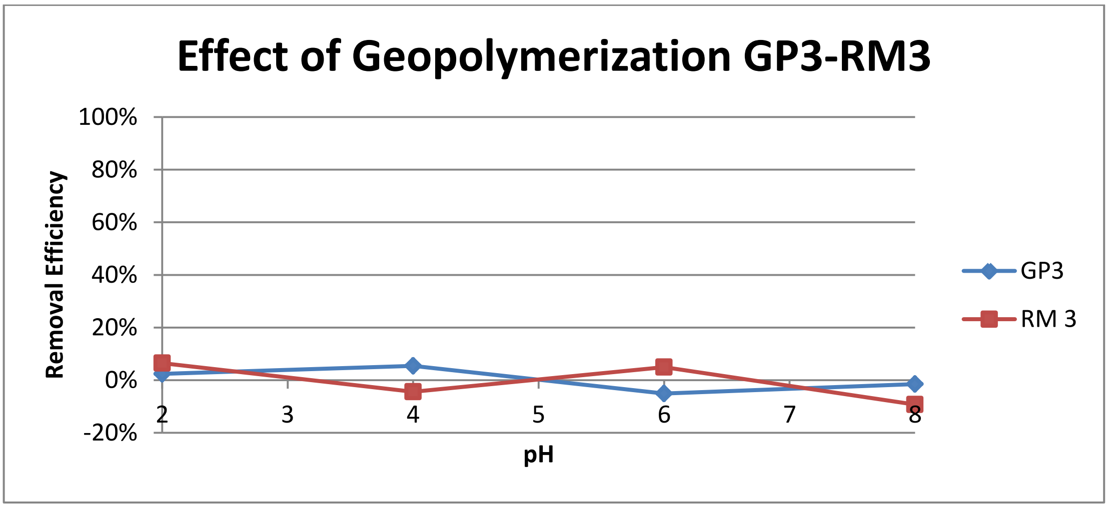
*Graph 1.* Effect of geopolymerization in adsorption experiments for RM1 and GP1.

- *RM2 vs GP2:*



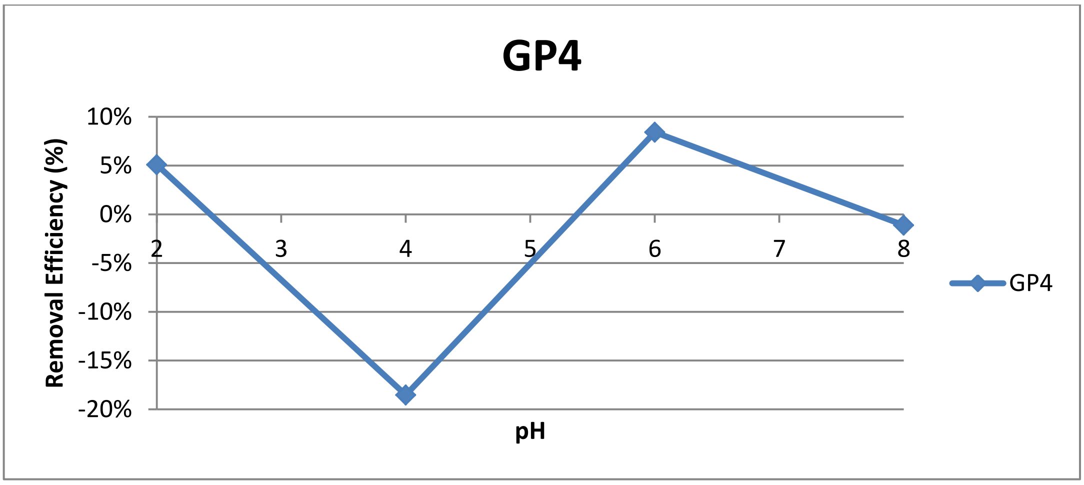
*Graph 2.* Effect of geopolymerization in adsorption experiments for RM2 and GP2.

- *RM3 vs GP3:*



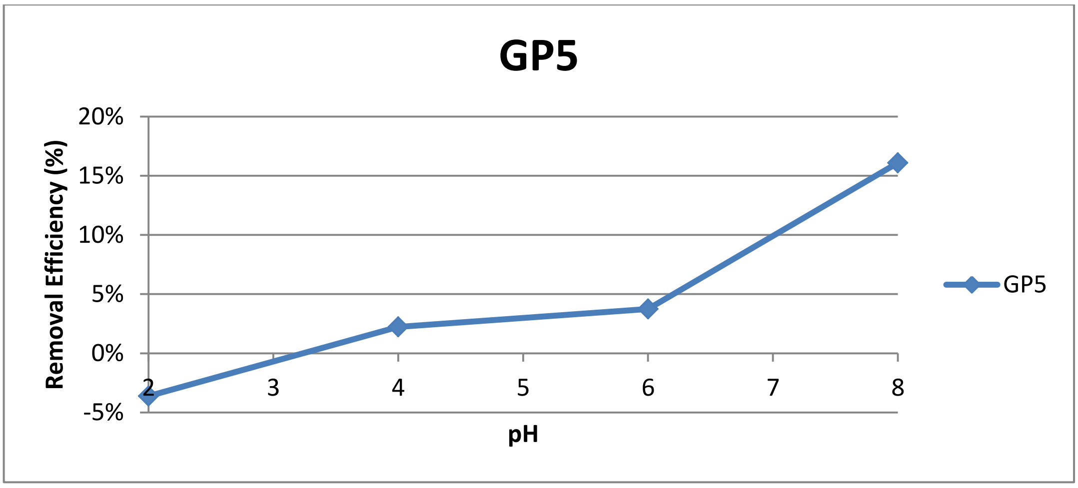
*Graph 3.* Effect of geopolymerization in adsorption experiments for RM3 and GP3.

- *GP4:*



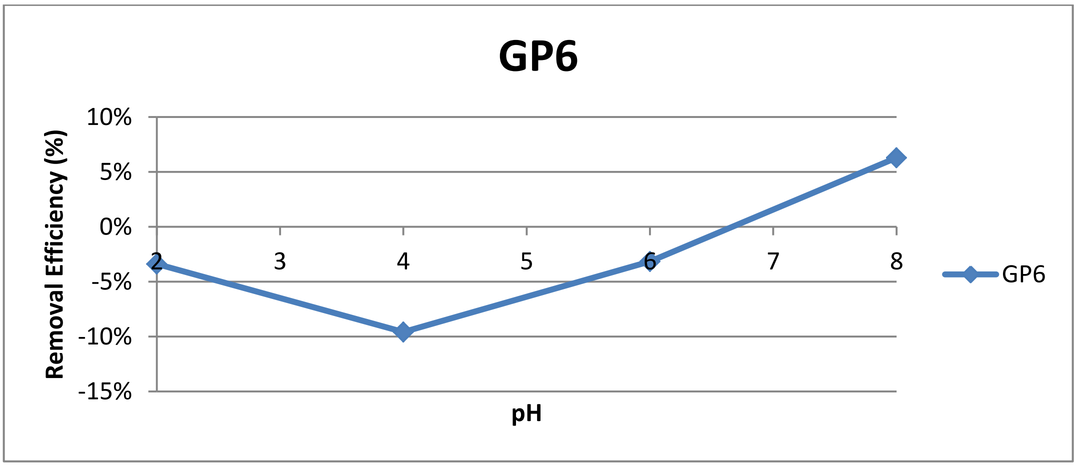
*Graph 4.* Removal efficiency of the GP4 at different pH.

- *GP5:*



*Graph 5.* Removal efficiency of the GP5 at different pH.

- *GP6:*



*Graph 6.* Removal efficiency of the GP6 at different pH.

## 7. Jarosite Study

For the Jarosite Study, a new alkaline activating solution had to be prepared. The experimental amount of each reagent used for that purpose is shown below.

*Table 28.* Experimental amount of each reagent used to prepare the alkaline activating solution 3.

| | |
|---|---|
| $w_{NaOH\ 10\ M}$ (g) | 75,02 |
| $w_{Na2SiO3}$ (g) | 75,02 |

### *7.1 Jarosite Study 1*

*Table 29.* Experimental quantities of each reagent in the synthesis of Jarosite geopolymer (Jarosite Study 1).

| | | $w_{RM}$ (g) | | $w_{Asol}$ (g) | $w_{Jarrosite}$ (g) | $V_{H2O}$ (mL) |
|---|---|---|---|---|---|---|
| **GP2 – FA** | 1 | 7,8000 | | 6,0464 | 7,8000 | 15 |
| | 2 | 9,1002 | | 7,0005 | 3,9029 | 15 |
| | 3 | 10,4001 | | 8,0073 | 1,6001 | 10 |
| **GP3 – GRANULATED BFS** | 1 | 7,8019 | | 6,0023 | 7,8001 | 15 |
| | 2 | 9,1685 | | 7,019 | 3,8925 | 10 |
| | 3 | 10,419 | | 8,0031 | 1,6001 | - |
| **GP3 – FINE BFS** | 1 | 7,8010 | | 6,0257 | 7,8248 | 10 |
| | 2 | 9,1017 | | 7,0063 | 3,9060 | 10 |
| | 3 | 10,4037 | | 8,0144 | 1,6118 | - |
| **GP 4 – MK+FA** | 1 | MK | FA | 6,0004 | 7,8000 | 10 |
| | | 3,9004 | 3,9008 | | | |
| | 2 | MK | FA | 7,0065 | 3,9008 | 10 |
| | | 4,5500 | 4,5500 | | | |
| | 3 | MK | FA | 8,0264 | 1,6008 | 5 |
| | | 5,2001 | 5,2003 | | | |
| **GP 6 – FA + GRANULATED BFS** | 1 | BFS | FA | 6,0031 | 7,8054 | 5 |
| | | 3,9011 | 3,9035 | | | |
| | 2 | BFS | FA | 7,0025 | 3,9020 | 10 |
| | | 4,5575 | 4,5529 | | | |
| | 3 | BFS | FA | 8,0006 | 1,6472 | 5 |
| | | 5,2003 | 5,2006 | | | |
| **GP 6 – FA + FINE BFS** | 1 | BFS | FA | 6,0183 | 7,8081 | 10 |
| | | 3,9002 | 3,9003 | | | |
| | 2 | BFS | FA | 7,0282 | 3,9005 | 10 |
| | | 4,9336 | 4,9324 | | | |
| | 3 | BFS | FA | 8,0081 | 1,6003 | - |
| | | 5,2333 | 5,2026 | | | |
| | 2’ | BFS | FA | 7,0086 | 3,9960 | 5drops |
| | | 9,1004 | - | | | |

- *GP2:*

Aspect of the GP2 samples at different curing times:

*Figure 3.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 once they were synthesized.

*Figure 4.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 (3rd curing day).

*Figure 5.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 (6th curing day).

*Figure 6.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 (12th curing day).

*Figure 7.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 (14th curing day).

*Figure 8.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 (18th curing day).

*Figure 9.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 (35th curing day).

*Figure 10.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 (40th curing day).

Figure 11. From left to right, aspect of the samples 1, 2 and 3 of the GP2 before crushed (42th curing day).

*Figure 12.* From left to right, aspect of the samples 1, 2 and 3 of the GP2 after crushing (physical stability test; 42th curing day).

Figure 13. Enlarged photo of the aspect of the sample 1 of GP2 after crushed (physical stability test; 42th curing day).

- *GP3 -Granulated:*

Aspect of the GP3 - Granulated samples at different curing times:

*Figure 14.* Aspect of the sample 3 of the GP3-Granulated once synthesized.

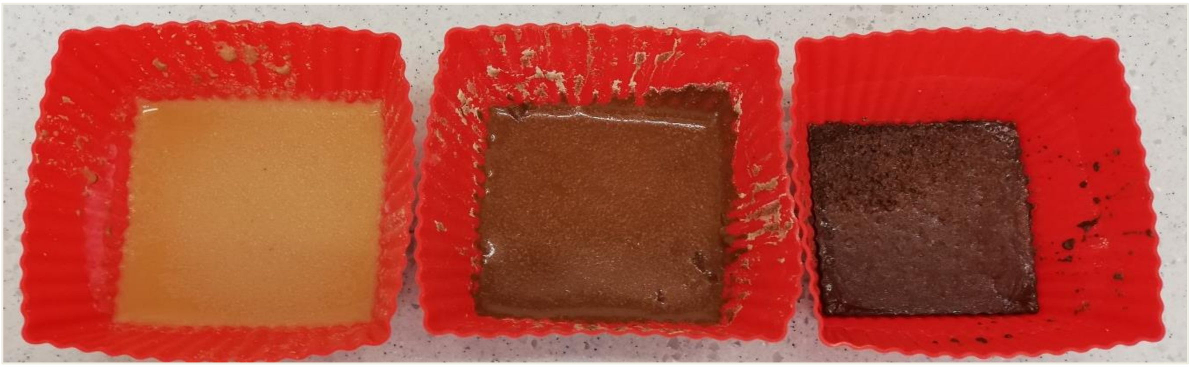


*Figure 15*. From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated. For the sample 1 and 2, aspect after being synthesized. For sample 3, aspect after 20 h of synthesis.

*Figure 16.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated after being one day curing.

*Figure 17.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated (2nd curing day).

*Figure 18.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated (6th curing day).

*Figure 19.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated (8th curing day).

*Figure 20.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated (12th curing day).

*Figure 21.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated (29th curing day**).**

*Figure 22.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated (34th curing day).

*Figure 23.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated (36th curing day).

*Figure 24.* Aspect of the sample 1 of GP3-Granulated. Geopolymer no homogeneous (36th curing day).

*Figure 25.* Aspect of the sample 3 of GP3-Granulated. (36th curing day).

*Figure 26.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Granulated after crushing (physical stability test; 36th curing day).

- *GP3 –Fine:*

Aspect of the GP3-Fine samples at different curing times:

*Figure 27.* Aspect of the sample 3 of the GP3-Fine once synthesized.

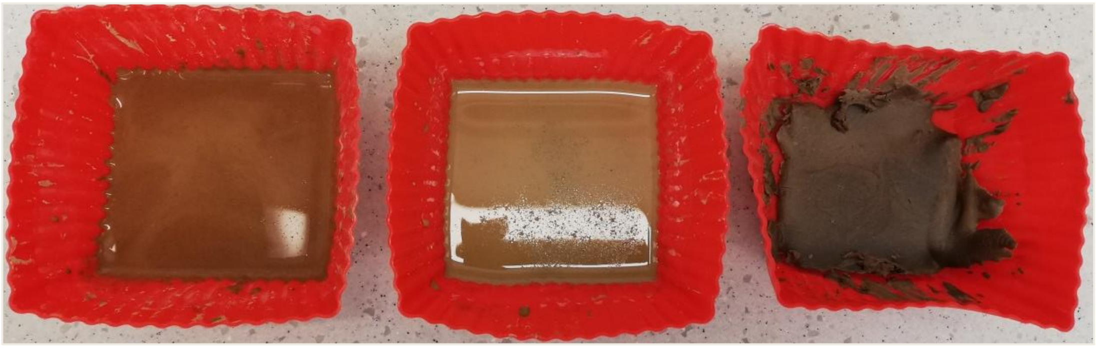


*Figure 28.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine**.** For the sample 1 and 2, aspect after being synthesized. For sample 3, aspect after 2 h of synthesis.

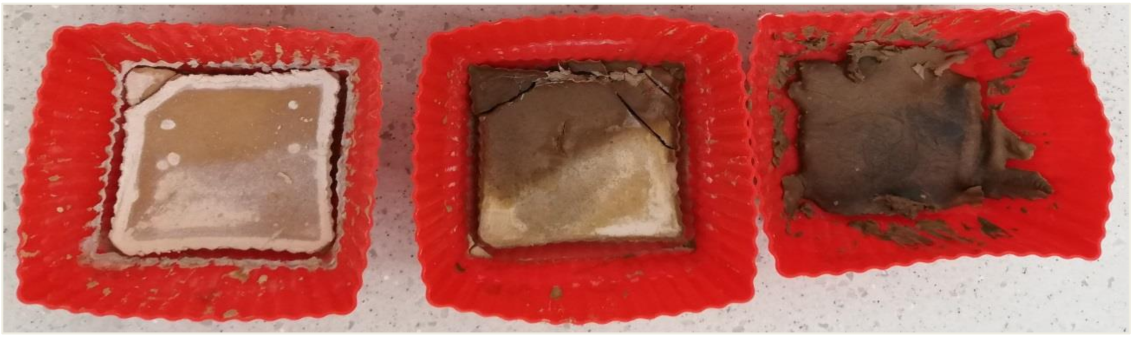


*Figure 29.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine after being one day curing.

*Figure 30.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine (2nd curing day).

*Figure 31.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine (6th curing day).

*Figure 32.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine (8th curing day).

*Figure 33.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine (12th curing day).

*Figure 34.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine (29th curing day).

*Figure 35.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine (34th curing day).

*Figure 36.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine (36th curing day).

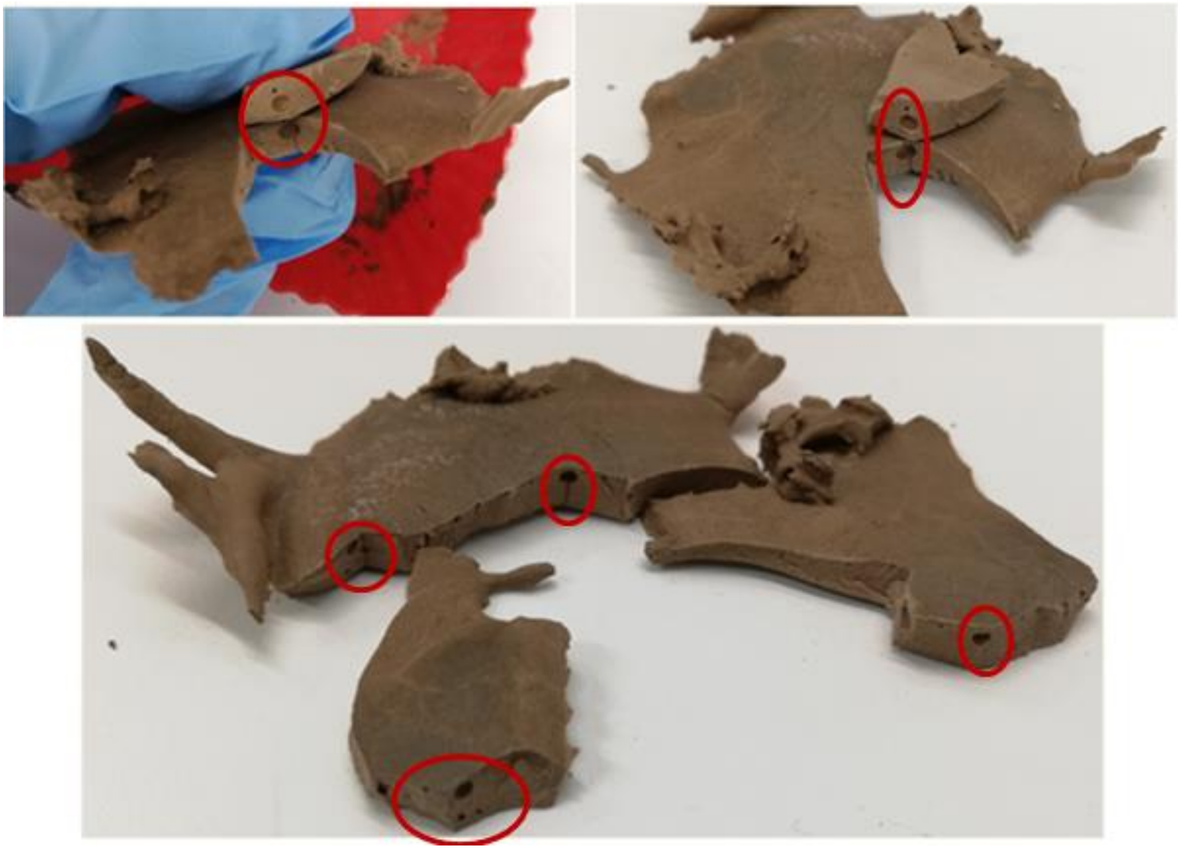


*Figure 37.* Aspect of the sample 3 of the GP3-Fine (36th curing day). Rupture due to imperfections (porous) in the geopolymer matrix.

*Figure 38.* From left to right, aspect of the samples 1, 2 and 3 of the GP3-Fine after crushing (physical stability test; 36th curing day).

- *GP4:*

Aspect of the GP4 samples at different curing times:

*Figure 39*. From left to right, aspect of the samples 1, 2 and 3 of the GP4 once they were synthesized.

*Figure 40.* From left to right, aspect of the samples 1, 2 and 3 of the GP4 after one day curing.

*Figure 41.* From left to right, aspect of the samples 1, 2 and 3 of the GP4 (5th curing day).

*Figure 42.* From left to right, aspect of the samples 1, 2 and 3 of the GP4 (7th curing day).

*Figure 43.* From left to right, aspect of the samples 1, 2 and 3 of the GP4 (11th curing day).

*Figure 44.* From left to right, aspect of the samples 1, 2 and 3 of the GP4 (28th curing day).

*Figure 45.* From left to right, aspect of the samples 1, 2 and 3 of the GP4 (33th curing day).

*Figure 46.* Aspect of the sample 1 of the GP4 (35th curing day).

*Figure 47.* Aspect of the sample 3 of the GP4 (35th curing day).

*Figure 48.* From left to right, aspect of the samples 1, 2 and 3 of the GP4 after crushing (physical stability test; 35th curing day).

- *GP6 – Granulated:*

Aspect of the GP6-Granulated samples at different curing times:

*Figure 49.* Aspect of the sample 3 of the GP6-Granulated once synthesized.

*Figure 50.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 after synthesis. Sample 3 after 1 curing day.

*Figure 51.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 on the 3rd curing day. Sample 3 on the 4th curing day.

*Figure 52.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 on the 5th curing day. Sample 3 on the 6th curing day.

*Figure 53.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 on the 6th curing day. Sample 3 on the 7th curing day.

*Figure 54.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 on the 10th curing day. Sample 3 on the 11th curing day.

*Figure 55.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 on the 27th curing day. Sample 3 on the 28th curing day.

*Figure 56.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 on the 27th curing day. Sample 3 on the 28th curing day (1).

*Figure 57.* Aspect of the sample 3 of GP6-Granulated on the 28th curing day.

*Figure 58.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated. Samples 1 and 2 on the 32th curing day. Sample 3 on the 33th curing day.

*Figure 59.* Aspect of sample 2 of GP6-Granulated after crushing (34th curing day). Structure no uniform of the geopolymer.

*Figure 60.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated after crushing (physical stability test). Samples 1 and 2 on the 34th curing day. Sample 3 on the 35th curing day.

- *GP6 –Fine:*

Aspect of the GP6-Fine samples at different curing times:

*Figure 61.* From left to right aspect of the sample 3 and 2 of the GP6-Fine once synthesized.

*Figure 62.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 and 2 after 1 h of the synthesis. Sample 3 after one day curing.

*Figure 63.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Samples 1 and 2 on the 1st curing day. Sample 3 on the 2nd curing day.

*Figure 64.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 and 2 on the 4th curing day. Sample 3 on the 5th curing day.

*Figure 65.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 and 2 on the 5th curing day. Sample 3 on the 6th curing day.

*Figure 66.* From left to right, aspect of the sample 1, 2, 2’ and 3 of GP6-Fine. Sample 1, 2 and 2’ on the 7th curing day. Sample 3 on the 8th curing day.

*Figure 67.* From left to right, aspect of the sample 1, 2, 2’ and 3 of GP6-Fine. Sample 1, 2 and 2’ on the 27th curing day. Sample 3 on the 28th curing day.

*Figure 68.* From left to right, aspect of the sample 1, 2, 2’ and 3 of GP6-Fine after crushing (physical stability test). Sample 1 and 2 on the 33th curing day. Sample 3 on the 35th curing day.

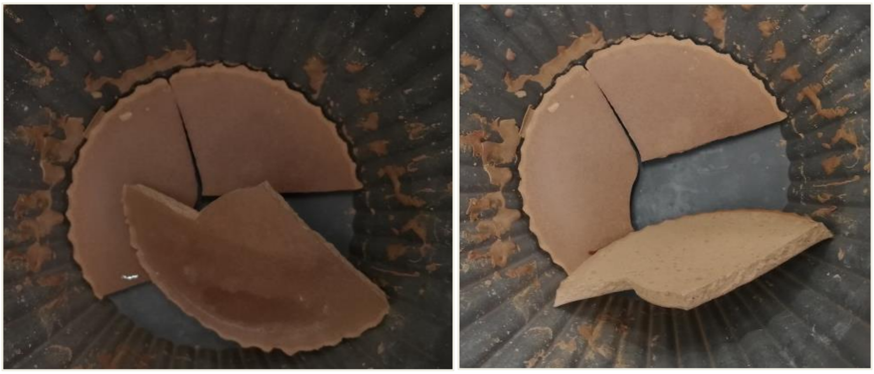


*Figure 69*. Aspect of the sample 2' of the GP6-Fine after crushing (33th curing day).

## *7.2 Study 2*

*Table 30.* Experimental quantities of each reagent in the synthesis of Jarosite geopolymer (Jarosite Study 2).

| | | $w_{RM}$ (g) | | $w_{Asol}$ (g) | $w_{Jarrosite}$ (g) | $V_{H2O}$ (mL) |
|---|---|---|---|---|---|---|
| **GP2 (FA)** | 1 | 7,8000 | | 6,0004 | 7,8002 | 10 |
| | 2 | 9,1001 | | 7,0016 | 3,9004 | 8 mL + 10 drops |
| | 3 | 10,4006 | | 8,0021 | 1,6007 | 5 |
| | 4 | 7,9067 | | 7,0008 | 7,8003 | 6 mL + 20 drops |
| **GP3 (FINE BFS)** | 1 | 7,8000 | | 6,0007 | 7,8000 | 5 |
| | 2 | 9,1000 | | 7,0008 | 3,9002 | 5 |
| | 3 | 10,4002 | | 8,0040 | 1,6001 | - |
| | 4 | 9,1000 | | 7,0007 | 3,0974 | 5 |
| **GP3 (GRANULATED BFS)** | 1 | 7,8059 | | 6,0003 | 7,8059 | 5 |
| | 2 | 9,1122 | | 7,0004 | 3,9004 | 3 |
| | 3 | 10,4007 | | 8,0001 | 1,6001 | 30 drops |
| | 4 | 9,4460 | | 7,0012 | 9,3 | 3 |
| | 5 | 9,1231 | | 7,0001 | 4,5649 | - |
| **GP4 (MK + FA)** | 1 | **MK** | **FA** | 6,0001 | 7,8002 | 10 |
| | | 3,9005 | 3,9002 | | | |
| | 2 | **MK** | **FA** | 7,0008 | 3,9000 | 8 |
| | | 4,5500 | 4,5500 | | | |
| | 3 | **MK** | **FA** | 8,0001 | 1,6159 | 5 |
| | | 5,2005 | 5,2000 | | | |
| | 4* | **MK** | **FA** | 6,0001 + 5mL | 7,8002 | 3 mL + 7 drops |
| | | 3,9002 | 3,9004 | | | |
| **GP6 (FA + FINE BFS)** | 1 | **FA** | **BFS** | 6,0008 | 7,8006 | 5 |
| | | 3,9006 | 3,9002 | | | |
| | 2 | **FA** | **BFS** | 7,0000 | 3,9000 | 5 |
| | | 4,5502 | 4,5506 | | | |
| | 3 | **FA** | **BFS** | 8,0000 | 1,6000 | - |
| | | 5,2000 | 5,2000 | | | |
| **GP6 (FA + GRANULATED BFS)** | 1 | **FA** | **BFS** | 6,0012 | 7,8005 | 3 + 4 drops |
| | | 3,9016 | 3,9013 | | | |
| | 2 | **FA** | **BFS** | 7,0004 | 3,9003 | 3 |
| | | 4,5505 | 4,6195 | | | |
| | 3 | **FA** | **BFS** | 8,0008 | 1,6025 | - |
| | | 5,2015 | 5,2020 | | | |

- *GP2:*

Aspect of the GP2 samples at different curing times:

*Figure 70*. From left to right, aspect of the samples 1, 2 and 3 of the GP2 once synthesized (Study 2).

Figure 71. From left to right, aspect of the sample 1, 2, 3 and 4 of GP2. Sample 1, 2 and 4 after one curing day. Sample 3 on the 3rd curing day (Study 2).

*Figure 72*. From left to right, aspect of the sample 1, 2, 3 and 4 of GP2. Sample 1, 2 and 4 on the 22th curing day. Sample 3 on the 24th curing day (Study 2).

*Figure 73*. Aspect of the sample 2 of GP2 (22th curing day).

*Figure 74.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP2. Sample 1, 2 and 4 on the 27th curing day. Sample 3 on the 29th curing day (Study 2).

*Figure 75.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP2. Sample 1, 2 and 4 on the 29th curing day. Sample 3 on the 31th curing day (Study 2).

*Figure 76.* Aspect of the sample 1, 2, 3 and 4 of GP2 after crushing (physical stability test). Sample 1, 2 and 4 on the 29th curing day. Sample 3 on the 31th curing day (Study 2).

Figure 77. From left to right, aspect of the sample 1 and 2 of GP2 on the 29th curing day after crushing (Study 2).

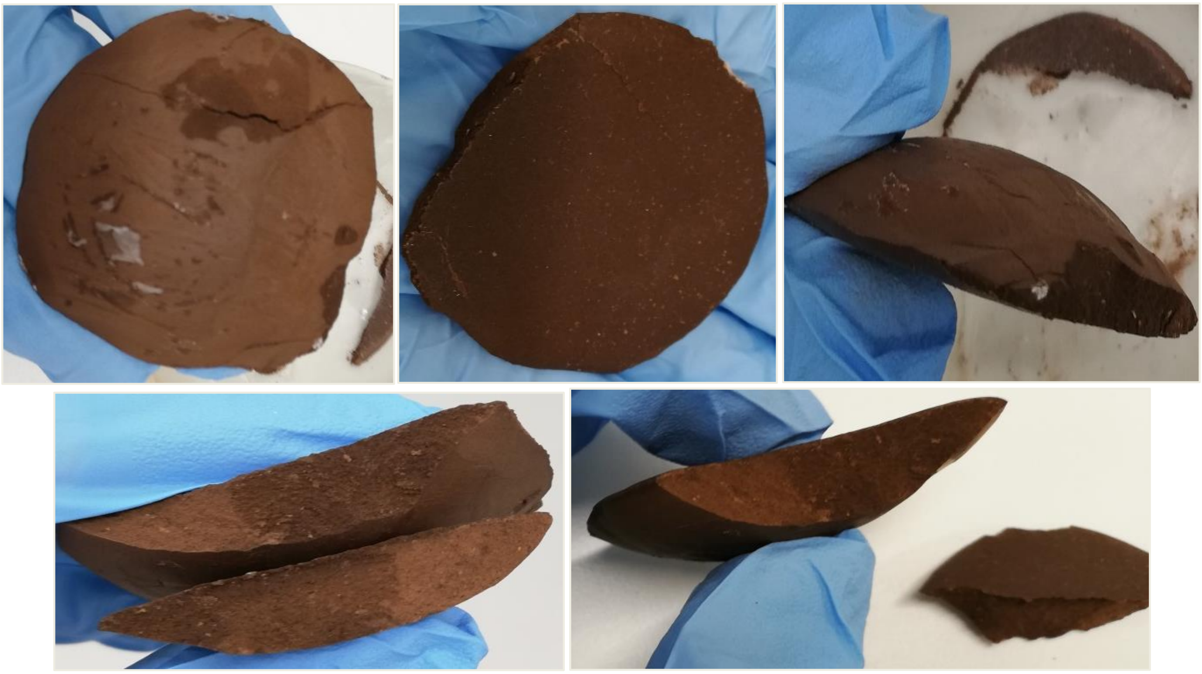


*Figure 78.* Aspect of the sample 3 on the 31th curing day after crushing (Study 2).

- *GP3 – Granulated:*

Aspect of the GP3-Granulated samples at different curing times:

*Figure 79.* From left to right, aspect of the sample 1, 2, 3, 4 and 5 of GP3-Granulated once synthesized (Study 2).

*Figure 80*. From left to right, aspect of the sample 1, 2, 3, 4 and 5 of GP3-Granulated (21th curing day). (Study 2).

*Figure 81.* From left to right, aspect of the sample 1, 2, 3, 4 and 5 of GP3-Granulated (26th curing day). (Study 2).

*Figure 82*. From left to right, aspect of the sample 1, 2, 3, 4 and 5 of GP3-Granulated after crushing (28th curing day). (Study 2).

*Figure 83.* Aspect of the sample 1 and 2 of GP3-Granulated once crushed (enlarged photo).

Figure 84. Aspect of the sample 3, 4 and 5 of GP3-Granulated once crushed (enlarged photo).

- *GP3 – Fine:*

Aspect of the GP3-Fine samples at different curing times:

*Figure 85.* Aspect of the sample 3 of the GP3-Fine once synthesized.

*Figure 86.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP3-Fine once synthesized. Sample 3 on the 3rd curing day (Study 2).

*Figure 87.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP3-Fine. Sample 1, 2 and 4 on the 24th curing day; sample 3 on the 27th curing day (Study 2).

*Figure 88.* Aspect of the sample 2 of GP3-Fine (24th curing day).

*Figure 89.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP3-Fine. Sample 1, 2 and 4 on the 29th curing day; sample 3 on the 32th curing day (Study 2).

*Figure 90.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP3-Fine after crushing (physical stability test). Sample 1, 2 and 4 on the 31th curing day; sample 3 on the 34th curing day (Study 2).

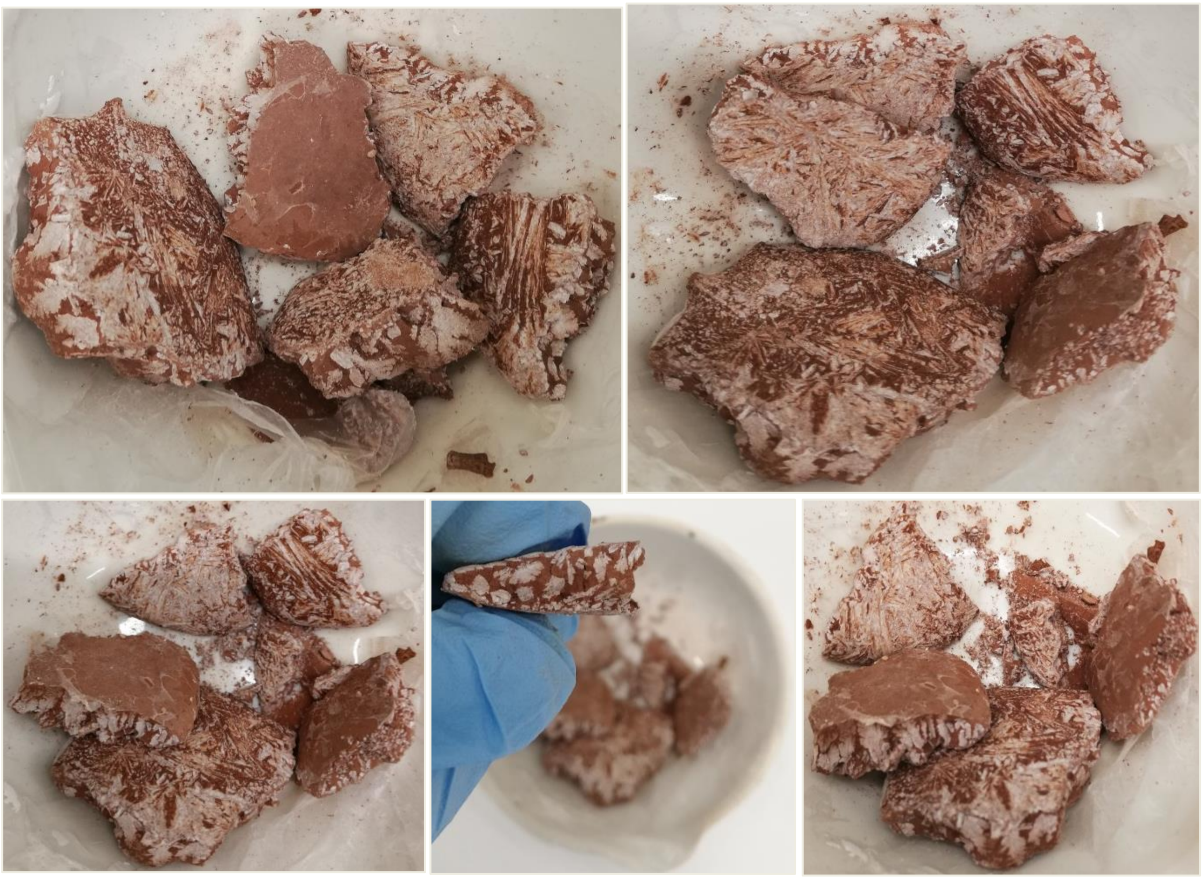


*Figure 91.* Aspect of the sample 2 of GP3-Fine once crushed (enlarged photo).

*Figure 92.* Aspect of the sample 3 of GP3-Fine after the physical stability test (enlarged photo).

*Figure 93.* Aspect of the sample 1 of GP3-Fine once crushed (enlarged photo).

*Figure 94.* Aspect of the sample 4 of GP3-Fine once crushed (enlarged photo).

- *GP4:*

Aspect of the GP4 samples at different curing times:

*Figure 95.* Aspect of the sample 3 of the GP4 once synthesized (Study 2).

*Figure 96.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP4 once synthesized. Sample 3 on the 3rd curing day (Study 2).

*Figure 97.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP4. Sample 1, 2 and 4 on the 24th curing day; sample 3 on the 27th curing day (Study 2).

*Figure 98.* Aspect of the sample 2 of GP4 (24th curing day).

*Figure 99.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP4. Sample 1, 2 and 4 on the 29th curing day; sample 3 on the 31th curing day (Study 2).

*Figure 100*. From left to right, aspect of the sample 1, 2, 3 and 4 of GP4 before crushing (physical stability test). Sample 1, 2 and 4 on the 31th curing day; sample 3 on the 33th curing day (Study 2).

*Figure 101.* From left to right, aspect of the sample 1, 2, 3 and 4 of GP4 after crushing (physical stability test). Sample 1, 2 and 4 on the 31th curing day; sample 3 on the 33th curing day (Study 2).

*Figure 102.* Aspect of the sample 3 of GP4 once crushed (enlarged photo).

- *GP6 – Granulated:*

Aspect of the GP6-Granulated samples at different curing times:

*Figure 103.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated once synthesized (Study 2).

*Figure 104.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated after one day curing (Study 2).

*Figure 105.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated on the 22th curing day (Study 2).

*Figure 106.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated on the 27th curing day (Study 2).

*Figure 107.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated before crushing (physical stability test) on the 29th curing day (Study 2).

*Figure 108.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Granulated after crushing (physical stability test) on the 29th curing day (Study 2).

*Figure 109.* Aspect of the sample 2 of GP4 once crushed (enlarged photo).

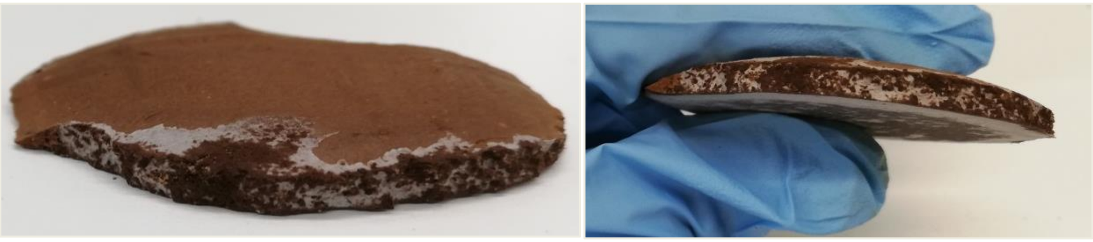


*Figure 110.* Aspect of the sample 3 of GP4 after physical stability test (enlarged photo).

- *GP6 – Fine:*

Aspect of the GP2 samples at different curing times:

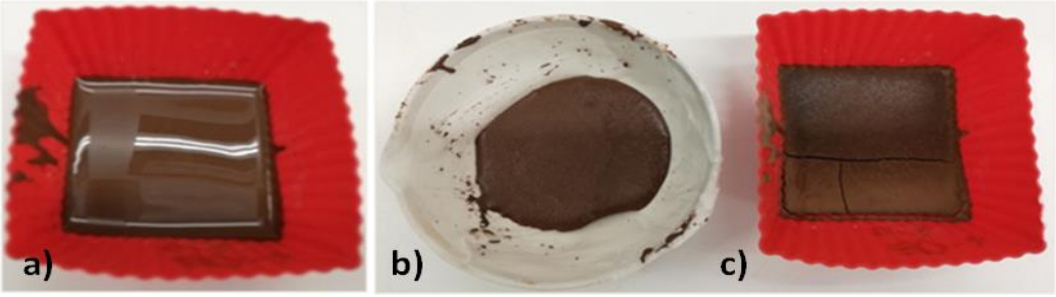


*Figure 111.* a) Aspect of the sample a) 3 of the GP6-Fine and b) 2 of the GP6-Fine once synthesized. c) Aspect of the sample 3 of GP6-Fine in the 3rd curing day.

*Figure 112.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 once synthesize; sample 2 on the 3rd curing day; sample 3 on the 6th curing day (Study 2).

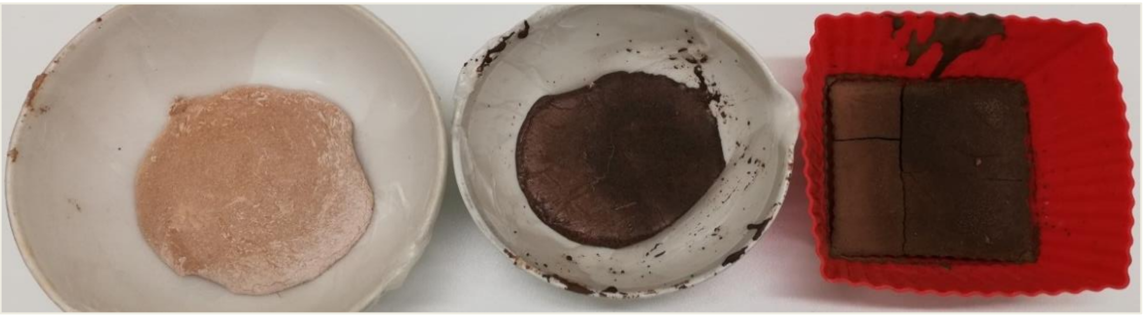


*Figure 113.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 on the 21th curing day; sample 2 on the 24th curing day; sample 3 on the 27th curing day (Study 2).

*Figure 114.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine. Sample 1 on the 29th curing day; sample 2 on the 32nd curing day; sample 3 on the 35th curing day (Study 2).

*Figure 115.* From left to right, aspect of the sample 1, 2 and 3 of GP6-Fine after crushing (physical stability test). Sample 1 on the 31th curing day; sample 2 on the 34th curing day; sample 3 on the 37th curing day (Study 2).

- ***All GP samples (Study 2):***

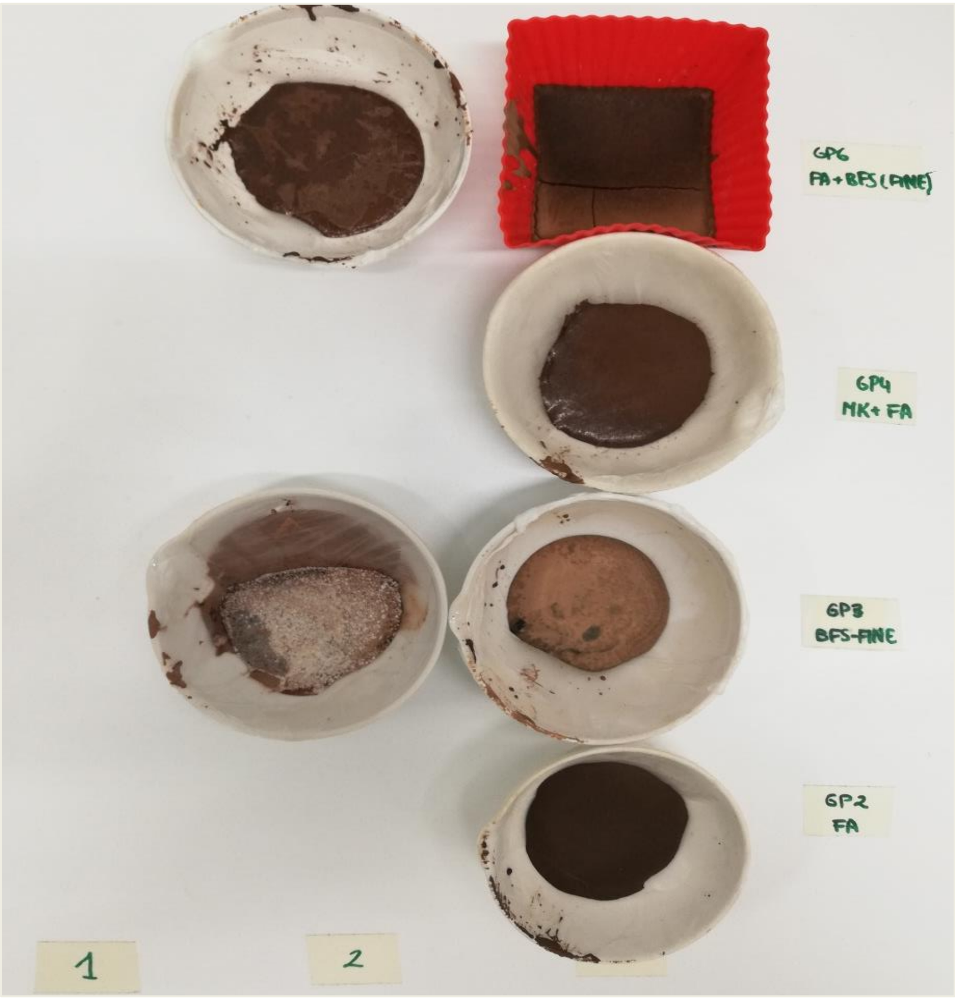


*Figure 116.* Samples in its 1st curing day unless GP6 sample 3, which is on the 4th curing day (Study 2).

*Figure 117.* All Study 2 geopolymer samples once synthesized. 2nd curing day for GP2-3, GP3-Fine-3, GP4-3 and GP6-Fine-2. 6th curing day for GP6-Fine-3.

*Figure 118.* All Study 2 geopolymer samples in its 4th curing day unless: GP2-3, GP3-Fine-3, GP4-3 and GP6-Fine-2 (6th curing day) and GP6-Fine-3 (10th curing day).

## *7.3 Jarosite Study 1*

The experimental results for Jarosite Study 1 are shown below.

- Study 3-1

*Table 31.* Experimental quantities of each reagent in the synthesis of Jarosite geopolymer (Jarosite Study 3-1).

| | $w_{ASol}$ (g) | $w_{RM}$ (g) | $w_{Mold}$ (g) | $V_{H2O}$ (mL) |
|---|---|---|---|---|
| **NaOH 8M** | 4,5000 | 20,5000 | 38,6312 | 10 |
| **NaOH 8M + $Na_2SiO_3$** | 4,5000 | 20,5000 | 40,0410 | 10 |

Aspect of the Study 3-1 samples at different curing times:

*Figure 119.* Aspect of the Jarosite Study 3-1 geopolymer once synthesized.

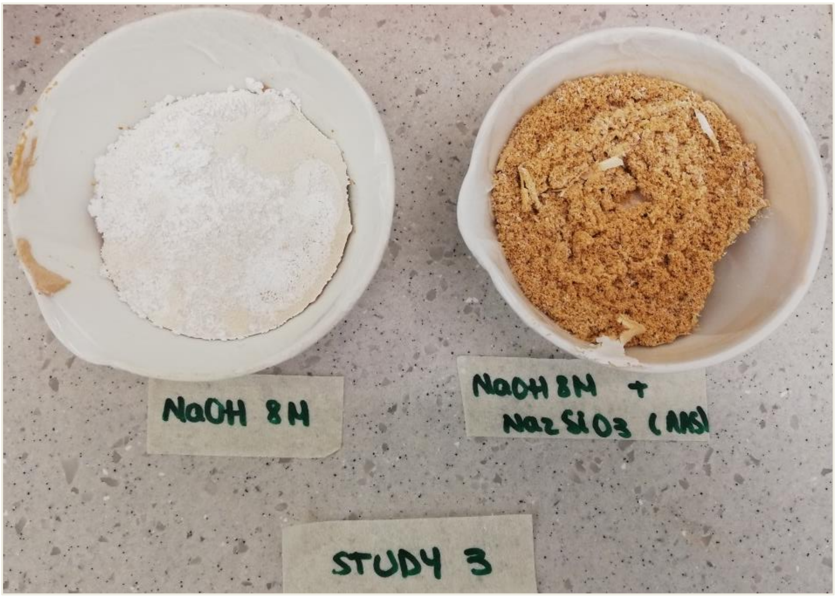


*Figure 120.* Aspect of the Jarosite Study 3-1 geopolymer on the 4th curing day.

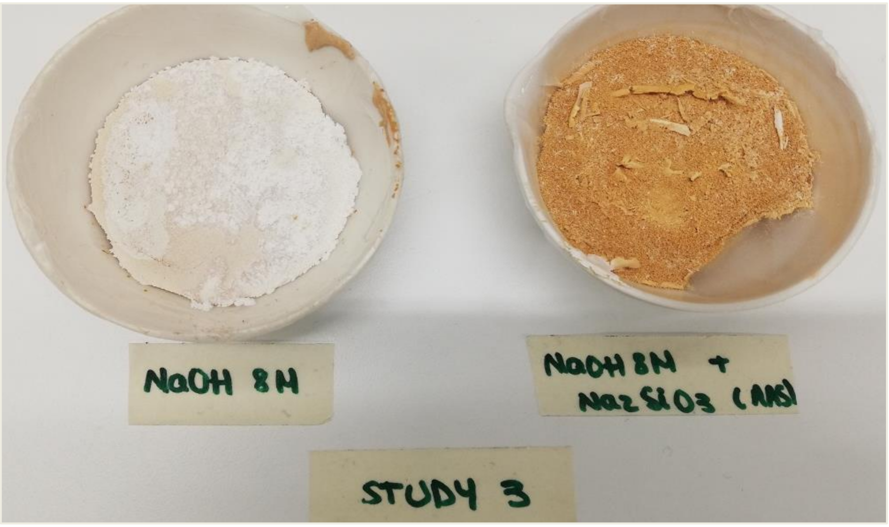


*Figure 121.* Aspect of the Jarosite Study 3-1 geopolymer on the 8th curing day.

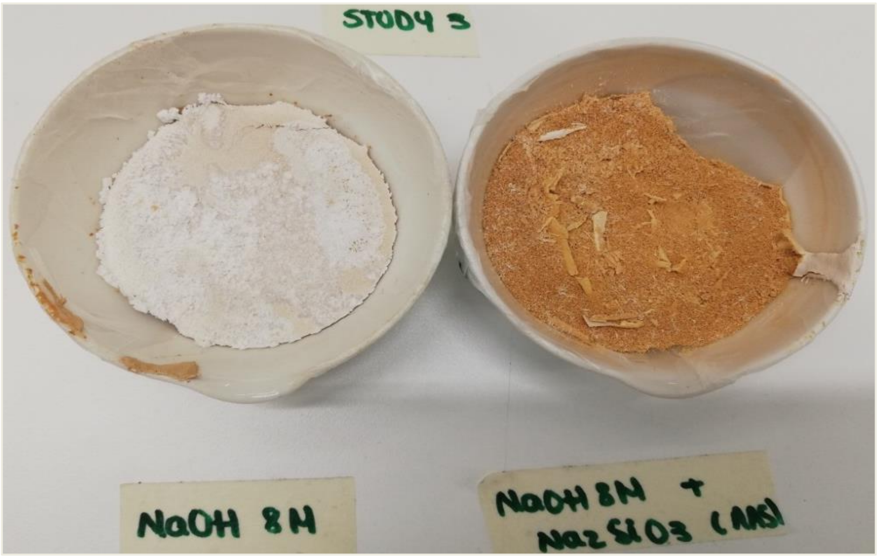


*Figure 122.* Aspect of the Jarosite Study 3-1 geopolymer on the 21th curing day.

*Figure 123.* Aspect of the Jarosite Study 3-1 geopolymer on the 26th curing day.

*Figure 124.* Aspect of the Jarosite Study 3-1 geopolymer on the 28th curing day after crushing (physical stability test).

- Study 3-2

*Table 32.* Experimental quantities of each reagent in the synthesis of Jarosite geopolymer (Jarosite Study 3-2).

| | $w_{ASol}$ (g) | $w_{RM}$ (g) | $w_{Mold}$ (g) | $V_{H2O}$ (mL) |
|---|---|---|---|---|
| **NaOH 8M** | 3,0525 | 14,0002 | 66,4929 | 5,6086 + 3mL |
| **NaOH 8M + $Na_2SiO_3$** | 3,0347 | 14,0002 | 48,5147 | 5,6067 + 3mL |

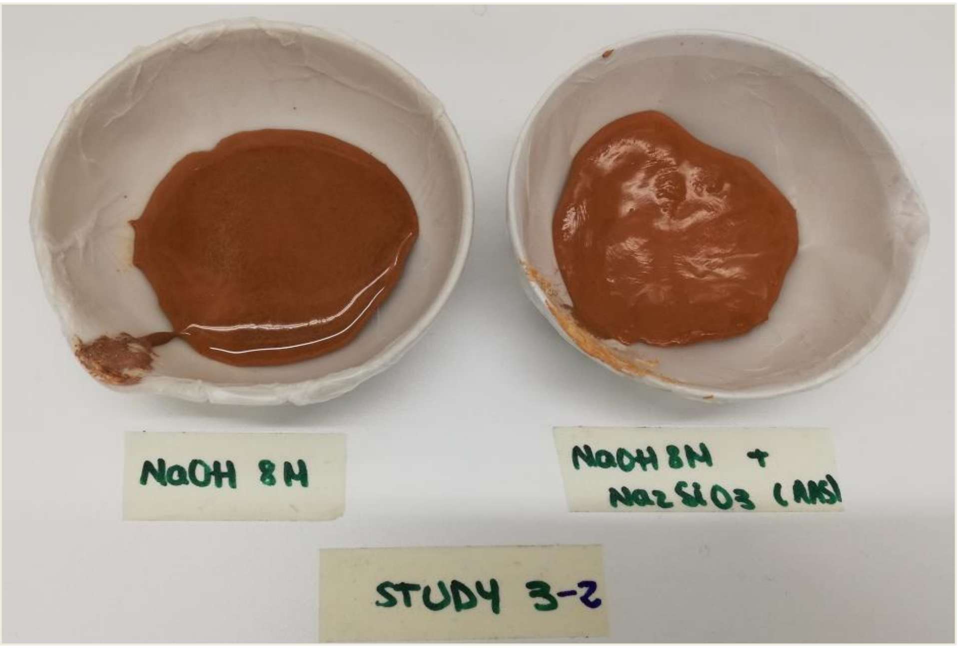


*Figure 125.* Aspect of the Jarosite Study 3-2 geopolymer once synthesized.

*Figure 126*. Aspect of the Jarosite Study 3-2 geopolymer on the 13th curing day.

*Figure 127.* Aspect of the Jarosite Study 3-2 geopolymer on the 18th curing day.

*Figure 128*. Aspect of the Jarosite Study 3-2 geopolymer on the 20th curing day after crushing (physical stability test).

- Study 3-3

*Table 33.* Experimental quantities of each reagent in the synthesis of Jarosite geopolymer (Jarosite Study 3-3).

| | $w_{ASol}$ (g) | $w_{RM}$ (g) | $w_{Mold}$ (g) | $V_{H2O}$ (mL) |
|---|---|---|---|---|
| **NaOH 8M** | 3,0525 | 14,0002 | 66,4929 | 5,6086 + 3mL |
| **NaOH 8M + $Na_2SiO_3$** | 3,0347 | 14,0002 | 48,5147 | 5,6067 + 3mL |

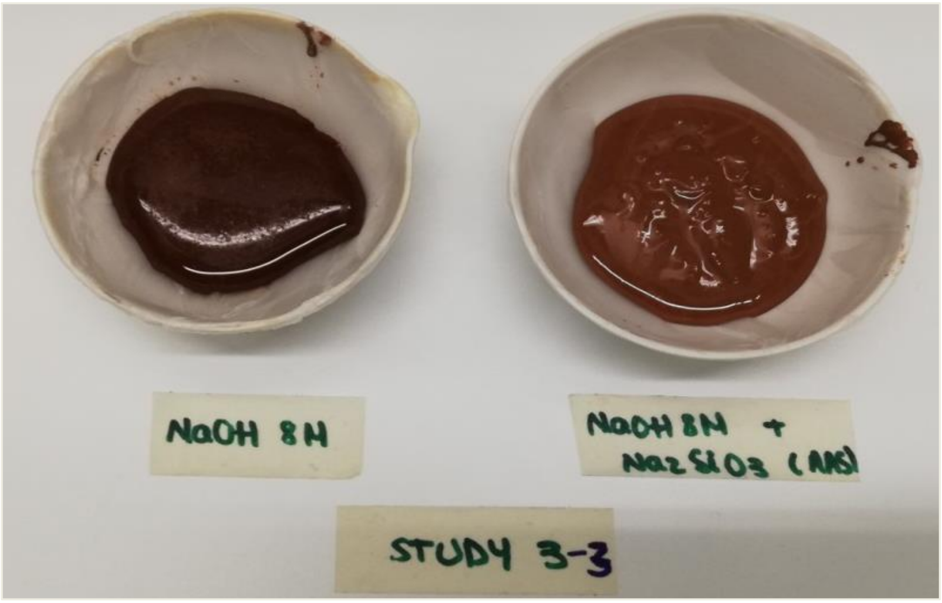


*Figure 129.* Aspect of the Jarosite Study 3-3 geopolymer once synthesized.

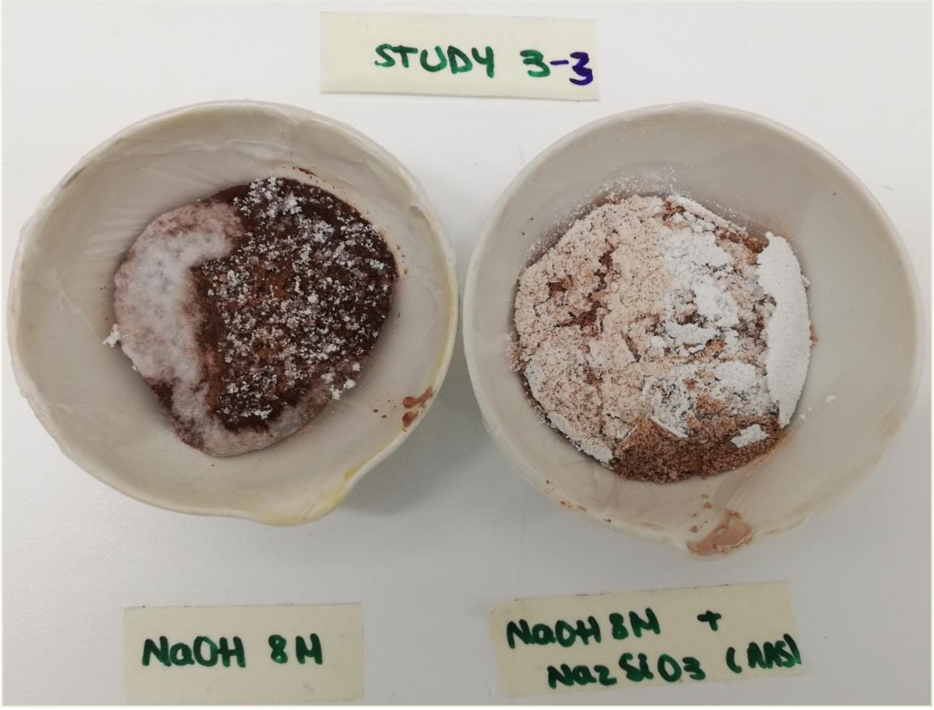


*Figure 130.* Aspect of the Jarosite Study 3-3 geopolymer on the 13th curing day.

*Figure 131.* Aspect of the Jarosite Study 3-3 geopolymer sample with NaOH 8 M on the 13th curing day.

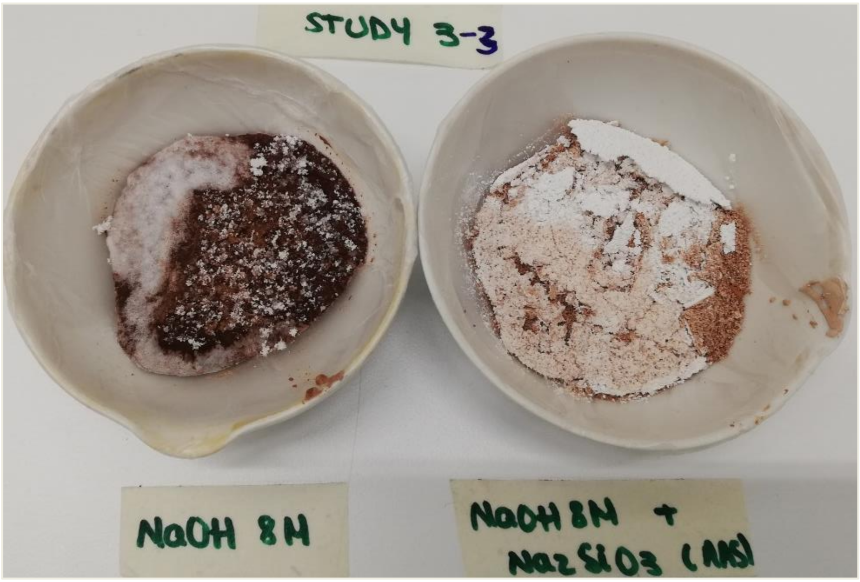


*Figure 132.* Aspect of the Jarosite Study 3-3 geopolymer on the 18th curing day.

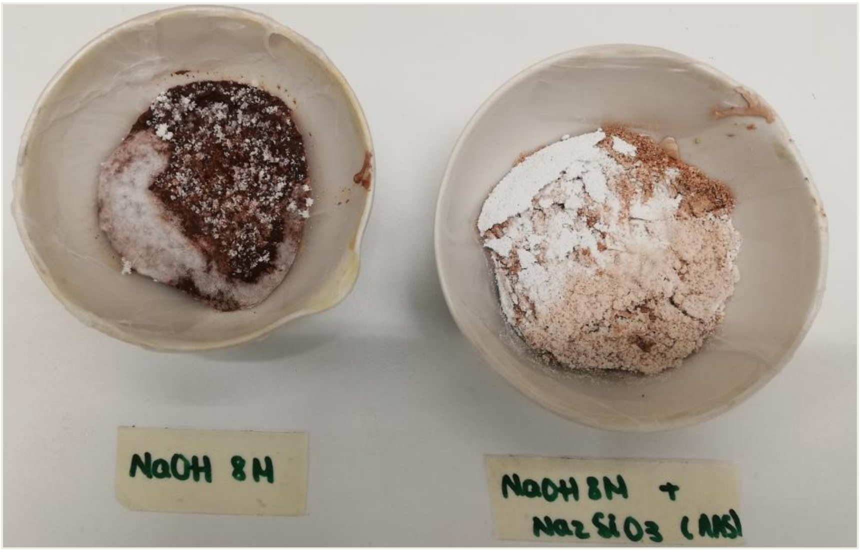


*Figure 133.* Aspect of the Jarosite Study 3-3 geopolymer on the 20th curing day before crushing (physical stability test).

*Figure 134.* Aspect of the Jarosite Study 3-3 geopolymer on the 20th curing day after crushing (physical stability test).

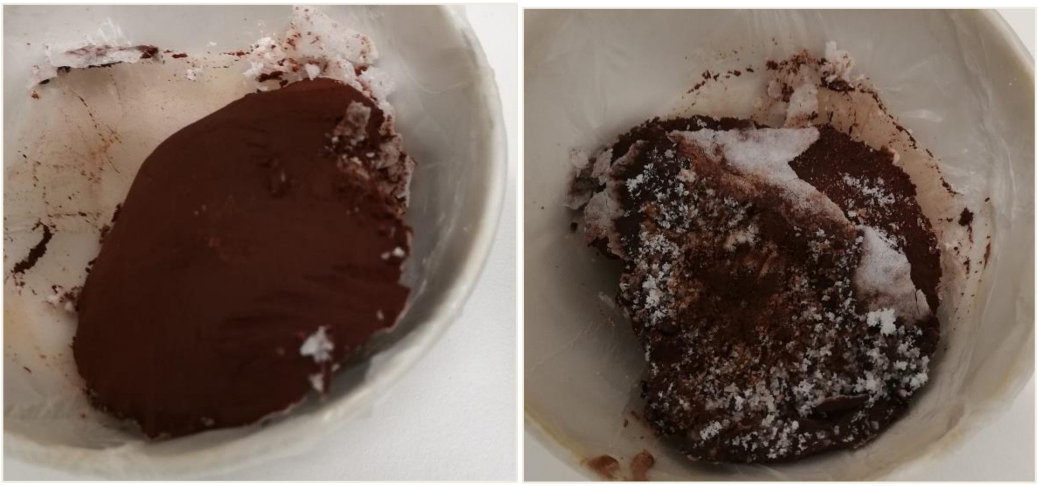


*Figure 135.* Aspect of the Jarosite Study 3-3 geopolymer sample with NaOH 8 M on the 20th curing day after crushing (enlarged photo).