FACULDADE DE CIÊNCIAS
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Universidade de Aveiro Departamento de Geociências
Ano 2019

Cristiana Sofia de Almeida Costa

DESENVOLVIMENTO E OTIMIZAÇÃO DE FORMULAÇÕES DE GEOMATERIAIS PARA REABILITAÇÃO E RESTAURO DE ADOBES

DEVELOPMENT AND OPTIMIZATION OF FORMULATIONS OF GEOMATERIALS FOR ADOBES REHABILITATION AND REPAIR

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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutora em Geociências, realizada sob a orientação científica do Doutor Fernando Joaquim Fernandes Tavares Rocha, Professor Catedrático do Departamento de Geociências da Universidade de Aveiro e coorientação da Doutora Ana Luísa Pinheiro Lomelino Velosa, Professora Associada do Departamento de Engenharia Civil da Universidade de Aveiro.

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Este trabalho é uma contribuição para o projeto DB- Heritage (PTDC/EPH-PAT/4684/2014).

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DEVELOPMENT AND OPTIMIZATION OF FORMULATIONS OF GEOMATERIALS FOR ADOBES REHABILITATION AND REPAIR

Thesis submitted to University of Aveiro to fulfill the requirements of the Doctoral Program in Geosciences, held under the scientific supervision of Doctor Fernando Joaquim Fernandes Tavares Rocha, Full Professor at the Geosciences Department of University of Aveiro and co-supervision of Doctor Ana Luísa Pinheiro Lomelino Velosa, Associate Professor at the Civil Engineering Department of University of Aveiro.

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This work is a contribution to DB-Heritage project (PTDC/EPH-PAT/4684/2014).

Dedico este trabalho aos meus pais, ao meu irmão e ao meu noivo pelo apoio incansável e pela compreensão!

o júri

presidente

Prof. Doutor Carlos Manuel Martins da Costa
Professor catedrático da Universidade de Aveiro

Prof. Doutor Fernando Joaquim Fernandes Tavares Rocha
Professor catedrático da Universidade de Aveiro

Prof. Doutor Iulius Bobos Radu
Professor associado com agregação da Universidade do Porto

Prof. Doutora Maria Paulina Santos Forte de Faria Rodrigues
Professora associada da Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa

Prof. Doutor João Paulo Pereira de Freitas Coroado
Professor coordenador do Instituto Politécnico de Tomar

Prof. Doutor Walid Hajjaji
Investigador Doutorado (Nível 1) da Universidade de Aveiro

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palavras-chave

Construção em terra, adobes, sustentabilidade, conservação do património, materiais activados alcalinamente, geopolímeros.

resumo

O presente trabalho aborda a construção em terra em Portugal, com foco na construção em adobe, e com particular incidência no desenvolvimento de novos materiais para a conservação e restauro destes mesmos tipos de construção.
A construção em adobe é predominante na zona litoral centro do país. No entanto, apesar de existirem inúmeros edifícios de adobe nesta região, muitos deles (alguns com valor patrimonial) carecem de intervenções adequadas de conservação e restauro. O conhecimento destes materiais antigos é uma necessidade prévia a qualquer intervenção e é essencial para a conservação do património arquitetónico destas regiões. O uso de materiais compatíveis com os adobes aumenta a eficácia e durabilidade das ações de conservação e restauro. Assim, a primeira parte deste trabalho consistiu na caracterização química, mineralógica e física de adobes de Aveiro e da Figueira da Foz (onde este tipo de construção é predominante).
O conhecimento adquirido sobre estes materiais consistiu na base necessária para o desenvolvimento de novos materiais passíveis de serem usados em intervenções de edifícios que tenham por base a construção em adobe.
Para além do princípio da compatibilidade dos materiais, no desenvolvimento de novos materiais teve-se ainda como pressuposto a sustentabilidade dos materiais.
A sustentabilidade dos materiais é um assunto de importância relevante devido às crescentes preocupações com o meio ambiente. A escolha de produtos que sejam ao mesmo tempo, eficazes para o fim a que se destinam e “amigos do ambiente” durante todo o seu ciclo de vida são aspetos fundamentais a ter em conta quando se estudam os materiais.
Assim sendo, neste trabalho foram desenvolvidos dois tipos de materiais: adobes ativados alcalinamente e geopolímeros. Estes materiais tiveram como matérias-primas principais lama da Pateira de Fermentelos, areia siliciosa, diatomito Português, caulinos Portugueses, metacaulino industrial e produzido em laboratório. 48 formulações de adobes activados alcalinamente e geopolímeros foram produzidas em laboratório. 23 formulações foram selecionadas como passíveis de serem usadas nas intervenções de conservação e restauro em adobes. 8 formulações de adobes ativados alcalinamente apresentaram a formação de eflorescências que requerem um estudo mais focado de forma a despistar os seus possíveis contributos para degradação futura do material.
Os objetivos do trabalho foram concluídos com sucesso, ficando como trabalhos prioritários a desenvolver no futuro os ensaios de compatibilidade dos materiais a realizar em edifícios de adobe.

keywords

Earth construction, adobes, sustainability, architectural heritage, alkaline activated materials, geopolymers.

abstract

The present work deals with the earth construction in Portugal, with a focus on the adobe construction, and with particular incidence in the development of new materials for the conservation and restoration of these types of construction.
The adobe construction is predominant in the central coastal zone of the country. However, although there are numerous adobe buildings in this region, many of them (some with architectural heritage value) lack adequate conservation and restoration interventions. Knowledge of these ancient materials is a pre-requisite to any intervention and is essential for the conservation of the architectural heritage of these regions. The use of materials compatible with adobes increases the effectiveness and durability of conservation and restoration actions. Thus, the first part of this work consisted in the chemical, mineralogical and physical characterization of adobes from Aveiro and Figueira da Foz (where this type of construction is predominant). The knowledge of these materials was the necessary basis for the development of new materials that can be used in building interventions based on adobe construction.
In addition to the principle of compatibility of materials, the development of new materials also presupposed the sustainability of materials.
The sustainability of materials is a subject of significant importance due to growing concerns about the environment. The choice of products that are both effective for the purpose and environmentally friendly throughout their life cycle are key issues to consider when studying materials.
Thus, in this work two types of materials were developed: alkaline activated adobes and geopolymers. These materials had as main raw materials Pateira de Fermentelos mud, silicic sand, Portuguese diatomite, Portuguese kaolins, industrial metakaolin and produced in the laboratory. 48 formulations of alkaline activated adobes and geopolymers were produced in the laboratory. 23 formulations were selected as likely to be used in conservation and restoration interventions in adobes. 8 formulations of alkaline activated adobes showed the formation of efflorescences that require a more focused study in order to mislead their possible contributions for future degradation of the material.

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“In and of itself, an ERROR is neither good nor bad.

First of all, for us an ERROR is “merely” a deviation from what we expect. But what does it mean, if we´re no longer able to recognize the deviation at all?”

(DRIVE, the Volkswagen Group Forum, Berlin)

CHAPTER 1

INTRODUCTION, OBJECTIVES, OVERVIEW AND OUTLINE

1. INTRODUCTION, OBJECTIVES, OVERVIEW AND OUTLINE

1.1 Background and motivation

Sustainability, particularly in construction materials, has been a subject of growing interest. Civil construction is one of the industries consuming more materials, which leads to high energy consumption and CO_2 emissions. Cement production, especially clinker, is largely responsible for these problems. Consequently, research for more sustainable building materials is increasing, as well as the interest on ancient building materials, especially earth construction materials, which are more sustainable and environmentally friendly than the contemporary ones.

Earth construction is the oldest known building material, with documented cases of the use of earth bricks since Mesopotamia around 10 000 BC (Heathcote, 1995). Close to 30% of the world population lives in buildings made of earth materials. These materials offer economic and environmental benefits; because of that the interest of these types of construction are being increased.

The practice of earth construction is predominant in less developed countries, where lack of advanced technology and often the availability of labor and local materials encourage the use of these building techniques that are quite simple. Nowadays, most of the earth buildings, in Portugal and in other developed countries, is in a high stage of degradation or need repair. In recent years there has been an increased interest on earth construction in order to preserve the cultural heritage focused in the rehabilitation and conservation of this type of buildings.

Portugal has favourable weather conditions for earth construction and it is possible to find different building techniques. There are three main techniques, namely (Silva *et al*., 2013) rammed earth (‘‘taipa’’), adobe and wattle-and-daub (‘‘tabique’’).

Adobe is an extremely simple form of earth construction and with this technique the shrinkage associated with the construction of large structures is avoided. In Portugal, adobe has been used predominantly on the central coast, particularly in the Aveiro district. Although many old adobe buildings in Aveiro have been demolished or abandoned, some of them later can be refurbished with minor maintenance and repair works. Studies of material characteristics are required in order to understand the composition and specific properties of earth buildings, their heterogeneity and their degradation mechanisms. Therefore, it is necessary to have deep knowledge of the different compositions, as well as of other properties of the adobes, to infer which compatible materials can/must be used in the interventions taking into account each type of adobe blocks.

The materials to be used in the restoration and rehabilitation actions should be compatible with the old ones and if possible with improved chemical, mineralogical, and mechanical properties.

The consolidation procedures (like with cement) that have been used are a short-time solution. The major problem is the clay minerals present in these types of materials that expand and contract with water changes. The problem of clay swelling can be decreased with alkaline activation. This process decreases the effect of expansibility and increases the cementing of materials (Elert *et al.*, 2015). Clay swelling could be reduced significantly by transforming clay minerals into non-expandable binding materials with cementing capacity using alkaline activation.

In this context, old materials can be consolidating with alkaline activators, and similar products can be developed like geopolymers. Geopolymers are inorganic polymers obtained by the alkaline activation of aluminosilicate, arise as potential materials, having more controlled costs and lower environmental footprint and improving the chemical and physical characteristics of the adobes.

1.2 Objectives

The main goal of this study is to optimize and develop formulations of geomaterials for adobes repair and rehabilitation, in order to preserve the architectural heritage. For this purpose the following levels were realize:

i. Mineralogical, chemical and physical characterization of adobe construction in Portugal, focus in predominance area, Aveiro region;
ii. Development of innovative formulations of geomaterials for intervention actions, compatible with original adobes;

a. Consolidation of adobe formulations by alkaline activation with NaOH and KOH solutions; structural, mineral, chemical and mechanical characterization.
b. Development of geopolymers formulations; structural, mineral, chemical and mechanical characterization.

This study contributes to carry out recommendations for the selection and use of geological materials to design new materials for earth construction for the rehabilitation of buildings in order to preserve an entire archaeological and architectural heritage, maximizing the sustainable use of local/regional geological features.

Technical solutions were developed for simple and cheap interventions on existing adobe buildings assuring their sustainable rehabilitation.

1.3 Outline and document organization

This section aims to describe the thesis outline and organization. Figure 1.1 shows the flowchart of thesis.

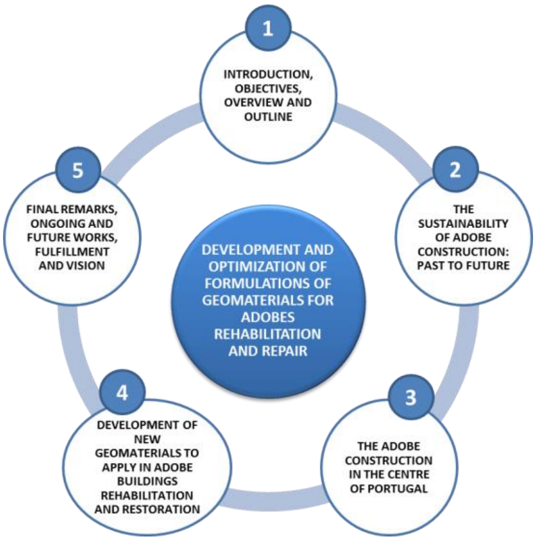


Figure 1.1 – Flowchart of the thesis.

The work herein presented is divided into six chapters developing on the following topics carried out:

The first chapter presents a brief introduction of the main topic of the developed work, followed by the description of the main objectives proposed for the next chapters. Then, the outline is depicted and as well as the document organization. The final section of this chapter presents, the research methodology strategy followed, illustrated using a flow diagram, to thoroughly understand the link between the chapters.

Chapter 2 is dedicated to the state of the art. This chapter deals with earth construction, namely, adobe construction, around the world and in Portugal. The main aspects of the construction in adobe are discussed, pointing out its fragilities and highlighting the state of high degradation of the still existing buildings. Some possible solutions are suggested for the sustainability of these materials on near future.

Chapter 3 is composed of 3 papers about adobe blocks characterization. The first two papers are focused on adobes of specific regions, and the last one includes all the adobe samples that were studied. In this chapter, the main characteristics of the different adobe blocks are assessed, to allow the selection of the best raw materials, in the next chapter.

Chapter 4 is composed by 3 papers. The first paper presents the development of adobe innovative formulations, alkaline activated, for rehabilitation of old adobe buildings. The second paper is about the development of geopolymers based on Portuguese diatomite, Portuguese kaolin and industrial metakaolin. The last one presents the development of geopolymers formulations based on low-grade Portuguese kaolins.

Finally, Chapter 5 presents the final remarks about characterization of original adobes and the development of new materials, ongoing and future work and fulfillment and vision of the work developed during the PhD.

The Figures and Tables were numbered according to the chapter and paper to which they belong to be easier to find.

CHAPTER 2

THE SUSTAINABILITY OF ADOBE CONSTRUCTION: PAST TO FUTURE

2. THE SUSTAINABILITY OF ADOBE CONSTRUCTION: PAST TO FUTURE

This paper was published in the **International Journal of Architectural Heritage.** Vol.13, nº5 (2019) p. 639-647. DOI: 10.1080/15583058.2018.1459954.

Abstract The Earth construction is the oldest building practice on the world. Around 30% of the world population lives in buildings made of earth materials. These materials offer economic and environmental benefits, because of that the interest of these types of construction are being increased. The practice of earth construction is predominant in less developed countries, where lack of advanced technology and often the availability of labor and local materials encourage the use of these building techniques that are quite simple. Nowadays, most of the earth buildings, both in Portugal and in the other countries are in a high stage of degradation. However, the interest of preservation of these buildings is increased. So, this works pretends a global vision of the earth construction on the past, and a new look at these materials in the future. It is important to develop new materials similar to these ones, with economic and environmental benefits, and which are compatible for interventions in these same old buildings. A new generation of materials, are geopolymers, these materials are alkaline activated and because of their properties as well as their ecological footprint they are promising to be a “kind” of materials that will follow the line of earth materials.

2.1 Introduction

Earth construction is the oldest building practice known, with documented cases of the use of earth bricks in Mesopotamia around 10,000 BC (Heathcote, 1995). According to Houben and Guillaud (1994), the “true” rammed earth technique was first developed during the Three Kingdoms Period (221–581 AD). Approximately 30% of the world population lives in buildings made of earth materials; this type of construction exists throughout the world in many different cultures, and for some countries it continues to be the main process of construction (Vega *et al*., 2011).

Earth construction offers economic and environmental benefits especially when used in developing countries where material costs overlap labor costs and where other construction materials and technologies may not be available (Fratini *et al*., 2011).

Earth construction is a type of sustainable architecture with large application in vernacular buildings. Vernacular architecture is based on localized requirements and building materials and reflects local traditions (Niroumand *et al*., 2013). Sustainable architecture, according to UNCED Brundtland Comission (1987), is a construction that fulfills the requisites of contemporary society without denying the future generation the ability to meet its needs. Earth construction is an environmentally friendly technique with a social and cultural contribution. The costs are minimized in this type of construction because local materials may be employed, and it is relatively simple and easy to perform. Earth buildings usually have a lower embodied energy and carbon footprint than the other buildings with sophisticated processes, like concrete, steel, or masonry (Bui *et al*., 2009b) (Bui *et al*., 2009a). This is because the earthen raw materials that are used do not need any kind of firing treatment before their use as a construction material, comprising only raw, sun-dried earth. There are several earth construction techniques employed worldwide such as cob, rammed earth (“pisé de terre”, “taipa”), “wattle and daub” (“tabique”), and adobe (Niroumand *et al*., 2013).

2.1.1 Cob

Cob is the simplest of earth-building technologies, it´s formed by the stacking of earth, usually with the addition of straw and posterior finishing of the surface. This technique makes use of a few tools and formwork and consists of piling and molding mud to create walls (Niroumand *et al.*, 2013).

2.1.2 Rammed earth

Rammed earth is a mixture of sand, gravel and soil (and sometimes lime is used to improve mechanical resistance) and construction is performed by using the rammed material and compacting it in layers between formworks (Jaquin *et al*., 2009). The soil in these constructions is normally found in mountainous areas and rivers, where it is possible to find sand, silt, and clay together (Jaquin, 2012). This technique is based on the experience of local practitioners (Beckett and Augarde, 2012), and it has been in use for thousands of years. There are therefore many historic structures constructed with rammed earth, such as the Potala Palace in Tibet and the Alhambra (rammed earth with lime) in Granada, Spain (Jaquin *et al.*, 2009).

2.1.3 Wattle and Daub

“Wattle and Daub” or “tabique” consists in placing earth in its plastic state, on a support cane wooden or wicker. According to Niroumand *et al.* (2013), the wattle and daub technique consists of two parts. A wattle is a woven structure of small plant elements held together in a stiff frame common materials used to create wattle are reeds, bamboo, branches, and twigs.

Daub or mud adheres to the irregularities and overhangs off the organic matrix. This mud mixture is similar to the one used for mud brick but with smaller aggregate size, and dung is often the organic binder.

2.1.4 Adobe

Adobe bricks were made with humid sandy soil which, once mixed and molded, is dried in the sun. For improving their mechanical performance the inclusion of lime or natural fibers, such as straw, was frequent. Adobe is an extremely simple form of earth construction and with this technique the shrinkage associated with the construction of large structures is avoided. The bricks can be cast from a great variety of soils and can be of two kinds: earth adobe and lime adobe. However, the clay content influences the humidity intake and swelling of adobe blocks as well as the continuous presence of moisture in the walls. In this sense, the clay content should be sufficient to promote workability but should not be very abundant because the associated swelling and shrinking may damage the walls (Burroughs, 2008). Adobe construction was performed in the ancient world, as recorded in the Old Testament, and archaeologists have discovered surviving examples in many places around the world (Quagliarini *et al*., 2010). An adobe building can last hundreds of years (if the materials used are the most appropriate), it is totally recyclable and it is executed with low energy consumption. It is possible to find adobe buildings around the world, hundreds of years old, that only need small interventions. This increases the present interest in adobe as an environmentally friendly material for sustainable construction (Calabria *et al.*, 2008).

2.2 Historical Background

There is no consensus regarding the origin of earth buildings. According to Minke (in Torgal *et al*., 2012), the first adobe buildings discovered in Turkmenistan are aged from between 8000 and 6000 BC. Other authors refer that in Europe this technique appears during the Iron Age (Chazelles, 1995; Daudon *et al*., 2014). The use of adobe construction in Cyprus is dated to the Neolithic Era (Illampas *et al*., 2014; Christoforo *et al*., 2016). The authors that discovered adobes in the Tigris River affirmed that the oldest adobe bricks found have an age that ammounts to 7500 BC, and they concluded that the earth construction could have been used for over 10 000 years (Torgal & Jalali, 2012). It is not possible to date the beginning of adobe construction; however, it is known that this type of construction appears in a period between 6000 and 10 000 BC. The earliest use of adobe in Europe can be dated at around 5300 BC in the settlement of Sesklo in Greece, with small homes built on stone foundations. The use of earth with timber in northern Europe means that many archaeological sites have decayed and only foundations remain, making assessment of the building materials difficult. In central Turkey, remains of adobe buildings have been found as far back as 1600 BC (Torgal, 2015).

The use of adobe construction is spread all over the world, especially in countries where the raw material is easily available. This happens because this is the simplest and easiest form of construction. However, what occurs over time with scientific and technological developments is that there is a certain abandonment of this technique, especially in more developed countries despite the advantages that this constructive technique offers in terms of sustainable development.

There are studies that report the existence of adobe buildings from South America to North America, Africa, and Europe. In the Iberian Peninsula this construction arose under the influence of the Phoenicians, Carthaginians, Romans, and Muslims. However, it was mainly Muslims who had greater influence and dissemination in terms of these constructive techniques (Torgal & Jalali, 2010).

2.3 Adobe construction in the World

Several authors report that almost 30% of the world's population lives in earth-based dwellings (Costa *et al*., 2016; Parisi *et al*., 2015; Silveira *et al*., 2012; Varum *et al*., 2015). Considering the information on the global variations of precipitation and temperature, there is no correlation between these parameters and the implementation earth construction; it's possible to visualize in the map of Figure 2.1 that earth construction is present in countries with climates that are totally different, due to thermal properties of soils.

Figure 2.1 – Earth construction in the world with heritage UNESCO (Daudon *et al*., 2014).

The practice of earth construction is predominant in less developed countries, where lack of advanced technology and often the availability of labor and local materials encourages the use of these building techniques that are quite simple. However, this type of construction occurs in some developed countries like Portugal, Germany, France, or even the UK (Varum *et al*., 2015).

The earth construction in Europe appears essentially in less developed countries; however, it is possible to find earth buildings throughout other European countries such as Germany, UK, and France (Torgal, 2015). In Europe, earth building traditionally takes many forms; it can be found buildings made in adobe and rammed earth in southern Europe, while in northern Europe, earth is used in conjunction with timber in wattle and daub and half-timbered techniques.

In Spain, earth construction can be found in the whole country (Figure 2.2), being predominant in the central area, especially in small towns. As in Portugal, Spain's earth construction is present in all kind of buildings, such as: urban and vernacular architecture; monuments; public buildings; walls, wells; and other construction elements. The tradition of earth construction in Spain was considered by UNESCO as world cultural heritage, because the country hosts five earthen monuments such as the historic center of the city of Córdoba, or the Alhambra, Generalife, and Albaicín in Granada (Delgado *et al*., 2006).

There are few new earth buildings in Spain but the majority are residential buildings using compressed earth blocks. In terms of rehabilitation and conservation works, this is still an area in need of expertise but some historic monuments, such as the Alhambra, have been intervened in close link with research work and using compatible materials and techniques. However, it still happens that as in Portugal, in Spain demolition is the most common choice instead of rehabilitation of these buildings.

Figure 2.2 – Map of Earth Construction in Spain (adapted from Delgado *et al.*, 2006).

In Italy, according to Pagliolico *et al.* (2010), it is normal to find earthen buildings. The adobe construction is mainly found in Sardinia, whereas cob is present in Marche and Abruzzo, and rammed earth, together with some adobe, constructions in Piedmont. However, most of these buildings are in a high state of degradation because often times the used soils used aren´t adequate for this type of constructions, and sometimes the soil/sediments proportions adopted may not be the best (Pagliolico *et al.*, 2010).

There are some authors (Daudon *et al.*, 2014; Obafemi & Kurt, 2016) that refer the importance of earth construction in Greece where there is availability of the materials reported that the city of Athens was being constructed entirely from adobe (Jaquin, 2012). The vernacular architecture reveals Greek lifestyle and cultural values of the past and the buildings can be studied as models of environmentally responsive and sustainable architecture. Some examples are in Sernikaki and Cyprus (Obafemi & Kurt, 2016). Cyprus is one of the oldest islands in the Mediterranean Sea. Obafemi & Kurt (2016) studied the building materials from Louroujina, in Cyprus, that are adobe and mortars of the same material as the adobe units. Like in Portugal, the earthen blocks are usually produced manually and are called “adobe” or “sun-dried block”.

In the UK around 60% of monuments and archeological sites were built using earth materials or have earthworks associated. Nowadays, just 2% of earth buildings are found in the UK, because earth became regarded as a material of limited durability and thus inferior to more permanent materials, such as stone or fired clay bricks (http://www.earthstructures.co.uk/history.htm). In the developed countries like UK, the preservation and rehabilitation of earth buildings has fallen into disuse, not only by the development of building materials but also by a lack of awareness of the preservation of heritage.

2.4 Adobe construction in Portugal

In Portugal, earthen materials have been used in load bearing walls in the form of adobe or rammed earth for the construction of buildings especially in the southern and central coast. Earth construction was extensively used in Portugal during the Islamic domination period (between 7th and 13th centuries), both to build military and civil constructions. The military constructions are mainly constituted by fortresses, which were firstly built between the 7th and 9th centuries. From then on, earth has often been employed in both rural and urban buildings, and the various building techniques associated to earth construction are present throughout the country, with distinct regional expression. Most of the adobe buildings are confined mainly to the central coast. The adobe construction in these locations has economic and environmental benefits, because the raw material (soil) is sourced *in situ* (Ciancio *et al.*, 2013). In Portugal, earth construction was also a very common technique used in the past and widespread throughout the territory with the employment of different techniques (Figure 2.3). Locally, it is divided into three different types or building techniques: rammed earth, “taipa”; wattle-and-daub, “tabique”; and “adobe”. In the present work, adobe construction type will be emphasized.

Figure 2.3 - Earth construction in Portugal (Martins, 2009).

The term “adobe” is derived from the Arabic “attob” which means sun-dried brick. This constructive technique is one of the oldest; the adobe bricks have been used in ancient Egyptian and Mesopotamian civilizations. This indicates that this technique will have reached the Iberian Peninsula during the Arab occupation. In southern and central Portugal there are many buildings with adobe masonry, due to the existence of sandy soils and the presence of lime, used as a stabilizing agent. Some of these buildings date from the 20th century and are still in a reasonable conservation state (Varum *et al*., 2015). The manufacture of adobes consists in forming small blocks normally using wooden molds, which are demolded in the fresh state and left to dry at natural environmental conditions. How to build adobe is simple, similar to the placement of the conventional brick forming masonry. The settlement of the adobes is accomplished with earth-based mortar in order to obtain a better connection between the materials, since it keeps the same level of shrinkage, thus avoiding the appearance of fissures or posting of material. Portugal has favorable weather conditions for earth construction. However, with the evolution of building materials, this construction technique was almost abandoned. Despite this, in recent years there has been an increased interest on earth construction in order to preserve the cultural heritage focused in the rehabilitation and conservation of this type of buildings. Most adobe buildings are confined to the central coast, particularly to the Aveiro district. In Aveiro, there has been an obvious degradation and abandonment of many buildings; however, some of these old buildings can be rehabilitated with minor maintenance and repair works. Over recent years, particular attention has been given to rehabilitation in order to preserve and protect this heritage (Costa *et al*., 2013).

Adobe has been used in several types of construction: rural and urban buildings, many of which are still in use; walls for the boundary of properties; water wells; churches; warehouses. The use of adobe construction in the Aveiro district reflected the properties of the existing available raw materials applied, which were sand, clay sediments, soils and lime (Silveira *et al*., 2012), and there is an evident heterogeneity of the adobes linked to the geographic distribution of the available resources. In Aveiro there was a semi-industrial production of adobe, some small companies employing “adobeiros”, for the manufacture of blocks of adobe, along with a domestic self-production (Costa *et al*., 2016).

2.5 Composition and properties of adobes

Adobe is associated with a very simple technique of manufacturing and building. For this reason many ancient adobe buildings are still inhabited today. In Aveiro, due to the lack of raw materials, lime adobes were mostly used. There are many different formats and several dimensions of adobe blocks, depending on the intended application. In Portugal, common adobe blocks dimensions, despite the existence of numerous typologies depending on use, are approximately 0.45 × 0.30 × 0.12 m, when used in houses, and 0.45 × 0.20 × 0.12 m, when used in the construction of boundary walls (Silveira *et al*., 2012). The adobe building technique requires the use of a plastic soil and clay, being mainly used in places where it is possible to find water. The use of clay soil leads to the appearance of

cracks during the drying stage due to shrinkage of the material. For this reason straw or other plant fibers are usually mixed in the adobe raw materials in order to avoid cracking (Christoforo *et al.*, 2016). Adobe walls should also be thick to obtain the best mechanical and thermal properties. Consequently, there is a high risk of cracking during drying, and the axial shrinkages are significant. The particular aspects of the manufacture of adobes, require skilled labor. According to literature, soils used for the manufacture of adobes must contain a percentage of clay between 15–16% (Calatan *et al.*, 2016). To obtain the best possible results, the employed soils must have adequate workability and plasticity. The introduction of fibers in adobes is controversial, the opinions of different authors diverge; some claim that this can prevent cracking others understand that degradation of the fibers may confer a decrease in the mechanical strength of adobe blocks (Parisi *et al.*, 2015; Calatan *et al.*, 2016; Sharma *et al.*, 2015). According to Calatan *et al.* (2016), the addition of 9–10% (by volume) of fibers is the optimum value to have benefits on the properties of the adobe bricks. The mechanical strength values mentioned in the literature vary between 0.6 and 8.3 MPa, however the frequent of resistance in adobes focuses on values between 0.8 and 3.5 MPa, (Illampas *et al.*, 2014; Coroado *et al.*, 2010).
The capillary water absorption varies between 3–21 $kg/m^2/h^{1/2}$, and this heterogeneity is correlated with the compositional differences of adobes and their differential degradation due to exposure (Coroado *et al.*, 2010). The mineralogical composition shows the occurrence of quartz and calcite as main phases with presence of K-feldspars and phyllosilicates minerals (like kaolinite). In adobes, where there is an adequate amount of kaolinite, its properties such as water absorption and mechanical strength are improved. It should be noted that the amount of clay minerals should be moderate to avoid cracking in the material.

The adobe building technique is also simple and similar to the placing of the conventional brick, forming masonry. The settlement of the adobes is accomplished with earth-based or lime mortars in order to obtain a better connection between the materials, since it keeps the same level of shrinkage, contributing to compatibility of materials and improved behavior of masonry.

2.6 Sustainability

Sustainability deals with three key areas: environmental, economic and social. It's known that sustainable construction has become a significant factor in recent times, because this type of industry is one of the most materials consuming, producing a significant environmental impact.

Nowadays, there is a growing concern with the consumption and production of materials due to the effects on the environment and economy. It is known that the construction industry is one of the largest consumers of materials with high CO_2 emissions associated with the production process of these materials, especially when it comes to concrete. One of the biggest problems of cement production is the temperature for the production of this material, which implies high energy consumption. The use of the earth reduces energy consumption, what makes that material friend of the environment. In this context, there is an increase in the interest by developing and using more sustainable materials, and therefore earth construction has become a subject of growing interest.

Earth construction was one of the most used types of construction all over the world, by using simple techniques and locally available materials. This type of construction is directly related to economic and environmental advantages. However, most of the buildings that still exist are in a high degree of degradation which causes a growing concern with the preservation of this specific kind of cultural heritage. For many, the solution is to demolish these buildings rather than incorporate rehabilitation actions in order to preserve the built heritage. It is important to introduce the subject of the sustainability of these materials that are often ignored due to their supposed frailty. As such, an attempt must be made in order to find materials that are compatible for restoration purposes. Adobe is an eco-friendly, low energy, and cost-efficient construction material. The adobe material offers indoor thermal comfort and adequate sound insulation, and allows the economization of carbon dioxide during its production (Christoforo *et al.*, 2016). The soils used for this type of construction are usually located immediately below the soil top layer. Often, this earth is located very close to the building and as such there is no pollution even in the transport of materials, contrary to other materials such as ceramic bricks or concrete. The waste of the earth construction can be deposited at the site of extraction in the absence of any environmental hazard.

Conservation of buildings is, in itself, a sustainable action and the development of compatible materials and re-use of old materials should become a growing concern. For this purpose, further characterization is mandatory as well as the widespread of knowledge. However, the use of materials with improved properties may also have its role. There are some examples of adobe buildings with cultural heritage relevance in Portugal, particularly in Aveiro district, which were success stories after small interventions and rehabilitation, such as the Art Nouveau Museum (in Aveiro city centre), or the Gandareza House (in Vagos).

Several recent scientific articles concluded that the characteristics of the adobe can be improved by adding different natural additives. According to Corrêa *et al.* (2015), the incorporation of bamboo particles and “synthetic saliva” allows the improvement of the physical and mechanical stabilization. These materials reduced linear shrinkage, water absorption, and loss of mass of adobe when exposed to water. The bamboo particles increased the compressive strength, interrupting the cracks that form during the compressive test of the adobes. Other authors such as Calatan *et al.* (2016) stated that the addition of 9–10% (v/v) hemp fiber or 10–30% of straw can increase the mechanical behavior of adobes. Parisi *et al*. (2015) also concluded that the addiction of straw fibers can reinforce the adobe bricks.

Sharma *et al*. (2015) studied the improvement of mechanical strength in adobes with fibers and they concluded that this addition can increase the compressive strength between 50–225%. Sharma *et al*. (2015) also concluded that the presence of fibers can improve the durability of adobes. There are several studies that prove the efficacy of certain additives in improving the properties of adobes, as such, it is possible today to obtain a sustainable material with adequate properties.

Other sustainable materials have been studied as potential resources for rehabilitation and even for the construction of new buildings, in particular geopolymers. A geopolymer is an inorganic polymer, obtained by the alkaline activation of an aluminosilicate, under certain temperature and pressure conditions (Davidovits, 2002). Its properties depend mainly on the chemical structure. In addition to the replacement of cements, these products can also be applied as other materials, such as composites with fire-resistant fibers, bricks, anti-fire protection, in the ceramic industry, encapsulation of toxic and radioactive waste, among others. Geopolymers can be produced from naturally high-strength natural phyllosilicates being cured at room temperature. As such, they have good physicochemical characteristics, such as: high workability, fast hardening, surface finish, rapid development of mechanical strength, surface hardness, good chemical resistance, and heat and fire resistance (Davidovits, 2015). These characteristics reveal the great potential for application in construction materials. Geopolymers will contribute decisively to increase sustainability in the construction industry, because, compared to traditional cement, they have the advantage of reducing CO_2 emissions, as well as lower energy embodiment when compared to the high energy consumed during the production of clinker in a traditional cement.

2.7 Conclusions

The earth construction, both in Portugal as in other countries where this is still a reality, is based on the use of simple techniques that guarantee the sustainability of buildings. This type of construction should be preserved to ensure the legacy of this built heritage and also due to its characteristics. For the rehabilitation of this type of building it is necessary to know the materials and to create new materials that are compatible; these materials should ensure the longevity of the conservation and restoration actions. It is important that the materials used have a low energy consumption and low CO_2 release to the environment, because it is intended that the developed materials needs to be environmentally and economically sustainable. In construction due to excessive consumption of materials this concern becomes larger, mainly due to the production of cement, in addition to consuming different materials, carries an high energy expenditure and a release of CO_2, which corresponds to at least 5 of the 7% of global emissions (McLellan *et al.*, 2011).

In Portugal, particularly in the Aveiro district, there has been an obvious degradation and abandonment of many adobe buildings; however, some of these old buildings can be rehabilitated with minor maintenance and repair works. The materials used in to the conservation actions should be compatible with the base materials. The compatibility of the materials used in the adobe buildings rehabilitation are the key point for the success of the preservation of these buildings. These materials need to assure the sustainability offers by adobe and other earth construction materials.

Nowadays, since there is a growing concern with the sustainability of building materials, the preservation of earth buildings should be taken as a focus of preservation of heritage and guarantee economic and environmentally sustainable buildings. In addition to the development of new materials for the rehabilitation of adobe/earthen buildings, there is also a concern with the use of more sustainable materials for construction of new buildings. The first approach of the geopolymers arises from this perspective, as most sustainable capable materials with potential to replace the usual concrete maintaining its properties and leading to lower energy consumption and release of CO_2 to the environment.

CHAPTER 3

THE ADOBE CONSTRUCTION IN THE CENTRE OF PORTUGAL

In this chapter 3 the following papers are presented:

1) ***Influence of the mineralogical composition on the properties of adobe blocks from Aveiro, Portugal***. (Published in *Clay Minerals. Vol. 48 (2013) p. 749–758*. DOI: https://10.1180/claymin.2013.048.5.07).

This paper focused on the characterization of twenty different adobe samples with two provenances, ten of them from Anadia and the other ten from Murtosa (both in Aveiro region). The mineralogical composition, capillary water absorption and mechanical strength are the main characteristics that distinguish these adobes with different provenances, which means, with different raw materials available.

Anadia adobes reveal better results, presenting the best results of mechanical resistance, related to mineralogical composition (richer in kaolinite than the Murtosa adobes), and absence of calcite nodules (present on Murtosa adobe samples).

It must be stated that the obtained values are from materials in their current state of conservation, which does not mean that at the time of their production these different adobes did not present better resistance results.

2) ***Sustainability in earthen heritage conservation.*** (Published in *Construction Practice. Geological Society, London, Special Publications, Vol. 416 (2016) p. 91-100.* DOI: https://10.1144/SP416.22).

This paper arises as a consequence of the previous paper. Studied adobe samples are from the same provenance sites.

The properties of these materials were studied creating two groups of adobes that represent the adobes found in the Aveiro region (where a large part of the adobe study area is located).

On the other hand, this paper aims to emphasize the environmental character of the earth construction, being a sustainable material, with great ecological advantages. It is shown that the conservation of this type of construction should be a priority at present and for the future.

3) ***Adobe blocks in the center of Portugal: main characteristics.*** (*In press* in April 2019 in the *International Journal of Architectural Heritage. DOI:* https://10.1080/15583058.2019.1627442).

This paper is an essential basis for the knowledge of the characteristics of the studied original adobes as a basis for the development of new materials for the conservation and restoration actions.

A total of 41 old adobes were studied, from Aveiro and Figueira da Foz sectors (Figure 3.3.1), presenting the main visual characteristics (color and texture) and mineralogical, chemical and mechanical characterization. Depending on the properties, it is concluded that there are 5 essential adobe groups in this region. The compositions and characteristics of the studied adobes should be considered for any action of conservation or restoration of buildings with similar materials.

3.1 INFLUENCE OF THE MINERALOGICAL COMPOSITION ON THE PROPERTIES OF ADOBE BLOCKS FROM AVEIRO, PORTUGAL

Abstract Earth materials have been used in the form of adobe or rammed products for the construction of load-bearing walls in buildings. In Portugal, the adobe has been used predominantly on the central coast, particularly in the Aveiro district. Although many old adobe buildings in Aveiro have been abandoned, some of them can be refurbished with minor maintenance and repair works. Representative samples from typical adobe blocks, from various constructions in the region were collected and characterized for their mineralogical composition, particle size, aggregate content, water uptake, durability and strength. These basic properties provide a basis for the development of adequate interventions, preserving the characteristics of the buildings. This study compares the main characteristics of adobes from two different locations (Anadia and Murtosa). The most important differences between the two groups of adobes are the particle size distribution, the mineralogical composition, the water absorption and the mechanical and durability properties. The study improved the knowledge of the traditional construction methods and will enable decisions for rehabilitation of adobe buildings to be made. Knowledge of the main characteristics of adobes allows those participating in the rehabilitation process to obtain the basis for the rehabilitation and conservation of old buildings.

3.1.1 Introduction

Approximately 30% of the world population lives in buildings made of earth materials. The earth construction offers economic and environmental benefits especially when used in developing countries where material costs overlap labor costs and where other construction materials and technologies may not be available (Fratini *et al*., 2011).

The earth construction includes different building techniques; for example, in Portugal, there are three main techniques namely rammed earth (‘‘taipa’’), adobe and wattle-and-daub (‘‘tabique’’), (Silva *et al*., 2013).

In general, the adobe blocks were made with humid sandy soil which, once mixed and moulded, were dried in the sun. For improving their mechanical performance the inclusion of lime or natural fibres, such as straw, was frequent. The current adobe blocks dimensions, despite the existence of numerous typologies depending on use, are ~0.45m*0.30m*0.12 m when used in houses and ~0.45m*0.20m*0.12m when used in the construction of walls (Silveira *et al*., 2012).

Adobe is an extremely simple form of earth construction and with this technique the shrinkage associated to the construction of large structures is avoided. The bricks can be cast from a great variety of soils. However, the clay influences both the humidity intake and swelling of adobe bricks and may keep moisture in the walls. In this sense, the clay content should be sufficient to promote workability but should not be very abundant because the associated swelling and shrinking may damage the walls (Burroughs, 2008). An adobe building can last hundreds of years and it is totally recyclable. This behaviour increases the present interest in adobe as environmentally friendly material for sustainable construction (Calabria *et al.,* 2008).

In Portugal, earthen materials have been used in load-bearing walls in the form of adobe or rammed earth for the construction of buildings especially in the southern and central coast. Most of the adobe buildings are confined mainly to the central coast, particularly in the Aveiro district. The adobe construction in these locations has economic and environmental benefits, because the raw material (soil) is sourced in situ (Ciancio *et al*., 2013).

In Aveiro, there has been an obvious degradation and abandonment of many adobe buildings; however, some of these old buildings can be rehabilitated, with minor maintenance and repair works. Over recent years, particular attention has been given to rehabilitation in order to preserve and protect this heritage.

Adobe has been used in several types of construction: rural and urban buildings, many of which are still in use; walls for the delimitation of properties; water wells; churches and warehouses. The use of adobe construction in the Aveiro district reflected the properties of the existing available raw materials in the region. The principal raw materials applied were sand, clayey earth and lime (Silveira *et al*., 2012) and there is an evident heterogeneity of the adobes, linked to the geographic distribution of the available resources.

The study of the mineralogical composition and properties of the adobe yields a better understanding of these materials, their heterogeneity and of their degradation mechanism. This characterization is essential for the rehabilitation of old buildings, by highlighting options for the selection of compatible materials in any conservation action.

The purpose of this study is the mineralogical, textural and mechanical characterization of ten adobes from the Anadia area and ten from the Murtosa area in Aveiro district.

3.1.2 Methods

Acid dissolution removed the soil binder and created a residue composed of the aggregate fraction. Adobe samples of ~50 g were dried at 110+/- 5ºC until reaching a constant weight. The carbonate fraction, mainly lime which is often added to adobes, was dissolved in 20% HCl and the sample was agitated prior to filtering. An approximate value of the binder/aggregate ratio was obtained, since the acid dissolution technique used totally dissolves carbonates but may only partially dissolves soluble SiO_2. The residue obtained was dried until reaching a constant weight. Particle size analysis of the aggregate fraction was performed by dry sieving on the insoluble residue obtained from acid dissolution, corresponding to the aggregate fraction, using the E196-66 series for analysis of soil samples, with the largest sieve corresponding to a 19 mm opening. The sand fraction between 0.075 and 0.050 mm and the silt and clay fractions were quantified by an X-ray sedigraph (Micromeritics1 Sedigraph 5100).

Mineralogical studies were carried out on the bulks sample and on the <0.075 mm and <2 µm (clay) fractions of the samples with X-ray diffraction (XRD). The mineralogical composition was determined with random powder mounts for the bulk samples and <0.075 mm fraction and with oriented samples for the clay fractions. The clay fractions were separated by sedimentation according to Stokes law, using 1% sodium hexametaphosphate solution to avoid flocculation. For the preparation of oriented clay mounts, the suspension was sedimented into a thin glass plate and dried in the atmosphere. XRD measurements were performed with a Philips PW 3050 and a X'Pert PW 3040/60 equipment using Cu-Ka radiation. Scans were run between 2º and 60º 2θ (random powder mounts) and between 2º and 20º 2θ (oriented clay mounts) in the air-dried state, after previous glycerol saturation and heat treatment (500ºC). Qualitative and semi-quantitative mineralogical analyses followed the criteria recommended by Schultz (1964), Thorez (1976) and Mellinger (1979). Semi-quantitative estimation of the principal minerals, was obtained from peak areas of the specific reflections and weighted by empirically estimated factors, according to Galhano *et al.* (1999) and Oliveira *et al. (*2002). The methylene blue test was performed following standard NP EN 933-9 (2002). Methylene blue dye solution (10 g of anhydrous dye/L) was added progressively until the test sample no longer adsorbed the dye. The methylene blue value was calculated in g of anhydrous dye per kg of the <2 mm fraction of the aggregate.

Capillary water absorption was performed on cylindrical samples extracted from each adobe, taking into account water intake and subsequent drying. This specific testing procedure was developed at LNEC (Veiga, 2005). Cubic samples of 20 specimens were submitted to compressive strength tests, using a universal mechanical compression testing machine (Shimadzu Autograph AG 25 TA). This test was made with a 50 N/s simple compression.

The Geelong test was used to determine the durability of adobe blocks. This test consists of adding dropwise a certain amount of water from a height of 400 mm using a soaked felt over a specimen placed at an angle of 30º. The test ends when the water volume reaches 100 mL, which usually happens after 30 min. The degree of erosion encountered is given by the depth of wear caused by the fall of water on the adobe block. Water depth erosion greater than 15 mm signifies that the specimen should be rejected (Silva *et al*., 2013). The durability of adobe buildings is dependent on appropriate maintenance and repairs that are compatible with the original construction, because it is extremely important to study the characteristics of adobe blocks from different buildings (Torgal & Jalali, 2012).

3.1.3 Results

3.1.3.1 Acid dissolution to evaluate binder/aggregate ratio

After acid dissolution the percentage of the insoluble residue for the samples from Anadia ranged from 84 to 92%, and for the samples from Murtosa between 86 and 93% (Table 3.1.1).

Table 3.1.1 – Percentage of the insoluble residue (Ins. Res.), mean diameter of fine fraction (Ø50), and MB results.

Sample	% Ins. res.*	Ø50 (µm)	MB (g MB/kg fraction 0/2)	Sample	% Ins. res.*	Ø50 (µm)	MB (g MB/kg fraction 0/2)
A2-1	87	12	0.3	M1-2	93	12	0.3
A2-2	89	12	0.6	M1-3	90	12	0.2
A3-1	92	11	0.6	M1-4	90	7	0.3
A3-2	89	8	0.5	M2-2	90	14	0.4
A3-4	88	12	0.7	M2-3	90	14	0.3
A8-1	84	19	0.3	M10-2	89	8	0.2
A8-2	85	17	0.6	M10-3	86	8	0.2
A8-3	86	9	0.8	M11-3	86	8	0.2
A8-4	89	12	0.7	M11-5	87	9	0.3
A8-5	88	15	0.5	M11-6	87	9	0.4
Average	88	12	0.6	Average	90	9	0.3

Therefore the two groups of samples displayed comparable behaviour in terms of the aggregate/binder percentages. The samples are actually Si-rich aggregates, essentially free of carbonates, and thus they are resistant to acid attack.

3.1.3.2 Particle size analysis of the aggregate

In general the samples of Anadia are finer than their Murtosa counterparts (Figures 3.1.1 and 3.1.2). In the Anadia samples three groups with different particle size distributions are in evidence (Figure 3.1.1). The first group is composed of samples with a Ø50 of 0.425 - 0.85 mm, the second group represents the samples with a Ø50 between 0.85 and 2 mm, and finally the third group of samples has a Ø50 between 2 and 4.75 mm.

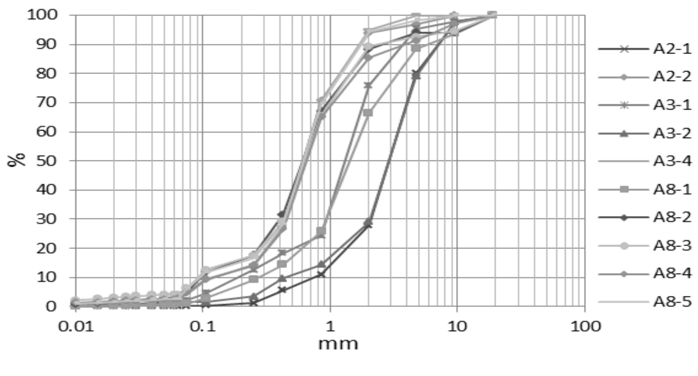


Figure 3.1.1 – Particle size distribution curves of the Anadia samples.

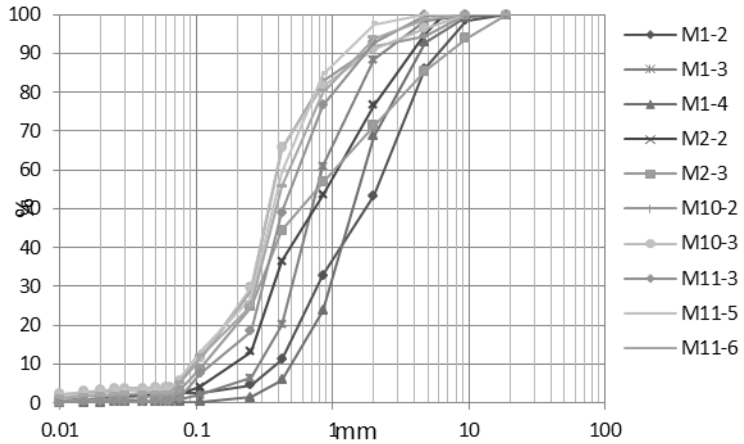


Figure 3.1.2 – Particle size distribution curves of the Murtosa samples.

The Murtosa samples also consist of three groups with distinct particle size distributions (Figure 3.1.2). A first group with a lower Ø50 (between 0.25 and 0.425 mm), that represents samples with finer particle size, an intermediate group with Ø50 between 0.425 and 0.85 mm and a third group with coarser samples having Ø50 between 0.85 and 2 mm, which features a dispersed sample behaviour.

The particle size distribution was based on acid dissolution with HCl. The fraction of coarser particles in the Anadia samples clearly decreases, compared to the original samples after acid dissolution (Figure 3.1.3). Moreover all samples have comparable particle size distributions. This behaviour can be explained by the mineralogical composition of the adobes; indeed the larger particles include mainly calcite, feldspars and iron hydroxides, which are susceptible to acid attack. Hence they dissolve, thereby explaining the particle size distribution differences with the acid attack. In the Murtosa samples there is a slight increase of the fraction of particles with diameter below 2 mm after dissolution. However, the coarse fraction of the adobes is heterogeneous (Figure 3.1.4) due to the variation of the mineralogy. It is considered that the Murtosa samples have some calcite ‘‘clusters’’ affecting the particle size distribution of samples after acid dissolution.

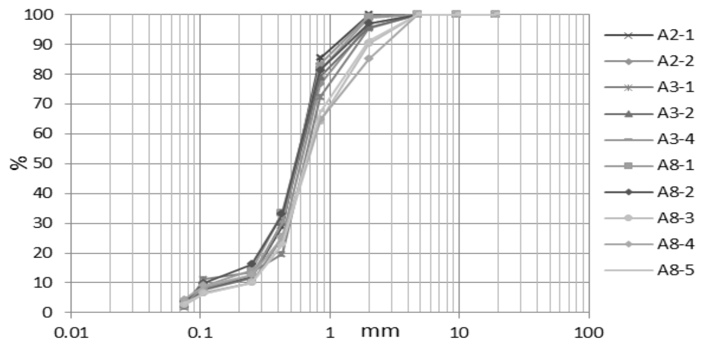


***Figure 3.1.3* – Particle size distribution curves of the Anadia samples after acid dissolution.**

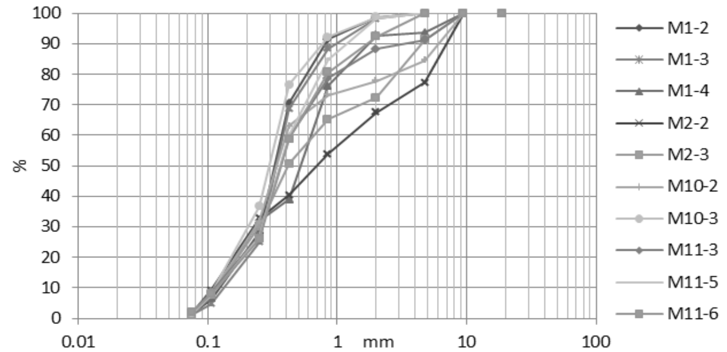


Figure 3.1.4 – Particle size distribution curves of the Murtosa samples after dissolution.

The results obtained by the X-ray sedigraph are presented in Figures 3.1.5 and 3.1.6. The Anadia samples consist of three groups between 2 and 15 mm (Figure 3.1.5). The first group presents the largest percentage of fine particles and the third group is clearly coarser in size. The Murtosa samples from two groups, the first consisting of particles over 2 mm (Figure 3.1.6).

For a clearer interpretation of the results obtained by X-ray sedigraph, the differences in Ø50 between the different groups of samples are presented in Table 3.1.1. The average particle diameter of the Anadia samples is larger than that of the Murtosa samples.

The results obtained for textural analysis represent only the adobes collected. It is important to note that there is a variety of adobes in the Aveiro district, suggesting that adobes with different particle size distributions than those obtained in this study may be present.

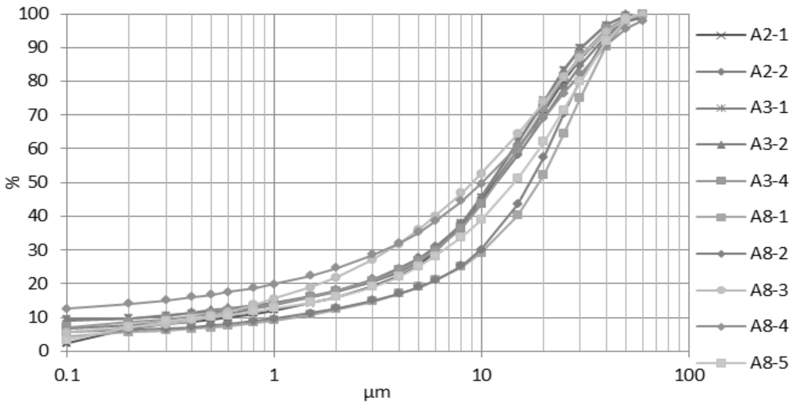


Figure 3.1.5 – Particle size analysis by sedigraph, for the Anadia.

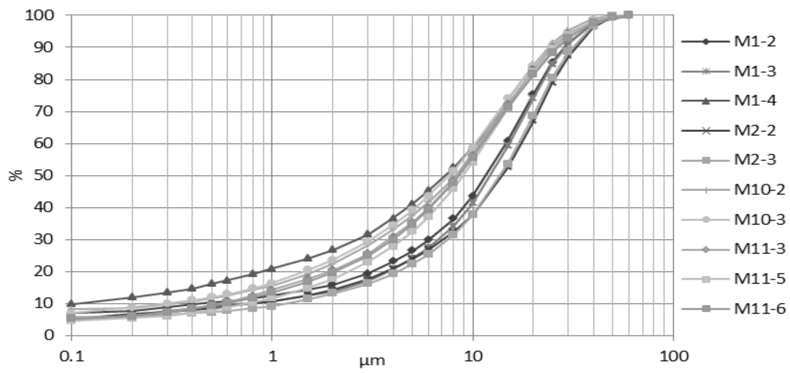


Figure 3.1.6 – Particle size analysis by sedigraph for the Murtosa samples.

3.1.3.3 Methylene blue test (MB)

The methylene blue test was used to estimate the percentage of the fraction <2 mm of the studied adobes. The results obtained are listed in Table 3.1.1. The Anadia samples have a higher clay fraction than the Murtosa samples, in accordance with the percentage of phyllosilicates determined from the mineralogical analysis (Table 3.1.2).

3.1.3.4 Mineralogy; X-ray diffraction (XRD)

The mineralogical qualitative and semi-quantitative analysis of the Anadia and Murtosa groups of samples are presented in Table 3.1.2. In general the two groups have different mineralogical compositions. The samples from both adobe groups contain carbonates (calcite and traces of dolomite), those from Murtosa being richer (59%), probably reflecting a higher percentage of added lime and/or the use of a distinct type of sand.

Adobes from Anadia contain a higher percentage of phyllosilicates (40%) compared with their Murtosa counterparts.

Table 3.1.2 – Mineralogical composition of samples (Anadia and Murtosa), (in percentages).

	Samples	Phyllosilicates	Tectosilicates	Carbonates	Iron Oxides and Hidroxides	Sulphates
Anadia	A2-1	35	18	34	8	5
	A2-2	35	19	44	0	2
	A3-1	44	17	29	8	2
	A3-2	47	11	35	5	2
	A3-4	50	16	28	3	3
	A8-1	39	16	36	7	2
	A8-2	41	20	33	4	2
	A8-3	28	20	45	2	5
	A8-4	37	13	44	3	3
	A8-5	48	7	38	7	0
	Average	40	16.5	35.5	4.5	2
Mutosa	M1-2	5	22	64	4	5
	M1-3	15	18	62	0	5
	M1-4	21	20	55	0	4
	M2-2	8	25	63	1	3
	M2-3	12	19	62	3	4
	M10-2	27	8	59	4	2
	M10-3	23	12	57	4	4
	M11-3	21	12	57	7	3
	M11-5	21	11	59	5	4
	M11-6	22	15	53	7	3
	Average	20	16	58	2	4

With respect to the clay mineralogical composition, the adobe samples consist essentially of kaolinite, illite and smectite (Table 3.1.3). Anadia adobes have a higher percentage of kaolinite (77%) and a small percentage of illite (13%). In some samples (A2-1, A3-1, A3-2 and A8-1) chlorite is also present. The Murtosa adobes are chlorite free and have a lower kaolinite content (54%) compared to the Anadia adobes. The two groups of adobe samples have in general the same amounts of tectosilicates, namely quartz, plagioclase and potassium feldspar. The Anadia adobes have a slightly higher percentage of iron oxides and hydroxides than the Murtosa adobes. The latter are more abundant in sulfates (mainly anhydrite) than their Anadia counterparts (42% and 22% respectively).

Samples belonging to the same building often have different mineralogical compositions. This may be due to heterogeneity in adobe execution and/or differential degradation of adobe samples located in distinct areas of external walls.

Table 3.1.3 – Clay minerals present in adobe sample (Anadia and Murtosa), in percentages.

Anadia					Murtosa				
Samples	Smectite	Kaolinite	Chlorite	Illite	Samples	Smectite	Kaolinite	Chlorite	Illite
A2-1	trace	70	30	tr	M1-2	trace	31	0	69
A2-2	3	85	0	12	M1-3	0	0	0	100
A3-1	17	42	26	15	M1-4	22	65	0	13
A3-2	9	75	16	0	M2-2	trace	trace	0	100
A3-4	2	80	0	18	M2-3	100	trace	0	trace
A8-1	trace	91	9	0	M10-2	0	50	0	50
A8-2	trace	100	trace	trace	M10-3	0	100	0	0
A8-3	0	93	0	7	M11-3	0	0	0	0
A8-4	0	68	0	32	M11-5	0	95	0	5
A8-5	0	71	0	29	M11-6	0	58	0	42
Average	2	77	8	13	Average	4	54	0	42

3.1.3.5 Water absorption and drying

The water absorption rates of the Anadia and Murtosa adobe groups are listed in Table 3.1.4. The capillary absorption coefficient of the samples was calculated representative samples from the Anadia and Murtosa groups are shown in Figure 3.1.7. Most of the Anadia samples show a greater water absorption rate than the Murtosa samples. Although a great heterogeneity in the values is observed, sample A3-1 (Anadia group) has the highest capillary absorption coefficient. This value is directly dependent on the quantity and type of porosity present in the samples. Adobes with a higher capillary coefficient have a faster water intake and may be more prone to degradation. Finally the

Anadia samples generally display a faster drying capacity than the Murtosa samples and a more homogeneous behaviour (Figure 3.1.8).

Table 3.1.4 – Capillarity absorption coefficient of adobe samples.

Anadia		Murtosa	
Sample	Capillary absorption coefficient (g/dm^3.min$^{1/2}$)	Sample	Capillary absorption coefficient (g/dm^3.min$^{1/2}$)
A2-1	3.1	M1-2	3.0
A2-2	-	M1-3	7.0
A3-1	12.8	M1-4	2.6
A3-2	10.7	M2-2	2.4
A3-4	-	M2-3	1.8
A8-1	4.4	M10-2	7.4
A8-2	8.4	M10-3	7.7
A8-3	7.3	M11-3	8.1
A8-4	-	M11-5	9.2
A8-5	-	M11-6	7.0
Average	7.9	Average	7.0

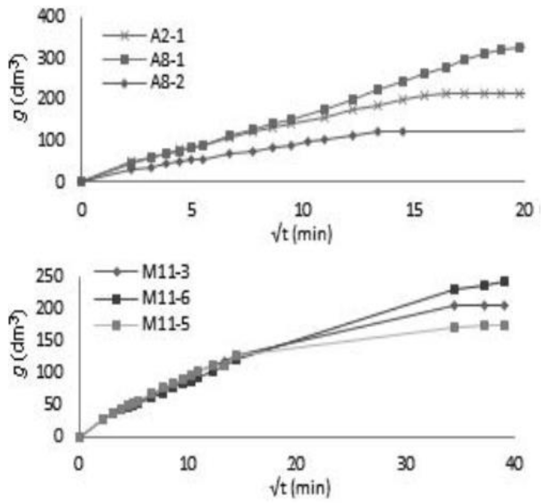


Figure 3.1.7 – Characteristic water absorption curves of Anadia and Murtosa samples.

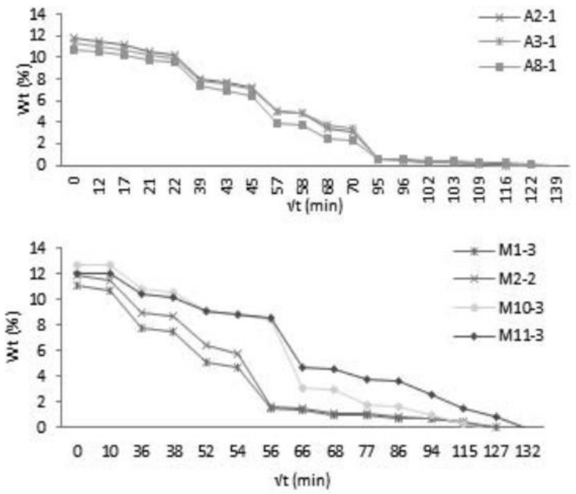


Figure 3.1.8 – Characteristic drying curves of two groups of adobes.

3.1.3.6 Compressive strength tests

In general, the Anadia adobes are more resistant than their Murtosa counterparts (Table 3.1.5). This may be due to the fact that Anadia adobes have higher kaolinite content, and Murtosa adobes contain lime clusters due to production conditions because the calcite was not disseminated in the adobe matrix. According to the Australian Standard or Middleton (Vega *et al*., 2011), the compressive strength for earthen materials should exceed 2 N/mm^2. All but one Anadia adobe samples have a strength greater than 2 N/mm^2; hence they meet this criterion. Sample A2-1 has a compressive strength slightly lower than the suggested value. In the Murtosa group only samples M1-3, M10-2, M11-3 meet the strength criterion, the remaining samples developing lower compressive strength than the reference value indicated in the standard.

Table 3.1.5 – Compressive strengths of the two Adobe groups (simple compression).

Anadia		Murtosa	
Samples	N/mm^2	Samples	N/mm^2
A2-1	1.97	M1-2	1.87
A2-2	2.05	M1-3	2.07
A3-1	2.31	M1-4	1.61
A3-2	2.09	M2-2	1.25
A3-4	-	M2-3	1.64
A8-1	2.35	M10-2	2.52
A8-2	2.55	M10-3	1.4
A8-3	3.43	M11-3	2.63
A8-4	3.58	M11-5	1.93
A8-5	2.39	M11-6	1.32
Average	2.52	Average	1.76

3.1.3.7 Geelong Test

The results obtained for the Geelong test are shown in Table 3.1.6. The water penetration is lower for the adobes from Murtosa. The higher water penetration in the Anadia adobes is attributed to their more porous structure, because of their textural and mineralogical composition.

Table 3.1.6 – Geelong test results.

	Samples	Penetration of water (cm)	Average penetration of water (cm)	Average
Anadia	A2-1	3.35	3.35	3.18
	A3-1	2.9	2.77	
	A3-2	2.63	3.08	
	A8-1	3.08	3.27	
	A8-2	3.25		
	A8-3	3.29		
Murtosa	M1-2	0.97	1.55	1.58
	M1-3	1.9		
	M1-4	1.77		
	M2-2	1.83	1.58	
	M2-3	1.32		
	M10-2	2.1	1.84	
	M10-3	1.58		
	M11-3	1.43	1.58	
	M11-5	2		
	M11-6	1.32		

3.1.4 Discussion

The Anadia adobe samples display a more homogeneous texture and a larger quantity of fine particles than the Murtosa samples. This is in accordance with the higher phyllosilicate content (in particular kaolinite) and the lower carbonate content in Anadia samples. The higher phyllosilicate content contributes to a higher methylene blue adsorption value. The Murtosa samples are richer in carbonates, forming lime nodules in some samples, which may be detrimental for the mechanical behaviour of these adobes.

The Anadia samples have a faster absorption rate than the Murtosa samples, most probably due to their higher phyllosilicates content, the more homogeneous texture and the larger amount of fine particles. Similarly, in the Geelong test results, the penetration of water is higher in Anadia samples because of their higher porosity, due to their textural and mineralogical composition. The Anadia samples display a higher mechanical strength compared to their Murtosa counterparts, which may be explained by the differences in compactness and by the presence of lime nodules in the Murtosa samples. There seems to be no clear link between the mineralogical composition and mechanical strength, which is determined by the particle size distribution of the aggregate, compactness and production procedure. Nevertheless, the higher kaolinite content, which is used as additive to improve mechanical strength in polymers and composites for industrial applications, may contribute to the higher mechanical strength of the Anadia samples.

Finally, from the performed tests it follows that the durability of adobe as a construction material prone to the action of water is not directly related to its mechanical strength.

3.1.5 Conclusions

This study permitted the distinction of the main characteristics of two groups of adobes (Anadia and Murtosa) used in Aveiro, Portugal. The most important differences between these two groups of adobe samples pertain to the particle size distribution, the mineralogical composition, the water absorption and the mechanical strength. The Anadia samples are more homogeneous and have a greater quantity of fine particles than their Murtosa counterparts.

Also, the Anadia samples have a faster water absorption rate than Murtosa samples. Since adobes are especially prone to degradation by the action of water, the Anadia samples may be less durable than the Murtosa samples. However, the Anadia samples display a higher mechanical strength than the samples from Murtosa due to differences in compactness and to the presence of lime nodules in the Murtosa samples. All samples show good behaviour in terms of compressive strength tests, and some samples have a high mechanical resistance.

The phyllosilicate content, in particular kaolinite abundance, makes a positive contribution to the textural, absorption/drying and mechanical properties of the adobes.

3.2 SUSTAINABILITY IN EARTHEN HERITAGE CONSERVATION

Abstract Earth construction is the oldest building material known, with documented cases of the use of earth bricks since Mesopotamia around 10 000 BC. Earth construction exists throughout most of the world in different cultures, and for some countries it continues to be the main process of construction. Around 30% of the world's population lives in buildings made from earth materials. Earthen construction is an environmentally friendly technique with a social and cultural contribution; this advantage is increased when this type of construction is applied in developing countries where the material costs counterbalance the labour costs, and where other materials and techniques are not available. Studies of material characteristics are required in order to understand the composition and specific properties of earth buildings, their heterogeneity and their degradation mechanisms. Results from two different types of adobes that represent these material characteristics in Aveiro district are shown, owing to the importance of determining and acknowledging the main characteristics of adobe buildings in order to have sufficient information to initiate conservation and rehabilitation actions.

3.2.1 Introduction

Earth construction is the oldest building method known, with documented cases of the use of earth bricks in Mesopotamia around 10 000 BC (Heathcote, 1995). According to Houben & Guillaud (1994), the 'true' rammed earth technique was first developed during the Three Kingdoms Period (221–581 AD).

'Rammed earth' is a mixture of sand, gravel and clay and construction is performed by using the rammed material and compacting it in layers between formworks (Jaquin *et al*., 2009). The soil in these constructions is normally found in mountainous areas and rivers, where it is possible to find sand, silt and clays together (Jaquin, 2012). This technique is based on the experience of local practitioners (Beckett & Augarde, 2012), and it has been in use for thousands of years. There are therefore many historic structures constructed with rammed earth (e.g. the Potala Palace in Tibet and the Alhambra in Granada, Spain) (Jaquin *et al*., 2009). Adobe construction was performed in the ancient world, as recorded in the Old Testament, and archaeologists have discovered surviving examples in many places around the world (Quagliarini *et al*., 2010). Earth construction exists throughout the world in many different cultures, and for some countries it continues to be the main process of construction (Vega *et al.*, 2011). Figure 3.2.1 shows that around 30% of the world population lives in buildings made from earth materials; however, nowadays it is thought that this percentage corresponds to a much larger distribution.

Earth construction is a type of vernacular and sustainable architecture. A vernacular architecture is an architecture based on localized requirements and building materials and reflecting local traditions (Niroumand *et al.*, 2013). Sustainable architecture, according to UNCED Brundtland Comission (1987) is a construction that fulfills the need of contemporary society without denying the future generation the ability to meet its needs. Earthen construction is an environmentally friendly technique with a social and cultural contribution; this advantage is increased when this type of construction is applied in developing countries where the material costs counterbalance labour costs, and where other materials and techniques are not available (Ciancio *et al.*, 2013).

The costs are minimized in this type of construction because local materials may be employed, and it is relatively simple and easy to perform. Earth buildings usually have a lower embodied energy and carbon footprint than the other buildings with sophisticated processes, like concrete, steel or masonry (Bui *et al.*, 2009a, 2009b). This is because the earthen raw materials that are used do not need any kind of firing treatment before their use as a construction material, comprising only raw, sun-dried earth.

An adobe building can last hundreds of years, it is totally recyclable and it is executed with low energy consumption. This increases the present interest in adobe as an environmentally friendly material for sustainable construction (Calabria *et al.*, 2008).

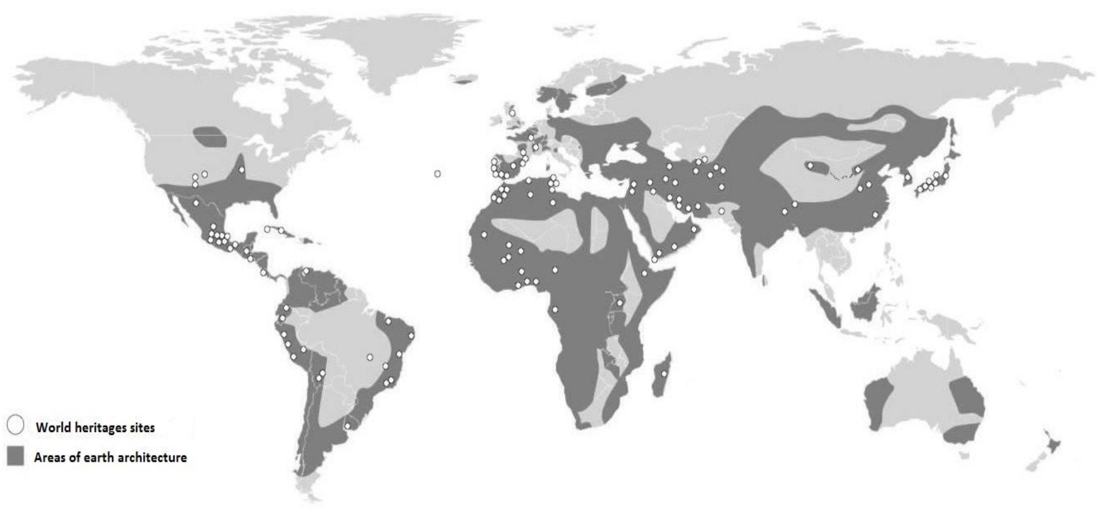


Figure 3.2.1 – Earth construction in world (CRATerre).

In Portugal, earth construction was also a very common technique used in the past (Figure 2.3, chapter 2). Locally, it is divided into three different types or techniques of construction: rammed earth, 'taipa'; wattle-and-daub, 'tabique'; and 'adobe'. The technique named taipa consists of compacting humid soil in layers between a removable formwork to build monolithic walls; this type of construction appears in southern Portugal. The tabique method consists of a wooden structure made up of vertical boards connected by laths which are boarded up with metal nails, creating internal divisions or external walls. This structure is then coated with an earthen material or a lime-based render. Adobe is an ancient form of brick that consists of earth (clay, silt and sand) and water; frequently, straw or other vegetable fibres are also included in the structure to improve resistance to shrinkage and cracking. Adobe bricks are executed without a firing process and the earthen blocks are therefore submitted to a prolonged period of drying, usually carried out by direct exposure to sunlight (Calabria *et al.*, 2008). The common adobe blocks dimensions, despite the existence of numerous typologies depending on use, are approximately 0.45 × 0.30 × 0.12 m when used in houses and 0.45 × 0.20 × 0.12 m when used in the construction of walls (Silveira *et al*., 2012). Adobe is an extremely simple form of earth construction and with this technique the shrinkage associated with the construction of large structures is avoided. The bricks can be cast from a great variety of soils. However, the clay content influences the humidity intake and swelling of adobe blocks as well as the continuous presence of moisture in the walls. In this sense, the clay content should be sufficient to promote workability but should not be very abundant because the associated swelling and shrinking may damage the walls (Burroughs, 2008).

In Portugal, earthen materials have been used in load-bearing walls, in the form of both adobe and rammed earth, for the construction of buildings especially in the southern and central areas. Most adobe buildings are confined to the central coast, particularly to the Aveiro district. The adobe construction in these locations has economic and environmental benefits, because the raw material is sourced on-site (Ciancio *et al*., 2013).

In Aveiro, there has been an obvious degradation and abandonment of many buildings (Figure 3.2.2); however, some of these old buildings can be rehabilitated with minor maintenance and repair works. Over recent years, particular attention has been given to rehabilitation in order to preserve and protect this heritage (Costa *et al*., 2013).

Figure 3.2.2 – Examples of degradation and abandonment buildings in Aveiro (Silva, 2011).

Adobe has been used in several types of construction: rural and urban buildings, many of which are still in use; walls for the delimitation of properties; water wells; churches; and warehouses (Figure 3.2.3). The use of adobe construction in the Aveiro district reflected the properties of the existing available raw materials applied, which were sand, clayey earth and lime (Silveira *et al*., 2012), and there is an evident heterogeneity of the adobes linked to the geographic distribution of the available resources. In Aveiro there was a semi-industrial production of adobe, some small enterprises having an 'adobeiro', making the blocks of adobe, along with a domestic self-production.

In recent decades, concern towards the conservation of ancient buildings has increased and the idea that these buildings can be rehabilitated and reused instead of demolished has become a common thought with repercussions in the market (Lourenço, 2005). There is an increased interest in preservation of old buildings because it is important to preserve the historic part of the cities with functioning and appealing characteristics both for inhabitants and for tourists.

Studies of material characterization are required in order to understand the composition and specific properties of the earth buildings, their heterogeneity and their degradation mechanisms. These studies are essential for the rehabilitation of old buildings, by highlighting options for the selection of compatible materials in distinct conservation actions. For this purpose, in the Department of Civil Engineering and in the Geosciences Department of University of Aveiro in Portugal, some studies of characterization of earthen constructions in Aveiro district are ongoing, particularly focused on adobe buildings. In this paper, results from two different types of adobes that represent these material characteristics in Aveiro district will be shown, owing to the importance of determining and acknowledging the main characteristics of adobe buildings in order to have sufficient information to initiate conservation and rehabilitation actions.

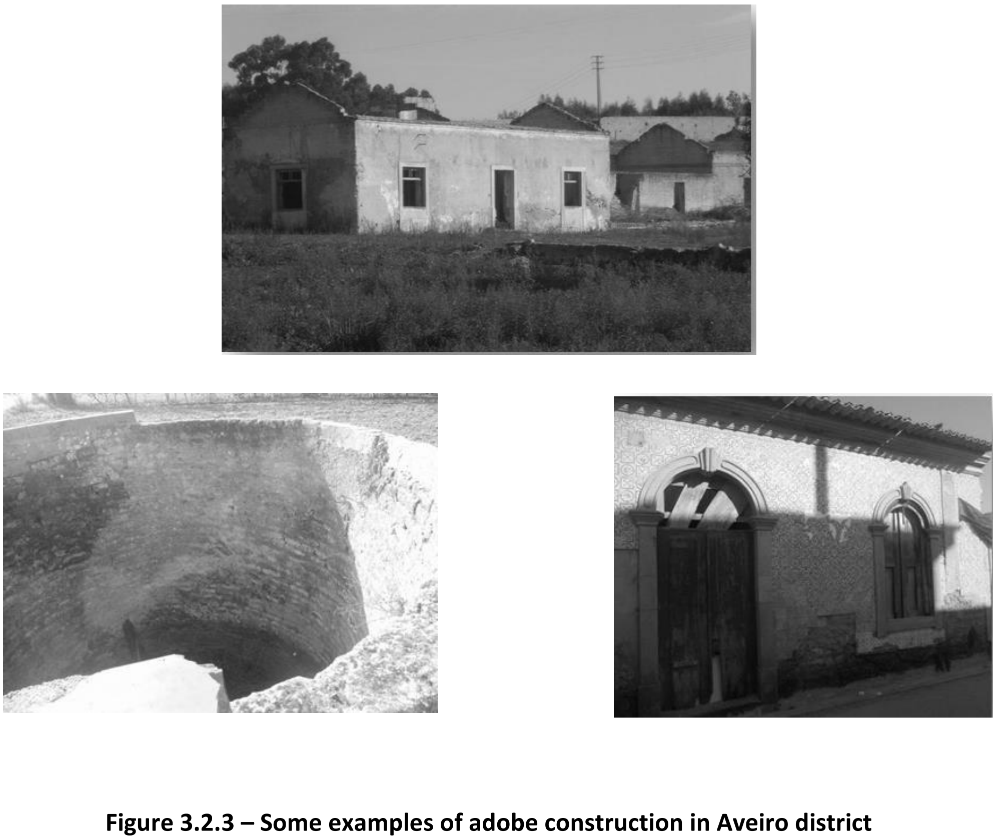


Figure 3.2.3 – Some examples of adobe construction in Aveiro district

3.2.2 Experimental

3.2.2.1 Samples

Twenty samples of adobe buildings were collected in Aveiro district, and divided into two groups according to the colour and grain size (Figure 3.2.4). The samples were extracted from the following locations: (a) Anadia region (in south of the district) and (b) Murtosa (in north of the district).

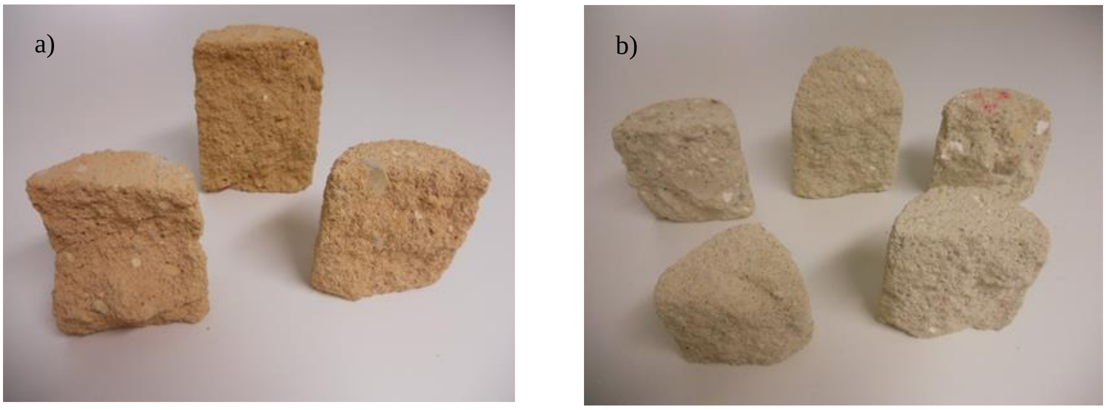


Figure 3.2.4 - Examples of samples, (a) group 1 and (b) group 2.

3.2.2.2 Methods

Mineralogy. Mineralogical studies were carried out on the <75 µm (fine) and <2 µm (clay) fractions of the samples through X-ray diffraction. The mineral composition was determined both on un-oriented powder mounts for <75 µm fraction analyses and on oriented aggregates for the clay fraction ones. The clay fractions were obtained by sedimentation according to Stokes's law, using 1% sodium hexametaphosphate solution to avoid flocculation. For the preparation of preferentially oriented clay mounts, the suspension was placed on a thin glass plate and air-dried. X-Ray diffraction measurements were performed using Philips PW 3050 and X' Pert PW 3040/60 equipment using Cu Ka radiation. Scans were run between 2 and 60º 2θ (unoriented powder mounts) or between 2 and 20º 2θ (oriented clay mounts) in the air-dried state after a previous glycerol saturation and heat treatment (500ºC). Qualitative and semi-quantitative mineralogical analyses followed the criteria recommended by Schultz (1964), Thorez (1976) and Mellinger (1979). For the semi-quantification of the identified principal minerals, peak areas of the specific reflections were calculated and weighed by empirically estimated factors, according to Galhano *et al*. (1999) and Oliveira *et al*. (2002).

Chemistry. The chemical composition of muds was assessed by X-ray fluorescence using a Panalytical AXIOS PW4400/40. Loss-on-ignition was determined by heating 1 g of the sample at 1000ºC for 1 h in furnace.

Insoluble residue. Acid dissolution tests were performed in order to dissolve the binder fraction, and therefore assess the aggregate fraction (Velosa *et al*., 2010). Adobe samples of 50g were dried at 110 +/-5 ºC until constant mass was achieved. In a 100 ml beaker, 1:5 hydrochloric acid was added and the sample was agitated prior to filtering. Hydrochloric acid was used in order to dissolve the carbonate fraction, since lime is commonly present in adobes.

Granulometry. Dry sieving was performed using the E196-66 sieves series for analysis of soil samples, with the largest sieve corresponding to a 19 mm opening. Particle size analysis of the aggregate fraction was performed on the insoluble residue obtained from acid dissolution, corresponding to the aggregate fraction. The sand fraction was assessed between 0.075 and 2 mm; silt and clay fractions were quantified by 'sedigraph' (Lima & Luz, 2001).

The methylene blue test was performed following standard NP EN 933-9 (2002).

Physical and mechanical properties. Twenty cylindrical specimens were extracted from the collected adobe bricks with diameters ranging from 80 to 90 mm. Specimens were subjected to compressive strength tests, using a universal mechanical compression testing machine (Shimadzu Autograph AG 25 TA). This test was made with a loading velocity of 50 $N.s^{-1}$ in uniaxial compression.

The Geelong test consists of dropping a certain amount of water, drop by drop, from a height of 400 mm using a soaked felt over a specimen placed at an angle of 30º. The test ends when the water volume is 100 ml, which should happen after 30 min. The degree of erosion consumed is given by the depth of wear caused by the fall of water on the adobe block. A water erosion depth greater than 15 mm signifies that the specimen should be rejected (Torgal *et al.,* 2012).

3.2.3 Results

3.2.3.1 Mineralogy

The qualitative and semi-quantitative mineralogical analyses of the samples (from Costa *et al*., 2013) are summarized in Table 3.2.1. According to these analyses (Figure 3.2.5), the samples of group 1 are composed essentially of phyllosilicates, carbonates and tectosilicates (quartz and feldspars), and some accessory minerals like iron oxides and hydroxides (hematite, goethite). The samples of group 2 are characterized by the high content of carbonates (essentially calcite and sometimes dolomite), and some phyllosilicates and tectosilicates. These samples have too, in minor percentages, some iron oxides, hydroxides and sulphates.

In terms of clay composition, the group 1 is constituted by a high percentage of kaolinite, and in minor occurrence illite, chlorite and smectite. In the group 2, kaolinite and illite are the principal clay minerals and the appearances of these two minerals are similar. Sometimes, smectite appears too.

Table 3.2.1 – Mineralogical composition of the two types of soils used for adobe production in Aveiro district (Portugal): 1 = Anadia region, 2 = Murtosa.

Minerals		Sample groups	
		1	**2**
Phyllosilicates	**Smectite**	0.8	0
	Kaolinite	30.8	11.2
	Chlorite	3.2	0
	Illite	5.2	8.8
Tectosilicates		17	17
Carbonates		36	59
Iron Oxides and Hydroxides		5	2
Sulphates		2	2

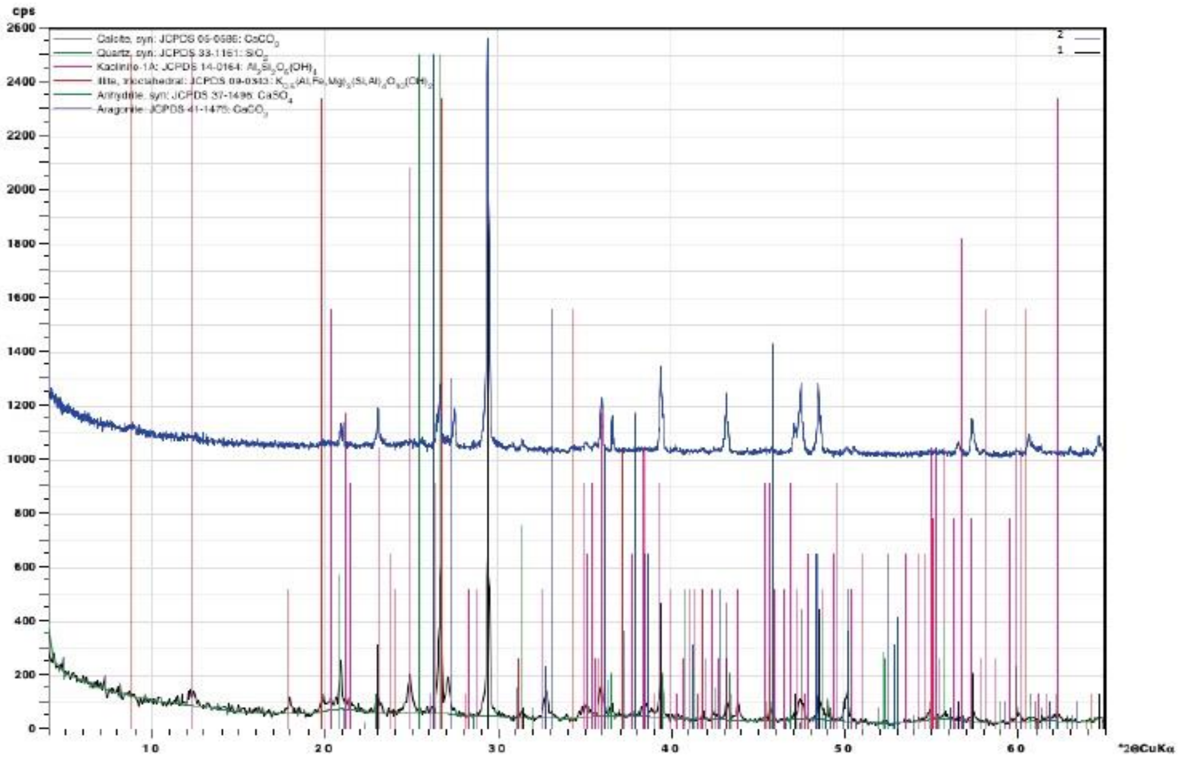


Figure 3.2.5 – Mineralogical results.

3.2.3.2 Chemistry

The chemical analyses shows some differences between the two groups of samples (Table 3.2.2), silica and iron showing higher content in group 1, whereas group 2 shows higher values for loss on ignition, calcium and titanium, this being coherent with the mineralogical results.

Table 3.2.2 – Chemical composition of the two types of soils used for adobe production in Aveiro district (Portugal), (1 = Anadia region, 2 = Murtosa).

	1 (%)	2 (%)
Loss-on-ignition	21.24	25.47
Na_2O	0.23	0.20
MgO	0.61	0.47
Al_2O_3	21.56	20.05
SiO_2	34.73	28.72
P_2O_5	0.53	0.07
SO_3	0.13	0.34
Cl	0.01	0.15
K_2O	0.71	0.62
CaO	16.83	18.50
TiO_2	0.26	4.62
MnO	0.01	0.02
Fe_2O_3	3.10	0.70

3.2.3.3 Insoluble residue

To assess the percentage of aggregate and the chemical resistance, the samples were attacked with hydrochloric acid (1:5). The results of this test were similar between the two groups of samples with a high percentage of insoluble residues, group 1 having a range of 84–92% and group 2 87–93%.

The textural behaviour of the samples after acid attack is represent in Figures 3.2.6 and 3.2.7. The samples are actually Si-rich aggregates, essentially free of carbonates, so they are resistant to acid attack.

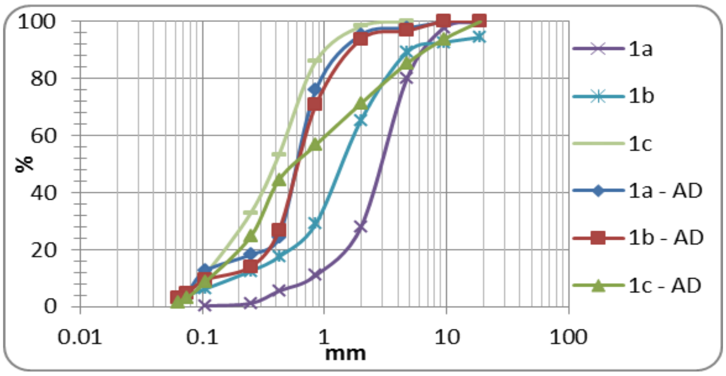


Figure 3.2.6 – Textural behaviour of group 1 of samples, 1a, 1b and 1c are examples of samples that represent in general the behaviour of this group of samples; -AD – after dissolution.

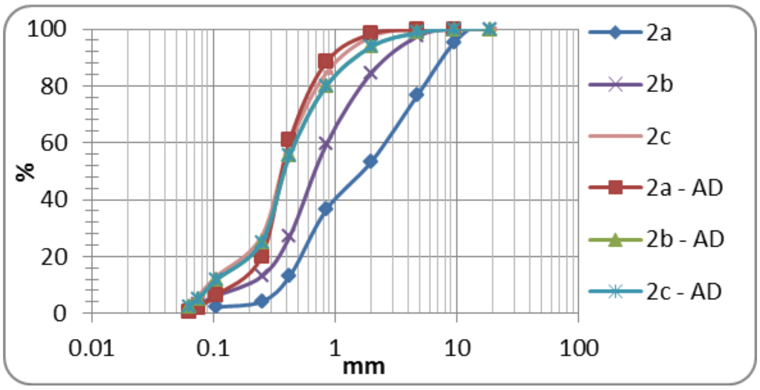


Figure 3.2.7 – Textural behaviour of group 2 of samples, 2a, 2b and 2c are examples of samples that represent in general the behaviour of this group of samples; -AD – after dissolution.

3.2.3.4 Textural analysis

The textural analysis shows that both groups of samples are essentially composed of sand particles. The first group have a range of 83–98% sand, 1–17% silt and 0.1–0.8% clay particles. The second group has 59–98% sand, 2–40% silt and 0.3–1% clay particles. However, in the second group the adobes are more heterogeneous. This was determined by visual analysis only, and then confirmed by results displayed in the textural curves, (Figures 3.2.6 and 3.2.7).

According to Dhandhukia *et al*. (2013) these clay percentages are not adequate and this will damage the compressive strength of the samples. In order to increase the mechanical strength, the percentage of the clay fraction needs to be around 5%.

The group 1 adobe samples display a more homogeneous texture and a larger quantity of fine particles. This is in accordance with the higher phyllosilicate content (in particular kaolinite) and the lower carbonate content in group 1. This may be due to the fact that group 1 has a higher kaolinite content, and group 2 contains lime nodules owing to production conditions, causing an irregular calcite dissemination in the adobe matrix.

Sedigraph. The results obtained by X-ray sedigraph are presented in Table 3.2.3. It is important to note that there is a variety of adobes in the Aveiro district, suggesting that adobes with different particle size distributions than those obtained in this study may be present.

Methylene blue test (fraction <2 mm). The methylene blue test was used to estimate the percentage of the fraction below 2 mm of the studied adobes. The results obtained are listed in Table 3.2.3. Group 1 has a higher fine (and clay) fraction than the samples of group 2, in accordance with the percentage of phyllosilicates determined by mineralogical analysis (Table 3.2.1). The higher phyllosilicate content contributes to a higher methylene blue adsorption value.

Table 3.2.3 – Physical properties of the two types of soils used for adobe production in Aveiro district (Portugal): 1 = Anadia region, 2 = Murtosa

Samples	1	2
Mean diameter (Ø50)	11.85	8.73
Methylene Blue (g MB/kg fraction <2mm)	0.60	0.30
Capillary Absorption Coefficient ($g/dm^3.m1/2$)	7.90	7.00
Average Penetration of water (cm) - Geelong test	3.18	1.58
Compressive Strength (N/mm^2)	2.52	1.76

3.2.3.5 Physical and mechanical properties

Compressive strength. In group 1, samples display a higher mechanical strength compared with their group 2 counterparts (Table 3.2.3); this behaviour may be explained by the differences in compactness and by the presence of lime nodules in the samples from group 2. There seems to be no clear link between the mineralogical composition and mechanical strength, which is determined by the particle size distribution of aggregates, compactness and production procedure. Nevertheless, the higher content of kaolinite, which is used as an additive to improve mechanical strength composites for industrial applications, may contribute to the higher mechanical strength of group 1 samples. Also, the clay percentage in these samples is very low. However according to Jaquin *et al*. (2009), it is widely accepted that unsaturated soils achieve a component of strength through matric suction, which can be considered as an apparent cohesion. As soils dry, so suction increases, and there is an increase in apparent cohesion and consequently strength. Group 2 is rich in carbonates, forming lime nodules in some samples, which may be detrimental for the mechanical behaviour of these adobes.

Geelong test. The water absorption rates of both groups of samples are presented in Table 3.2.3. The capillary absorption coefficient of the samples was calculated using the tangent to the absorption curve prior to stabilization. It is possible to observe that the samples of group 1 have a greater capillary absorption coefficient. This value is directly related on the quantity and type of porosity present in the samples. Adobes with a higher capillary coefficient have a faster water intake and may be more prone to degradation (Veiga, 2005). The results obtained for the Geelong test are shown in Table 3.2.3. The water penetration is lower for the adobes from group 2. The higher water penetration in the group 1 is attributed to their more porous structure, because of their textural and mineralogical characteristics. Likewise, in the Geelong test results, the penetration of water is higher in group 1 because of their higher porosity, owing to their textural and mineralogical composition.

3.2.4 Conclusions

This study allowed the distinction of the main characteristics of both groups of samples representing the most abundant adobes used in Aveiro district. The most important differences between these two groups are the particle size distribution, the mineralogical and chemical composition, the water absorption and the mechanical strength. These characteristics allowed us to determine the material’s characteristics and properties for use in conservation and rehabilitation actions. For this purpose materials compatible with the original ones as characterized in this study must be used. Although there is great diversity of materials, it is important to state that the studied adobes not only represent the main ones used in Aveiro but are also composed of the most available local raw materials. The performed tests also allow us to state that the durability of adobe as a construction material, prone the action of water, is not directly related to its mechanical strength.

This study is important to gain information on the adobes composition. In this case it is necessary to transform (in future studies) these adobes is terms of clay content. A higher percentage of clay fraction (around 5% is the best) will increase the strength of the adobes. According to Dhandhukia *et al*. (2013), there is a correlation between soil composition (sand, silt and clay content) and soil behaviour in terms of the compressive strength of adobes. The composition of the earth-based material (in this case adobe), including natural sand, silt and clay in optimized proportions, could generate higher strength.

The adobe bricks are an alternative of kiln baked bricks which has several advantages and one of the most important is that these materials are recyclable. Adobes are an excellent option for building construction, if composition is optimised.

3.3 ADOBE BLOCKS IN THE CENTER OF PORTUGAL: MAIN CHARACTERISTICS

Abstract Earth construction is the oldest building practice known. The adobe is a simple and sustainable type of earth construction. Many of adobe buildings are in an advanced state of degradation due to the effect of natural agents and to the ageing of constituent materials. There is a strong concern with these materials, because in addition to their sustainability, they are also the mark of generations and heritage of each region and country. Therefore, it is necessary to have deep knowledge of the different compositions, as well as of other properties of the adobes, to infer which compatible materials to use in the interventions taking into account each type of adobe blocks. In this work 41 different adobe blocks from the central coast of Portugal were characterized. It is concluded that there are 5 main types of adobes, which stand out for their visual properties (color and texture), 4 types of adobe blocks according to the mineralogy and three groups of adobe blocks regarding the other properties such as chemical composition and their mechanical behavior. In general terms, adobes consist mainly of quartz, calcite and phyllosilicates. The studied adobe blocks have mechanical strengths ranging from 0.30 to 3.50 MPa.

3.3.1 Introduction

Earth construction is the oldest building practice known, with documented cases of the use of earth bricks in Mesopotamia around 10 000 BC (Heathcote, 1995). Nevertheless, these records are observed in several localities around the world; in the form of old earth buildings that are still today partially preserved. The World Heritage list presents occurrences of adobe and mixed techniques in South America and the Caribbean, North America and Europe, Arab States, Africa and Asia-Pacific (Fernandes & Tavares, 2016). Peru and Mexico exhibit ruins of earth buildings (Torgal & Jalali, 2012) that used sun dried clay with vegetable fibers for the building of walls between 1000 and 1500 AD.

Neves & Faria (2011) point out that according to the displacement and processes of conquest and of Human colonization, construction techniques were diffused, adapted and organized according to the needs and particularities of each region. According to Dobson (2015), in most countries around the world there is some kind of earth construction, either old or currently under construction.

According to Dobson (2015), the earth buildings are sustainable, "healthy", with low emission of carbon dioxide and with aesthetics that vary from rustic to modern. These factors led to a process of industrialization and modernization of the construction processes in raw earth. Adobe is one of the most well-known earth building techniques. The adobe brick, as a construction material, was used in rural and urban buildings, walls for the boundary of properties, water wells, churches and warehouses (Costa *et al*., 2018). The manufacture of the adobe units consists of forming blocks in wood molds which are later sun dried. The molds are filled with a mixture of local soil and water, and in some cases stabilizers are added (Rotondaro, 2011). The application is similar to that of conventional masonry brick, with an earth based mortar being used as joint mortar, aiming at a better interaction between the materials and therefore avoiding cracks and eventual detachments (Costa *et al*., 2019a).

The first use of adobe in Europe refers to 5300 BC in the settlement of Sesklo, Greece, in small houses built on stone foundations (Torgal, 2015). Other authors refer that in Europe this technique appeared during the Iron Age (Chazelles, 1995; Daudon *et al*., 2014). The use of adobe construction in Cyprus is dated to the Neolithic Era (Illampas *et al.* 2014; Christoforou *et al*., 2016). According to Costa *et al*. (2019a) the authors that discovered adobes in the Tigris River affirmed that the oldest adobe bricks found go as back as 7500 BC.

Central and Northern Europe also have a tradition of earth building, although the most well-known buildings are concentrated in the Mediterranean area. The climatic and natural conditions together with the need to make use of the available material boosted the development of several earth-based techniques, either totally earth-based, hybrid, with addition of wood and plants, or as mortar in constructions with blocks of rock. There are records of earth-based constructions dating from the Neolithic period, made with wood and clay (a partition-like technique), for example in Austria (Volhard, 2015).

In the Iberian Peninsula, the development of earth construction remits its origins to the Phoenicians, Carthaginians, Romans and was later perfected by the Muslims (Ribeiro, 1969 in Torgal & Jalali, 2012).

Texts of Pliny (23 BC - 79 AD) concerning the walls of Carthage and Spain, built under Hannibal's rule, indicate that these were built with raw earth (Houben & Guillaud, 1989). Occurrence of earth buildings, specifically rammed earth, along the Iberian Peninsula, dating from the Muslim domination period (between the VIII and XV centuries), are common both in civil (buildings) and military (fortifications) architecture (Bruno, 2005).

The sustainability of earth construction and its vernacular character are the main qualities of this constructive method (Costa *et al.*, 2016). Among the masonry in raw earth presents characteristics that make it sustainable, well known due to the low energy and production costs, biodegradability and thermal capacity (Christoforou *et al.*, 2016); Torgal & Jalali, 2012).

However, like any other material, adobe also has its weaknesses. Among the disadvantages of adobe is its frailty against water and the related degradation that occurs hence. The most common problems found in adobe constructions are listed by Papayianni & Pachta (2017) as cracks due to earthquakes, vertical cracks due to overlapping of extra loads, cracking of the walls due to the compressions by movement of beams or wood floors, decay of beams, floors and roofs, mortar detachment, scratching and loss of material by abrasion, crystallization of salts on the surface (efflorescence), presence of insects, or plant growth.

The problem is spreading when inadequate conservation and restoration actions create further problems mostly felt in the long-term. The use of inadequate and incompatible materials is the problems that cause more disintegration and degradation of adobe buildings. One of the materials used in these actions that cause most problems is cement. The cement used mainly in coatings retains water, accelerating the negative effects of water intake and causing an increase in the disintegration of adobes (Illampas *et al.*, 2013). Another material that is widely used for restoration and rehabilitation of adobe is lime, whether air lime or hydraulic lime; hydrated lime, a common substitute for cement, by pozzolanic action becomes a binding agent that increases durability and strength in adobe (Millogo, 2008).

Like any other material the adobes need proper maintenance. The conservation and restoration actions must always be done taking into account the principle of compatibility of materials. Therefore, it is extremely important to have a deep knowledge of the materials before any intervention. It is considered that compatible materials must have, in regards to old adobes, similar chemical and mineralogical compositions, similar mechanical strength and water absorption and desadsorption capacity. Different mechanical resistances will make it harder the adhesion of materials and will eventually lead to detachment.

The present study aims to be a reference where one can find the characterization of the different types of adobe blocks found in the central coast of Portugal, for possible comparisons both for national and international studies of similar materials. Knowledge of the composition and physical and mechanical properties of adobe is the basis for any conservation and restoration action, useful for the application of compatible materials. Thus, this work intends to provide the main characteristics of the adobes being a database to consult before any intervention in buildings of the studied region, or others with the same characteristics.

3.3.2 The adobe construction in Portugal

In Portugal, many old buildings were erected with earth architecture. There are direct influences from Spain, Greece, Egypt, Tunisia and Syria, which in turn blended with the indigenous traditions, resulting in rammed earth and adobe constructions. Torres and Macias (1995) show the occurrence of earth constructions in the Algarve and Alentejo where the external walls were made of rammed earth, while the internal walls were executed in adobe.

Fernandes *et al*. (2016) describes a territorial zoning of the construction techniques: from the low Tagus to the Algarve where the constructions in rammed earth ("taipa") predominate; wattle and daub ("tabique") construction is characteristic of the Beiras and Trás-os-Montes as well as the coastal region between Douro and Minho rivers; the adobe construction is predominant in the Vouga and Mondego basins (Beira Litoral region), where there are more clayey and sandy soils, and water availability (Fernandes & Tavares, 2016). Further south, the adobe is also found in Ribatejo region, although more scarcely.

The buildings in adobe end up disappearing in places where the presence of fresh rocks predominates.

Figure 3.3.1 illustrates the occurrence of adobe constructions in Portugal, which are used both on exterior and interior walls.

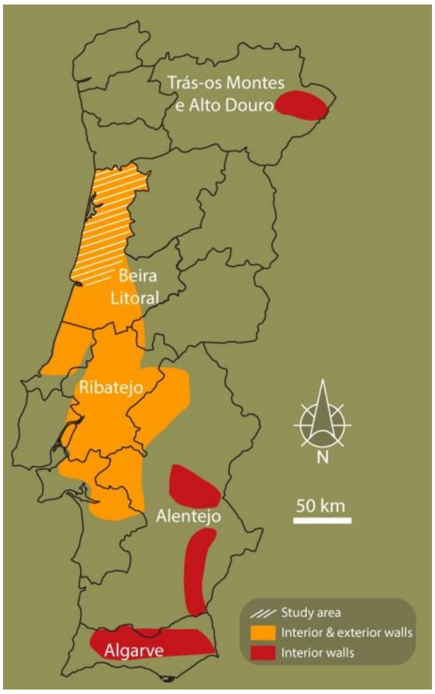


Figure 3.3.1 –Adobe construction in Portugal (adapted M. Fernandes & Tavares, 2016).

Portuguese adobe can be classified into two main types, namely the "adobo", denomination given to adobe stabilized with lime, and the adobes of earth itself. Air lime was a common stabilizer, being used in the area of Aveiro in adobes of very sandy composition. The soil adobes, however, were made of clayey soil and usually carried in their composition vegetable fibers, such as dry reed and straw. Concerning dimensions and masonry apparatus, a great diversity of Portuguese adobes is observed (Fernandes & Tavares, 2016).

Among Portuguese adobes made in molds, Fernandes & Tavares (2016) identify four types of predominant adobe compositions: earth-made, the formulation of which presents earth and water, stabilized with sand; "palhão", constituted by earth stabilized with reed or straw; mud or gravel made, with roots and vegetable remains already present in the soil itself that was used as raw material; and "adobo" that carries lime in its composition.

Thus, adobes present a great compositional diversity, since they reflect the characteristics of the place from which the earth is extracted. Fernandes & Tavares (2016) cite as examples the adobes of Vale do Cértima, that were made with mud material extracted from a local fresh water lagoon (Pateira de Fermentelos). In its composition, the mud extracted for the preparation of the adobes already carried remains of vegetable roots that were used as stabilizers in the confection of the adobes.

The great predominance of adobe in Portugal is in the Aveiro district. According to Varum *et al.* (2005), in the city of Aveiro between 20 and 25% of the construction is in adobe, and considering the district of Aveiro, the percentage rises to 35 to 40%, data that shows the importance of adobe as heritage and its potential as a construction method in the region.

On Aveiro and Ílhavo regions, many of the buildings built in adobe have cultural, social and architectural value associated with the Arte Nova period (Silveira *et al*., 2012; Tavares *et al*., 2012a). The adobe construction predominated up to 1940. From 1960 onwards, with the modernist influence, the use of reinforced concrete and ceramic in the adobe constructions was introduced, characterizing a mixed construction system. Due to the strong influence of the ceramic industries of the region, and the fact that the adobe production was not continuous but just seasonal (because of the weather), caused a progressive predominance of ceramic bricks used in the old adobe constructions, mainly in exteral walls, in order to avoid the traditional problems of adobe with water (Tavares *et al*., 2012b).

The typical adobe dimension in the central coast of Portugal region is 0,45mx0,15mx0,12m, although there are also other dimensions such as: three-quarter of standardized dimensions, for masonry trim or adobe walls; and 0,45mx0,30mx0,12m also for adobe walls (structural); and a curved shape for well walls (Fernandes & Tavares, 2016). Quinta do Areal is a local traditional production center (still running, by Mr. Manuel Duarte), in Esgueira, Aveiro, and still holds some of these typical adobe molds, made in the region until the mid-1960s, as shown in Figure 3.3.2.

Figure 3.3.2 – Typical wood adobe molds.

According to Costa *et al*. (2019a), the mineralogical composition of the adobe blocks usually reveals the occurrence of quartz and calcite as main phases, together with presence of K-feldspars and phyllosilicate minerals (like kaolinite). In adobes in which there is an adequate amount of kaolinite, properties such as water absorption and mechanical strength are improved. It should be noted that the amount of clay minerals should be moderate to avoid cracking in the material. The mechanical strength values mentioned in the literature range between 0.6 and 8.3 MPa, however the frequent of strength in adobes are values between 0.8 and 3.5 MPa, (Illampas *et al*., 2014; Coroado *et al.*, 2010).

The capillary water absorption is between 3–21 $kg/m^2/h^{1/2}$, and this heterogeneity is correlated with the compositional differences of adobes and their differential degradation due to exposure (Coroado *et al*., 2010).

In the adobe constructions in Portugal, especially in the Aveiro district, the wear of the facade is observed mainly by atmospheric interactions (rain, pollution, humidity and marine action) and cracks in the ceiling and walls due to redistribution of loads and stresses. In many adobe constructions the subsequent application of cement mortar is also observed to solve the coating and interaction problems of adobe with water. However, due to the incompatibilities between the two materials, they promote problems in the medium term, which lead to the release of the mortar (Tavares *et al.*, 2012).

This work aims to present the essential composition of the adobe blocks, to be consulted before any intervention in order to facilitate the more adequate choice of materials to be used in these actions.

3.3.3 Materials and Methodology

The adobe buildings, as previously mentioned, are located mainly in the central coastal region of Portugal, with a predominance of this type of construction in the Aveiro district. However, buildings eligible for rehabilitation and conservation works are usually in a high state of degradation (Figure 3.3.3). This leads to the fact that the collected samples are limited in size and conservation state, which makes it difficult to perform some tests.

Figure 3.3.3 – Adobe house in Figueira da Foz, showing the materials degradation.

Samples were selected aiming to understand the different regional/sub-regional characteristics and properties of the materials used in the adobe construction. The choice of the different adobes was mainly based on the difference of color and texture. Figure 3.3.4 shows the five principal adobes found according these two visual characteristics.

Figure 3.3.4 - Evidence of adobe colors and textures found.

A total of 41 samples was collected and characterized. Figure 3.3.1 shows the study area, which was selected as the area with the highest incidence of adobe construction in Portugal. The samples were selected to ensure that the different types of adobe are represented in this work. The samples were collected in vernacular dwellings and exterior walls that were in high stage of degradation. In Figure 3.3.5 it is possible to observe some sampling sites. The majority of the adobe samples studied is from buildings that have already been demolished. Wherever possible whole adobe blocks were collected for the analysis. The tests performed on the adobe samples were chosen in order to know the main characteristics in terms of composition and physical and mechanical properties, serving as a basis for the knowledge of the materials to be used in conservation and restoration activities.

Figure 3.3.5 – Examples of sampling sites.

Particle size distribution was carried out by dry sieving for the coarser fractions (>63 µm) and by wet sieving for the finer fractions (<63 µm); the standard used was EN 1015-1 (for mortars). The analyses of particle size followed the classification adapted from Wentworth scale. The percentage weight of straw it was obtained through the sieving and with the help of tweezer.

Mineralogical studies were carried out on the < 63 µm (fine) and < 2 µm (clay) fractions of the samples through X-Ray Diffraction (XRD). The mineral composition was determined both on un-oriented (random) powder mounts for < 63 µm fraction analyses and on oriented aggregates for the clay fraction ones. The clay fractions were obtained by sedimentation according to Stokes law, using 1% sodium hexametaphosphate solution to avoid flocculation. For the preparation of preferentially oriented clay mounts, the suspension was placed on a thin glass plate and air-dried. XRD measurements were performed using Philips PW 3050 and X' Pert PW 3040/60 equipment using Cu Kα radiation. Scans were run between 2° and 60° (unoriented powder mounts) or between 2° and 20° 2Θ (oriented to verify clay mounts) in the air-dry state after a previous glycerol saturation and heat treatment (500°C). Qualitative and semi-quantitative mineralogical analyses followed the criteria recommended by Schultz (1964), Thorez (1976) and Mellinger (1979). For the semi-quantification of the identified principal minerals, peak areas of the specific reflections were calculated and weighted by empirically estimated factors, according to Galhano *et al*. (1999) and Oliveira *et al.* (2002).

The chemical composition of adobes was assessed by X-ray fluorescence (XRF) using an XRF Panalytical AXIOS PW4400/40. Loss-on-Ignition (LOI) was determined by heating 1 g of the sample at 1000 ºC for 1 h in furnace.

Acid dissolution tests were performed in order to dissolve the binder fraction, and therefore assess the aggregate fraction (Velosa *et al*., 2010). Adobe samples of 50 g were dried at 110 ± 5 °C until constant mass was achieved. In a 100 ml beaker, 1/5 hydrochloric acid was added and the sample was agitated prior to filtering. Hydrochloric acid was used in order to dissolve the carbonate fraction, since lime is commonly present in adobes.

Cubical specimens were extracted from the collected adobe blocks with different sizes, because the size of specimens always depended of the quantity of sample available. Due to the high state of degradation of the most sampled adobes, it was impossible to follow a standard for the strength test, and in some samples it was impossible to perform the test. However, the procedure for simple compression follows the recommendations of "The Australian earth building handbook" (Walker, 2002). The recommendation in this document was taken as guideline, and were not strictly followed due to limitations of the available laboratory facilities, and due to the fact that these document refers to materials for new constructions while the present study is directed to materials collected from existing constructions. The obtained specimens were submitted to compressive strength tests, using a universal mechanical compression testing machine (Shimadzu Autograph AG 25 TA). This test was made with a loading velocity of 50 N/s in uniaxial compression.

3.3.4 Results

3.3.4.1 Particle size distribution

The grain size curves of 41 analyzed adobe samples are shown on the graph in Figure 3.3.6. Graph observation reveals a peculiar sample (28) with a grain size curve completely different from the others, being very rich in fine fraction. The other samples present similar curves, highlighting sample 29 presenting coarser aggregates and sample 33 which presents in its composition aggregates thinner than the other samples.

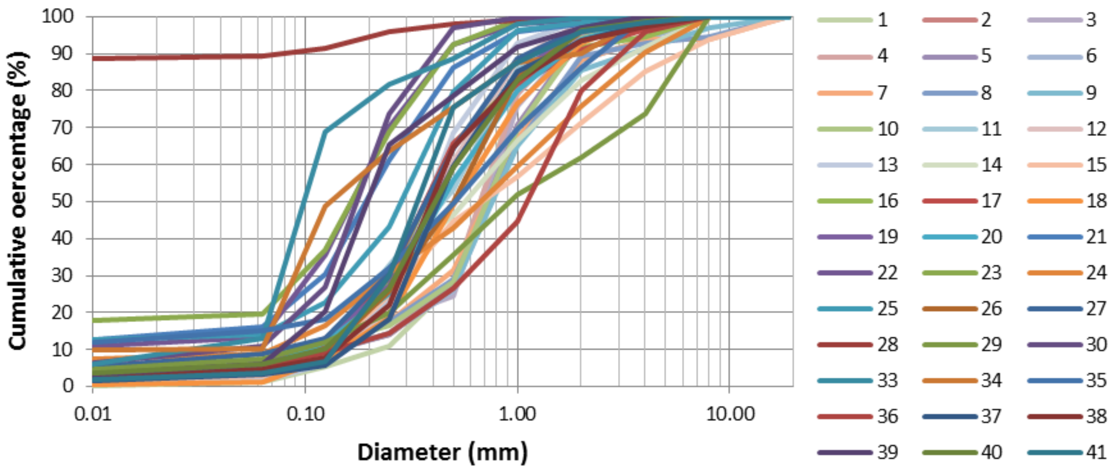


Figure 3.3.6 – Grain size distribution of adobe samples.

In general terms, the studied adobes are composed essentially by sands (0.063 to 2mm), presenting variable amounts of pebbles (>20mm), gravels (2 to 20mm), silts and clays

(<0.063mm) (Figure 3.3.7). Only samples 7, 8, 9 and 15 present aggregates with pebble dimensions. The percentage of silts and clays of most samples is around 5%, however, the samples 21, 22, 23, 25, 34 and 35, this percentage doubles to around 10% and the sample 25 reaches 18%. Sample 28 differs from the rest, being an adobe composed by fine soil and straw; 90% of its material is silts and clays, and the straw weight percentage is about 1%.

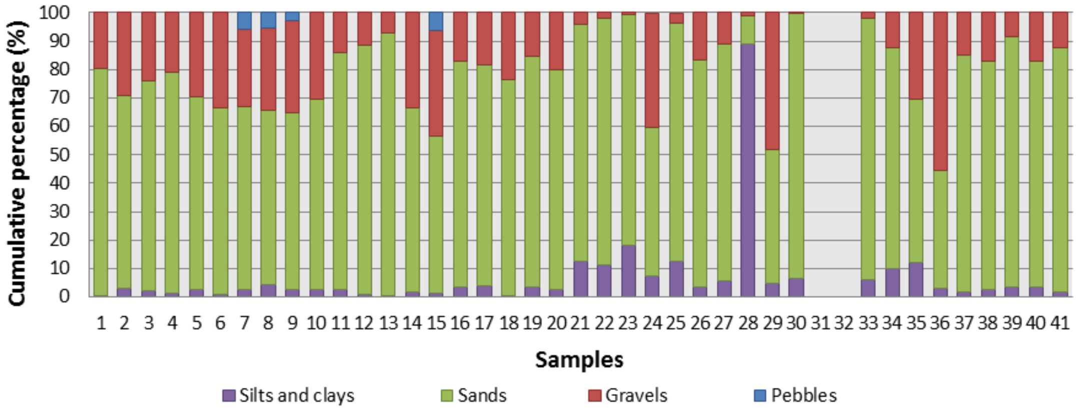


Figure 3.3.7 – Particle size distribution.

Taking into account the grain size distribution, we can distinguish 3 groups: “fine adobes” (for example sample 28) that are essentially fine soil and straw (or other type of fibers), without sand or other type of coarse fraction, being composed essentially by silts and clays; “coarse adobes”, whose aggregate is composed of a significant percentage of pebbles and gravels, around 40 to 50% in some samples (15, 24, 29, 36); “medium adobes” whose grain sizes are essentially sand, varying from 2 to 0.063mm.

3.3.4.2 Mineralogical composition

The mineralogical compositions was studied on the bulk samples and on fractions <63 µm and <2 µm. On bulk samples there is an absolute predominance of quartz, sometimes with calcite and /or feldspars; therefore on bulk samples it is difficult to check the existence of the other minerals. Figure 3.3.8 shows the mineralogical results for the fraction <63 µm. The analysis of this fraction allows us to know more precisely the composition of the silt-clay fraction of the adobes, dominated by quartz, calcite, phyllosilicates and K – feldspars; among the accessory minerals (Figure 3.3.9) predominates iron oxides and hydroxides, major responsible for the redder or orange tones of the adobe. Thus, the higher the content of these minerals redder are the adobes. White-gray adobes usually don´t have iron minerals or and present them in low amounts.

According to the mineralogical composition, these adobes can be classified in 4 groups: “lime-stabilized adobes”, where the percentages of calcite found are higher, ranging between 50 to 95% in the fraction <63 µm; “soil adobes”, where are found values of phyllosilicates between 30 to 60%; “medium adobes” that have a similar quartz and calcite content; “iron rich adobes” with iron oxides and hydroxides in higher content than the others.

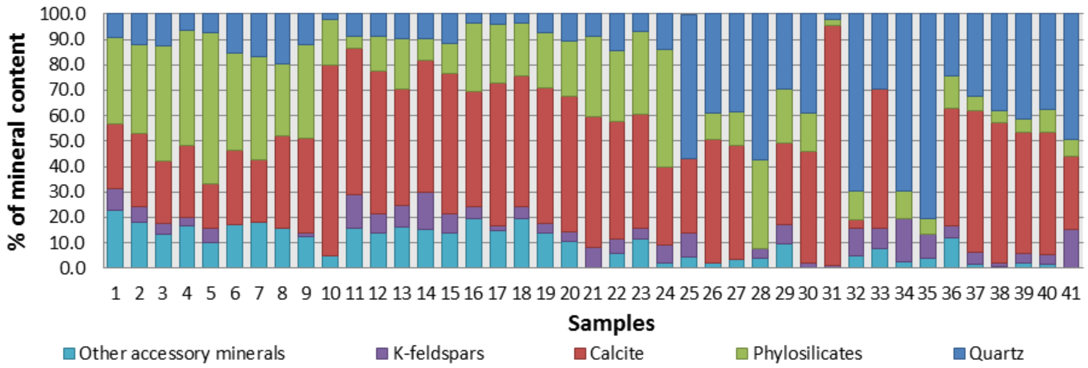


Figure 3.3.8 –Mineralogical composition of adobe samples (semi-quantification).

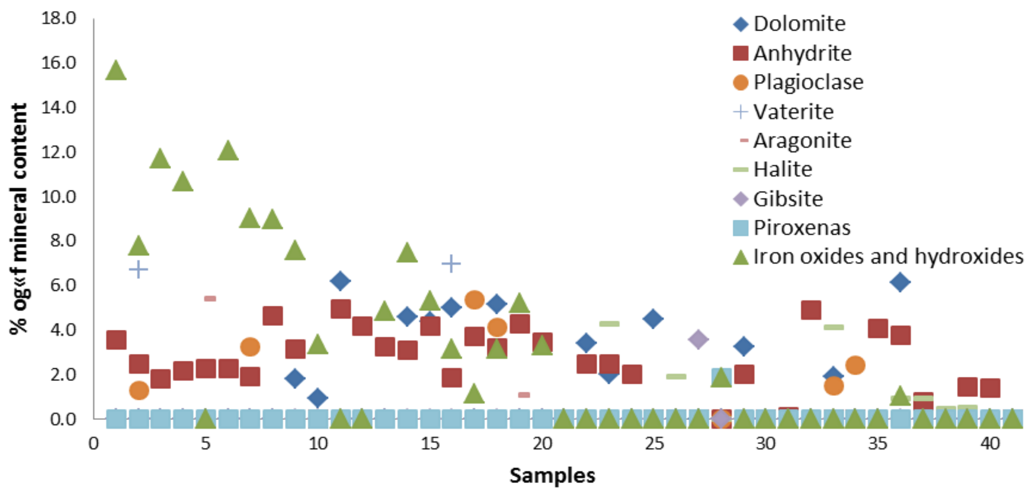


Figure 3.3.9 – Accessory minerals content.

The phyllosilicates were deeply studied in order to understand the actual clay minerals present in these adobes (Figure 3.3.10). The analysis of the phyllosilicates content also allowed to distinguish: adobes rich in phyllosilicates, with contents between 30 to 60%; adobes having around 30 to 10% of phyllosilicates content; and adobes poor in phyllosilicates with percentages below 10%. According to the analyzes performed on <2 μm fraction, phyllosilicates identified are the following clay minerals: kaolinite, illite, smectite, chlorite, vermiculite and illite-smectite (Figure 3.3.10). Taking into account the clay minerals semi quantification, three types of adobes can be distinguished: adobes composed mainly by kaolinite; adobes composed mainly by illite; adobes composed essentially by kaolinite with small amounts of illite and/or llite-smectite or vermiculite and/or chlorite; and adobes composed essentially by chlorite with lower contents of (and / or) illite, kaolinite and smectite.

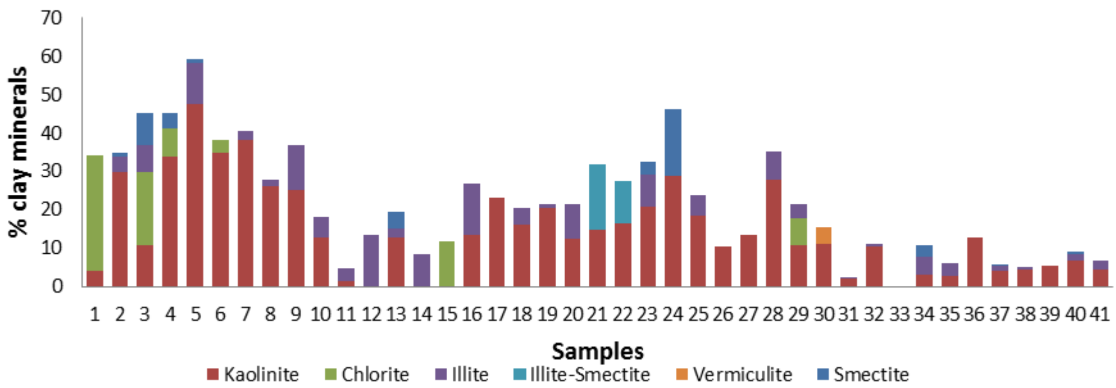


Figure 3.3.10 – Clay minerals content of the samples.

3.3.4.3 Chemical composition

The chemical composition of the adobe samples is presented in Table 3.3.1. Wherever possible the chemical analyses were carried out on the fraction <63 μm to support the mineralogical analysis. However, on samples marked with * the results presented are from the bulk samples due to the extremely low sample quantity. The chemical analyses support the mineralogical composition of the samples, being composed mainly of silica, calcium and aluminium. It should be noted that in the bulk samples, silica content is higher (and LOI values very low), due to the high content of coarse fraction (especially quartz rich sand) present in the adobes.

Table 3.3.1 – Chemical composition of the adobe samples

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	Fe_2O_3	MnO	LOI
1	0.1	0.5	22.8	33.6	0.1	0.1	0.0	0.7	17.4	0.3	3.1	0.0	21.2
2	0.1	0.5	22.7	33.5	0.1	0.1	0.7	17.1	0.3	0.0	3.1	0.0	21.9
3	0.0	0.5	22.8	34.0	0.1	0.1	0.0	0.7	16.6	0.2	2.8	0.0	22.0
4	0.1	0.5	23.1	33.7	0.1	0.1	0.0	0.7	16.8	0.2	2.8	0.0	21.9
5	0.1	0.5	22.9	34.8	0.1	0.1	0.0	0.7	16.6	0.3	3.0	0.0	20.8
6	0.1	0.7	22.4	37.0	0.1	0.1	0.0	0.7	16.6	0.3	3.1	0.0	18.9
7	0.1	0.7	21.4	35.9	0.1	0.1	0.0	0.7	17.2	0.3	3.3	0.0	20.1
8	0.9	0.7	20.3	34.1	2.3	0.1	0.0	0.7	16.3	0.3	3.1	0.0	21.3
9	0.1	0.7	20.1	35.1	0.1	0.2	0.0	0.8	17.7	0.3	0.0	3.0	22.0
10	0.1	0.7	21.8	36.5	0.1	0.1	0.0	0.7	16.5	0.3	3.0	0.0	20.2
11	0.2	0.4	20.6	30.2	0.1	0.2	0.2	1.0	20.6	0.1	0.7	0.0	25.6
12	0.2	0.4	20.7	30.2	0.1	0.0	0.2	1.1	22.4	0.1	0.7	0.0	23.8
13	0.1	0.4	20.3	30.2	0.1	0.0	0.1	1.0	21.1	0.1	0.6	0.0	25.9
14	0.1	0.4	18.1	28.9	0.1	0.1	0.0	1.0	26.3	0.1	0.7	0.0	24.1
15	0.1	0.5	17.6	28.5	0.1	0.2	0.0	1.0	27.2	0.1	0.7	0.0	24.1
16	0.1	0.5	20.0	28.0	0.1	0.4	0.0	0.7	22.6	0.1	0.7	0.0	26.9
17	0.2	0.5	19.2	28.0	0.1	0.3	0.1	0.7	23.7	0.1	0.7	0.0	26.4
18	0.3	0.5	20.4	29.0	0.1	0.3	0.3	0.8	22.3	0.1	0.7	0.0	25.1
19	0.2	0.5	19.8	28.5	0.1	0.4	0.1	0.8	23.3	0.1	0.7	0.0	25.7
20	0.2	0.5	20.9	30.1	0.1	0.3	0.2	0.8	22.9	0.2	0.7	0.0	23.3
21	0.7	1.0	13.4	26.4	0.1	0.3	0.4	1.3	26.9	0.2	1.8	0.0	27.6
22	0.9	0.9	18.6	32.6	0.1	0.5	1.3	2.3	16.7	0.3	1.3	0.0	24.7
23	2.8	1.6	10.8	17.2	0.2	0.4	4.3	7.9	15.9	0.1	0.6	0.0	38.3
24	0.0	11.7	15.3	27.5	0.2	0.0	0.0	0.8	16.2	0.2	2.0	0.0	26.1
25	0.7	0.6	22.3	32.3	0.1	0.0	0.1	1.3	17.0	0.2	1.1	0.0	24.4
26	0.1	0.5	12.4	20.5	0.1	0.1	0.0	0.8	34.4	0.1	2.0	0.0	28.9
27	0.1	0.8	21.2	27.3	0.2	0.3	0.0	1.1	20.6	0.3	4.6	0.0	23.5
28	0.3	1.0	21.1	52.4	0.2	0.4	0.0	3.3	0.9	0.6	4.7	0.0	14.8
29	0.2	0.5	19.0	32.8	0.2	0.1	0.0	3.5	18.7	0.2	6.8	0.0	17.7
30	0.1	4.1	18.1	25.3	0.1	0.1	0.1	1.3	22.7	0.2	1.4	0.0	26.5
31	0.2	0.5	12.9	26.9	0.1	0.2	0.1	1.3	28.7	0.2	1.9	0.0	26.8
32	0.4	0.3	14.5	69.8	0.1	0.1	0.0	2.3	0.7	0.6	2.2	0.0	8.9
33*	0.6	0.5	6.3	55.3	0.1	0.2	0.1	2.8	24.8	0.3	1.0	0.0	8.0
34*	0.4	0.9	15.4	74.5	0.1	0.1	0.0	3.5	0.3	0.5	3.1	0.0	1.2
35*	0.4	0.7	9.9	80.3	0.1	0.1	0.0	2.4	0.5	0.4	1.7	0.0	3.5
36*	0.2	0.4	10.2	74.1	0.1	0.1	0.1	1.9	7.5	0.1	0.9	0.0	4.4
37*	0.1	0.2	7.4	82.2	0.0	0.0	0.0	1.4	5.1	0.1	0.3	0.0	3.2
38*	0.1	0.3	8.7	80.8	0.1	0.0	0.0	1.3	6.3	0.1	0.4	0.0	1.9
39*	0.3	0.3	11.5	74.3	0.1	0.0	0.0	4.2	5.1	0.1	0.4	0.0	3.7
40*	0.1	0.3	7.1	77.8	0.0	0.0	0.0	1.3	8.0	0.2	0.4	0.0	4.8
41*	0.1	0.3	8.4	82.5	0.0	0.1	0.0	1.8	3.4	0.1	0.6	0.0	2.7

3.3.4.4 Percentage of aggregate

The results obtained from acid dissolution are shown in Figure 3.3.10, ranging from ~85 to 99%. The graph (Figure 3.3.11) allows the division, once again, in 3 groups: the first one with a higher percentage of insoluble residue (up to 95%), a second group showing insoluble residue values between 90 to 95%, and the last group between 85 to 90%. The percentage of insoluble residue is a proxy of the chemical resistance of the adobe, since the binder is prone to acid dissolution; it is also possible to have an idea of the amount of binder in relation to the aggregate present in the adobe. However, depending on the binder, the acid attack may be more or less effective, compromising a precise correlation of these results with the amount of aggregate / binder present in the adobes.

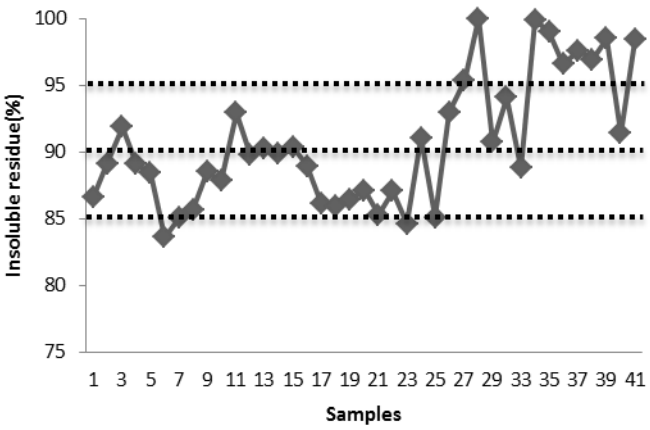


Figure 3.3.11 – Graph of the percentage of the insoluble residue.

3.3.4.5 Mechanical strength

The results of mechanical strength are presetend in Figure 3.3.12. The studied adobes have mechanical strengths ranging from 0.30 to 3.50 MPa. The obtained results allowed to distinguish three groups (like the previous parameters) of adobes: group 1, gathering samples showing lower strength (<1 MPa); group 2 with those presenting medium strengths (from 1 to 2 MPa), and group 3 with those presenting higher strengths (> 2 MPa).

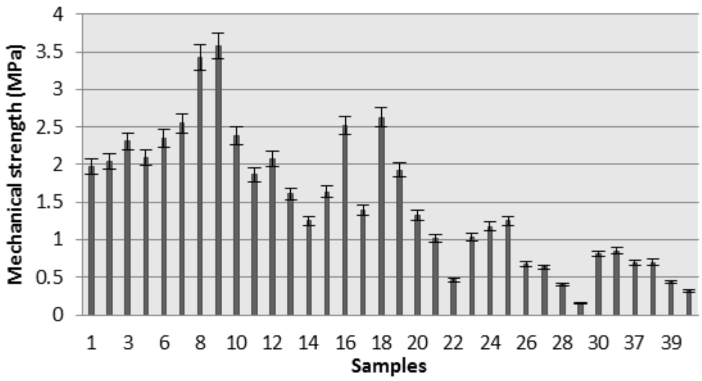


Figure 3.3.12 – Mechanical strength of the adobe studied samples.

Low compressive strengths can be related with the material degradation, as expected taking into account that these materials are old and have already suffered much wear and tear.

The mechanical strength values mentioned in the literature for old adobe blocks (Illampas *et al*., 2014; Coroado *et al*., 2010) range between 0.6 and 8.3 MPa; however the most frequent values of resistance in adobes are comprised between 0.8 and 3.5 MPa (Illampas *et al*., 2014).

3.3.5 Discussion of results

Grain size distribution of adobes is very variable being affected by the original textures of the used soil and aggregate. The predominantes textural classes are sand and clay/silt fractions for all samples. The other grain sizes may or may not be present but always in lower percentages (Illampas *et al*., 2014; Miccoli *et al*., 2014; Castrilho *et al*., 2017).

According to studies carried out by other authors in other adobe samples, the mineralogical composition varies according to the soil and material available in the study area. However, all refer to the appearance of quartz as the main mineral, making this part of the aggregate that constitutes the adobes (Miccoli *et al*., 2014; Faria *et al*., 2015; Abanto *et al.*, 2017; Fratini *et al*., 2011). The authors also describe the presence of calcite, feldspars (plagioclase and potassium feldspar) and phyllosilicates (montmorillonite, illite and kaolinite), and in smaller amounts sometimes dolomite, gypsum and iron oxides and hydroxides (mainly hematite, goethite). Mineralogically, the samples analyzed in this study, and by other authors, differ mainly in the accessory minerals that are directly related to the composition of the raw soil used in the execution of each adobe.

According to Miccoli *et al*. (2014), the SiO_2 percentages range between 10 to 45%, however in this study this percentages range between 14 to 82%. The same author refers 20 to 80 percent for CaO and 1 to 9 percent for Fe_2O_3. In the present study CaO percentages between 0 to 35% and for Fe_2O_3 percentages between 0 to 7% were found. These differences are correlated with the different provenience of the studied adobes and the different methodology used (FTIR vs XRF).

The insoluble residue depends mainly of chemical and mineralogical composition of the adobes. This test gives an idea of the amount of aggregate of the material, however, it works better in mortars, and in adobe the conclusions to be drawn are more limited.

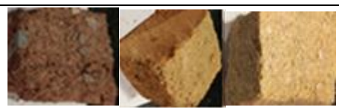
The mechanical strength of different adobes studied range between 0.30 to 3.50 MPa. According to Silveira *et al.* (2013), the mechanical strength for cubical specimens ranges between 0.28 to 1.21 MPa, whereas for the cylindrical specimens the values range between 0.23 to 1.02 MPa. Fratini *et al*. (2011) finds compressive strength values for cubic specimens varying between 0.5 and 1.32 MPa. Miccoli *et al.* (2014) describe mean values of compressive strength of the adobe blocks of 5.21 MPa. The mechanical strength values of the adobe depend on the material, its state of degradation, the sample preparation and the standards followed. However, the values of the different authors are all around the same order of magnitude.

The composition, and consequently the properties of the adobe are mandatory knowledge before any conservation and restoration intervention. Upon this knowledge depends the quality and efficiency of any intervention. The use of compatible materials is essential and indispensable in these actions.

3.3.6 Conclusions

The main characteristics of the adobes studied are shown on Table 3.3.2. Regarding texture, the studied adobes present mostly sand as the main constituent; pebbles, gravels and silts and clays are presented in different minor proportions. Mineralogically, the main minerals are quartz, calcite, feldspars, phyllosilicates (mainly kaolinite, illite and chlorite) and other accessory minerals (iron oxides and hydroxides, anhydrite and halite). The insoluble residue ranges between 85 to 99%. Mechanical strength results vary between 0.3 to 3.50 MPa. The iron oxides and hydroxides are correlated with the color of the adobes and also with mechanical strength (Figure 3.3.13).

Table 3.3.2 – Principal characteristics of the 3 groups of studied adobes

Main characteristics	**Adobe - 1**	**Adobe - 2**	**Adobe - 3**
Color			
Texture	Essentially sand (2 to 0.063mm)	Coarse adobes	Thinner adobes
Composition	Lime adobes (rich in calcite)	Rich in iron oxides and hydroxides	Soil adobes (rich in phyllosilicates)
Compressive strength	Acceptable strengths (from 1 to 2 MPa)	Good strengths (> 2 MPa)	Low strength (<1 MPa)

Adobes are materials strongly dependent on the availability of the local source material for their production. The adobes presented characteristics similar to adobes from other countries, such as Spain, Morocco, Italy and Angola (Daoudi *et al*., 2018; Duarte *et al*., 2015; Vega *et al*., 2011; Miccoli *et al*., 2014).

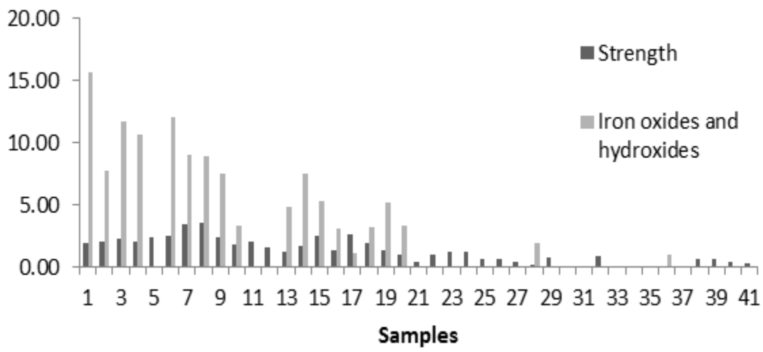


Figure 3.3.13 - Relation between mechanical strength and iron oxides and hydroxides content.

According to the geological materials available in the study areas and taking into account the results obtained in this study, there are essentially 3 to 5 types of adobes in the central coast of Portugal, depending on the properties analysed. Lime-stabilized adobes (usually grey to white in color) are the most frequent, due to the great availability of raw materials. The earth adobes (usually, brownish color) are not so frequent, due to their commonly very low mechanical strength (less than 0.50 MPa) and negative behaviour when in the presence of large amounts of water; the inclusion of natural fibers and straw in the earth adobes was quite frequent. A third type of adobes (commonly reddish to orange color) “sandy-adobes” is composed essentially by quartz rich sandy soils with small amounts of binder (often clays).

According to Costa *et al.* (2019a) the knowledge of the adobes composition is extremely important for the use of compatible materials with them in possible conservation and restoration of buildings with these materials. On this knowledge depends the quality and efficiency of any intervention. The use of compatible materials is essential and indispensable in these actions. This study aims to be a relevant contribution towards a better knowledge of the basic composition of adobes in Portugal, serving as a knowledge basis for future interventions in the conservation and restoration of adobe buildings in the central coastal region of Portugal, or for others in which the adobe materials have a similar composition.

3.4 CHAPTER SYNTHESIS

The analysed set of adobe samples represents the studied region, Central Portugal. The main assessed characteristics were: colour, texture, chemical and mineralogical composition, water absorption and mechanical resistance.

In terms of colour, the studied adobes can be divided in three groups: grey, yellowish to orange, and brown.

Concerning texture, the studied adobes present mostly sand as the main constituent; pebbles, gravels, and silts and clays are present in different minor proportions. However, the brown adobes usually are finer than the others.

Chemically, adobes consist essentially of silica (from the aggregate), aluminium and calcium. Aluminium increases when the phyllosilicates content increase and calcium when the content of lime increases. Iron is also found associated with the presence of iron oxides and hydroxides, which are responsible for the orange tones of some adobes.

According to the mineralogical studies the adobes are composed mainly of tectosilicates (quartz and feldspars), followed by carbonates (calcite and sometimes dolomite) and phyllosilicates (kaolinite> illite, sometimes discrete smectite and chlorite). As accessory minerals, iron oxides and hydroxides have been identified; in some samples occur salts (mainly halite) and sulphates (gypsum).

The capillarity absorption coefficient range between 3 to 13 $g/dm^3.m^{1/2}$. Adobes with a higher capillary coefficient have a faster water intake and may be more prone to degradation.

Mechanical strength results vary between 0.3 to 3.5 MPa. The lower values are correlated negatively with the materials stage of degradation. The higher results usually are influenced by iron oxides and hydroxides.

These are the main properties of the original adobes that may be used as base for any intervention in buildings with these materials. In addition, due to the principle of material compatibility, knowledge of these characteristics is crucial for the development of new materials, which will be the object of study of the next chapter.

CHAPTER 4

DEVELOPMENT OF NEW GEOMATERIALS TO APPLY IN ADOBE BUILDINGS REHABILITATION AND RESTORATION

In this chapter 3 papers are presented focused on the development of new materials.

Two groups of new materials were used: alkaline activated and geopolymers.

Alkaline activated materials don´t need a specific ratio Si:Al, and don´t have specifications for used raw materials; in this study, for all alkaline activated materials there is no addition of sodium silicate. Geopolymers are products demanding specific raw materials with high content in silica and aluminium; in this study, sodium silicate was added to develop geopolymers in order to increase reactive silica to faster process.

1. ***Adobe innovative formulations alkaline activated for rehabilitation of old adobe buildings.*** (S*ubmitted to International Journal of Architectural Heritage)*

   In this paper new adobes are developed with improvement of their properties using alkaline activation (with NaOH and KOH).

   The raw materials used in the development of the new adobes were chosen within the old studied adobes area in order to: i) minimize transport costs, thus reducing their ecological footprint; aiming that the possible market for these materials will be focused in the Aveiro region, where there is a great predominance of this type of construction; ii) assure the desired compatibilities with the old adobes.

   The developed adobes have the potential to be applied in the field, which will be the next step of this research.

2. ***Diatomite based geopolymers as restoration materials.*** (submitted to *Construction and Building Materials)*

   This paper is focused on the development of geopolymers with a Portuguese diatomite as additive (as a silicon source); the same kaolin and metakaolin of the previous paper were used, too.

   Geopolymers are alkaline activated aluminosilicates, arise as potential materials, having more controlled costs and lower environmental footprint and improving the chemical and physical characteristics of the adobes. It was evaluated the influence of the diatomite as an additive in these materials, and it was verified that about 10% of the addition is ideal for obtaining an increase in mechanical strength. The mineralogical, chemical and physical properties of the developed geopolymers are promising. The next step will be to test the compatibility of these materials with the old adobes.

3. **Development of geopolymers formulations based on low-grade kaolins as a potential construction material.** (Submitted to *Minerals,* preprint DOI: https://doi.org/10.20944/preprints201906.0170.v1)

   This third paper focused in the development of geopolymers with other raw materials, such as: two kaolins were supplied by a Portuguese company (Mibal - Minas de Barqueiros SA).

   The kaolins were calcined at different temperatures (300, 500 and 750°C) in order to test the effect of temperature on the performance of the produced geopolymers. The materials were activated with NaOH and sodium silicate. Concerning mechanical strength, the better results were obtained with natural and 300°C calcined kaolins; water absorption results showed opposite trend. The developed geopolymers have the mineralogical and physical properties necessary to be promising materials in terms of compatibility with the old adobes.

4.1 ADOBE ALKALINE ACTIVATED INNOVATIVE FORMULATIONS FOR THE REHABILITATION OF OLD ADOBE BUILDINGS

Abstract In Portugal, earthen materials have been used in load-bearing walls in the form of adobe masonry or rammed earth for the construction of buildings especially in the southern and central coast. In recent years there has been an increased interest on earth construction in order to preserve the cultural heritage focused in the rehabilitation and conservation of this type of buildings. The materials to be used in these actions should be compatible with the old ones and, if possible, improved, mainly in terms of durability and, namely, capability to withstand the action of water.

The most conventional consolidation treatments used in the past have not succeeded in providing a long-term solution because they did not tackle the main cause of degradation, the expansion and shrinkage of constituent clay minerals in response to moisture changes. This taken into account, in this study adobes produced with water (non-activated), NaOH-activated and KOH-activated were developed and tested. The adobes developed solely with water were used as reference (blank). The obtained results allowed the conclusion that the adobes with NaOH and KOH have an improvement in terms of properties; it´s possible to guarantee compatibility between the developed materials and old adobes.

4.1.1 Introduction

Earth construction is the oldest building practice known and approximately 30% of the world population lives in buildings made of earth materials; this type of building technique exists throughout the world in many different cultures, and for some countries it continues to be the main process of construction (Vega *et al*., 2011). Earth construction offers economic and environmental benefits especially when used in developing countries where material costs overlap labour costs and where other construction materials and technologies may not be available (Fratini *et al*., 2011). The costs are minimized in earth construction because local materials may be employed, and it is relatively simple and easy to perform. Earth buildings usually have lower embodied energy and carbon footprint than the other buildings with sophisticated processes, like concrete, steel or fired brick or concrete blocks masonry (Bui *et al*., 2009a, 2009b). This is because the earthen raw materials that are used do not need any kind of firing treatment before their use as a construction material, comprising only raw, sun-dried earth.

There are several earth construction techniques worldwide like cob, rammed earth ("pisé", "taipa"), "Wattle and Daub" (tabique), and adobe (Niroumand *et al*., 2016). Cob is performed by stacking an earth mortar, usually with the addition of straw and posterior regularization of the surface. In Portugal, earthen materials have been used in load-bearing walls, in the form of both adobe and rammed earth, for the construction of buildings especially in the southern and central areas. Most adobe buildings are confined to the central coast. The adobe construction in these locations has economic and environmental benefits, because the raw material is sourced on-site (Ciancio *et al*., 2013). In the central coast, there has been an obvious degradation and abandonment of many buildings; however, some of these old buildings can be rehabilitated with minor maintenance and repair works. Over recent years, particular attention has been given to conservation and rehabilitation in order to preserve and protect this heritage (Costa *et al*., 2013). The use of adobe construction in the Aveiro district reflected the properties of the existent available raw materials applied, which were sand, clayey earth and lime (Silveira *et al*., 2012), and there is an evident heterogeneity of the adobes linked to the geographic distribution of the available resources. In Aveiro there was a semi-industrial production of adobe, some small companies having 'adobeiros', a group of people making the adobe, along with domestic self-production (Costa *et al*., 2016).

In recent decades, concern towards the conservation of ancient buildings has increased and the idea that these buildings can be rehabilitated and reused instead of demolished has become a common thought with repercussions in the market (Lourenço, 2005). There is an increased interest in the preservation of old buildings because it is important to maintain the historic part of cities with functioning and appealing characteristics both for inhabitants and for tourists.

Taken this into account, several studies about these materials are being developed, trying to improve some properties and find compatibility among the materials used in the rehabilitation of these types of constructions.

The studied consolidation procedures are, actually, a short-time solution. The major problem is related to the specific type of clay minerals present (in these materials) which can expand and contract with water changes. This problem of clay swelling can be reduced with alkaline activation. This process decreases the effect of expansibility and increases the cementing of materials (Elert *et al.*, 2015). Taking this into account, this study developed adobes with water (non – activated), and activated with NaOH and KOH to evaluate the compatibility with old adobes focused in the improvement of mechanical strength.

4.1.2 Methods and materials

4.1.2.1 Methodology used

The chemical composition of samples was assessed by X-ray fluorescence (XRF) using an XRF-Panalytical AXIOS PW4400/40 spectrometer equipped with Rh tube, argon/methane gas and IQ+ (major elements) and Pro-Trace (minor elements) data processing programs for complete chemical analysis. Loss-on-Ignition (LOi) was determined by heating 1 g of the sample at 1000 ºC for 1h in a furnace Cassel, model MF20, series 83215.

Qualitative mineralogical analyses were carried out by X-ray diffraction (XRD) using a Philips®/Panalytical X'Pert-Pro MPD, Cu Kα (λ= 1,5405 Å) radiation, with 2º to 60º 2θ s^{-1} steps in goniometer speed. The identification of the different mineral phases followed the criteria recommended by Brindley and Brown (1980), the Joint Committee for Powder Diffraction Standards, and Mellinger (1979).

The microstructural characterization was carried out by scanning electron microscopy (SEM – Hitachi, SU 70) and energy dispersive X-ray spectrometry (EDS – EDAX with detector Bruker AXS, software: Quantax) operated at 3–30 kV.

The specific surface area analysis was accomplished in Micromeritics Gemini 2.0 equipment according to the BET method (Brunauer *et al*., 1938).

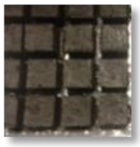
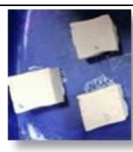
The cubical specimens were submitted to compressive strength tests, using a universal mechanical compression testing machine (Shimadzu Autograph AG 25 TA). The testing procedure was carried out with a maximum force of 5 kN at the speed of 50 N/s as per the standard EN 1015-11 (Moutinho *et al*., 2019).

4.1.2.2 Materials used for adobe formulations

The innovative adobe formulations in their composition incorporate materials available in Aveiro district (Figure 4.1.1) the geomaterials used being previously identified (Sabir *et al*., 2001, Vejmelková *et al*., 2012, Andrejkovičová *et al*., 2013) as good for application in construction materials. The location of the samples was chosen considering the high occurrence of ancient adobe buildings that have been previously studied and that many require urgent interventions (Costa *et al*., 2013; Costa *et al*., 2016, Costa *et al*., 2019a). One of the criteria for raw materials selection was the location in order to avoid large transportation costs reducing the ecological footprint of the final product. As a source of silicon sand from Quinta do Areal, a farm in Aveiro, where there was adobe production, was used. In order to replace a clayey soil by a material with improved properties, a low-grade kaolin from an exploration in Ovar area was used (Figure 4.1.1). Pateira de Fermentelos mud (Figure 1) was also used as a source of clay, as it is a material with good properties for the intended purpose and because it is available within the study area. Industrial metakaolin (1200S, AGS Mineraux, France) was also used to compare with the remaining materials sources of aluminum silicates. With these three materials a variety of formulations were developed in which water was used as a blank and alkaline activation with sodium hydroxide and potassium hydroxide, both to 6M solutions. The formulations performed are in Table 4.1.1.

Figure 4.1.1 – Map with the area of studied old adobes and of the materials used in the new formulations of adobes.

Table 4.1.1 – Performed formulations

Materials			**Solutions (33% volume)**	
Mud from Pateira de Fermentelos	**1.1**	Mud + Fibers (10%)	**H_2O** **NaOH (6M)** **KOH (6M)**	
Sand + Commercial Metakaolin	**2.1**	Sand + Metakaolin (20%)		
	2.2	Sand+ Metakaolin (40%)		
Sand + Kaolin	**3.1**	Sand + Kaolin (20%)		
	3.2	Sand + Kaolin (40%)		
Mixture	**4.1**	Sand+ Mud (10%) + Metakaolin (10%)		
	4.2	Sand + Mud (10%) + Kaolin (10%)		
	4.3	Sand+ Mud (20%) + Metakaolin (20%)		
	4.4	Sand + Mud (20%) + Kaolin (20%)		

4.1.2.3 Adobes formulation

The raw materials used in the production of the adobes were mixed by placing them in plastic bags and shaking these several times to assure some homogeneity. After this, mixing water or the alkaline solutions were added slowly and the mixture was promoted with the aid of a mechanical stirrer. After the mixture was adequately homogeneized it was placed in wood moulds with dimensions of 4cmx4cmx4cm. The compaction was carried out only with a wooden rod. The blocks were dried at room temperature and were demolded after 48 hours and placed in a laboratory table with greater sun exposure, still without any protection.

4.1.3 Results and discussion

4.1.3.1 Materials characterization

<u>Chemical composition</u>

The chemical composition is essential for better knowledge of the material. The chemical compositions of raw materials used in each formulation are shown in Table 4.1.2.

The principal component of sand is silica (SiO_2 ~87%). The principal components of mud, kaolin and metakaolin are silica and aluminium. The main difference between the kaolin and metakaolin is in the amorphous phases, which are impossible to evaluate by XRF. However, the difference between the loss on ignition (LOI) of these two materials, ~13% for kaolin and ~2% for metakaolin, is revealing in terms of the difference between them.

Table 4.1.2 – Chemical composition of raw materials

	Sand	*Mud*	*Kaolin*	*Metakaolin*
Na_2O	0.10	0.28	0.11	0.08
Al_2O_3	8.68	21.56	36.17	39.88
SiO_2	87.17	51.24	47.37	52.05
P_2O_5	0.04	0.19	0.02	0.06
SO_3	0.03	0.71	0.03	0.05
Cl	0.01	0.01	0.01	0
K_2O	1.60	3.13	1.87	1.28
CaO	0.08	0.49	0.05	0.12
TiO_2	0.13	0.64	0.11	1.55
MnO	0	0.02	0.02	0
MgO	0	1.01	0.31	0
Fe_2O_3	0.49	5.03	1.15	2.17
LOI	1.64	15.48	12.71	2.31

Mineralogical composition

The mud from Pateira de Fermentelos is composed mainly by quartz and, in minor concentrations, phyllosilicates (illite and kaolinite), feldspars (plagioclase and potassium feldspar), anatase, anhydrite, pyroxenes and iron oxides and hydroxides (Figure 4.1.2). The sand from Quinta do Areal in Esgueira is composed essentially by quartz and some potassium feldspars (Figure 4.1.3). The kaolin used on the adobe formulations is constituted by quartz and kaolinite as mainly components, and plagioclase and illite in minor quantities (Figure 4.1.4). The metakaolin is composed by quartz, illite, anatase and by an amorphous phase (Figure 4.1.5).

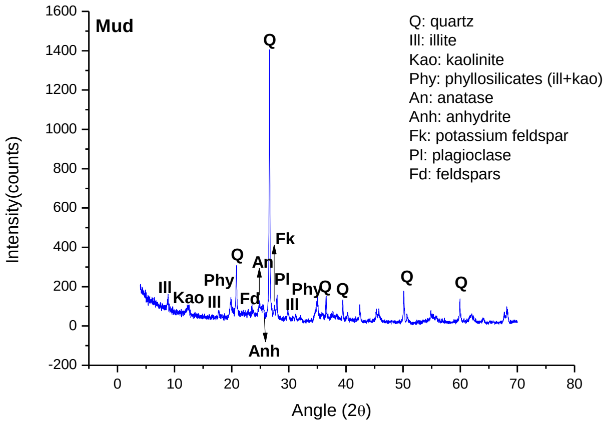
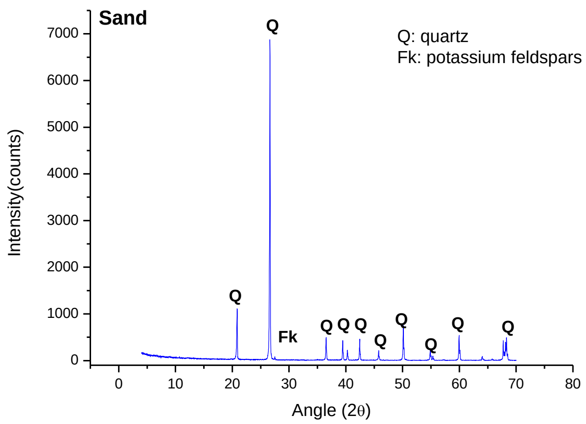


Figure 4.1.2 – Mineralogical composition of mud from Pateira de Fermentelos.



Figures 4.1.3 – Mineralogical composition of sand from Quinta do Areal in Esgueira (Aveiro).

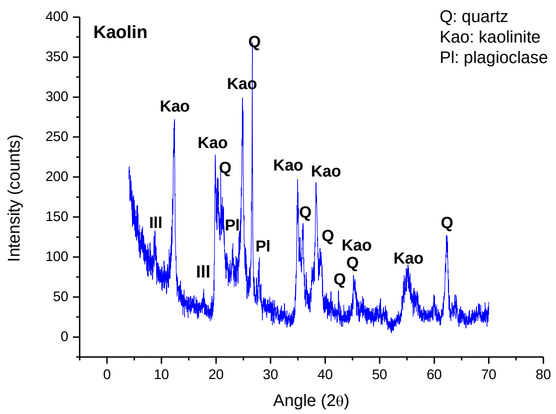


Figure 4.1.4 – Mineralogical composition of kaolin from São Vicente (Ovar).

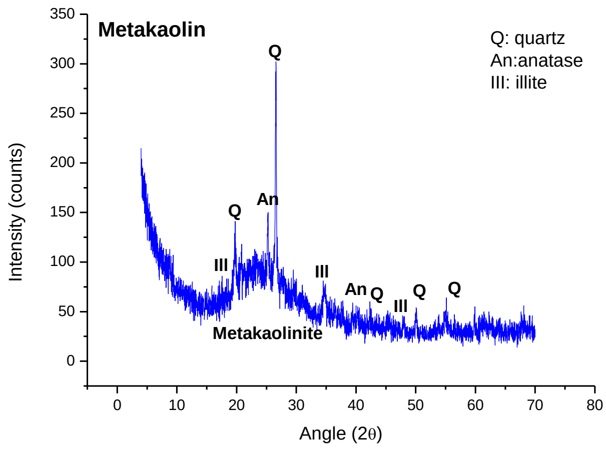


Figure 4.1.5 – Mineralogical composition of metakaolin (industrial).

4.1.3.2 Adobe formulations characterization

Chemical composition

The chemical results of the samples subject to different curing times did not show significant changes, only errors associated to the technique. The results presented are an average of the 4 curing times analyzed (28, 60, 90 and 180 days), (Table 4.1.3). The chemical composition of the formulations is a reflection of the materials used in each of them. The SiO_2 predominates in all formulations with sand ranged between 50 to 73%, these amounts depending of the sand quantities used in each formulation. In the formulation 1.1 with mud and addiction of sand the percentage of SiO_2 decrease to 38 to 48%. The Al_2O_3 percentages range between 16 to 32%, this compound depends essentially of phyllosilicates content; in the 2, 3 and 4 formulations depends of the metakaolin and kaolin percentages used. The Na_2O and K_2O contents increase in formulations activated with NaOH and KOH solutions. The iron contents are correlated with the use of mud, increasing with this component on the formulations. The poor Cl quantities show that the formation of salts does not pass beyond the surface of the materials and is not found within them. The loss on ignition is higher in formulation number 1, because of the use of straw. In the other formulations the loss on ignition is greater in those that present greater amount of mud.

Table 4.1.3 – Chemical composition of adobe formulations

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	Fe_2O_3	LOi
1.1 H2O	1.08	0.96	20.82	48.31	0.18	0.90	0.03	3.20	0.39	0.66	5.03	18.23
1.1KOH	0.30	0.76	16.94	38.53	0.14	0.58	0.02	18.44	0.32	0.59	4.39	18.81
1.1NaOH	11.85	0.81	17.83	41.71	0.15	0.63	0.03	2.73	0.31	0.56	4.26	18.96
2.1H2O	0.10	0.24	22.55	72.34	0.05	0.04	0.01	1.35	0.08	0.53	0.84	1.61
2.1KOH	0.21	0.24	24.75	49.50	0.06	0.04	0.01	17.77	0.10	0.81	1.27	4.39
2.1NaOH	12.99	0.22	24.51	54.03	0.06	0.06	0.01	1.49	0.12	0.69	1.11	3.82
2.2H2O	0.10	0.29	32.62	60.86	0.06	0.05	0.00	1.36	0.10	0.95	1.34	2.17
2.2KOH	0.19	0.25	27.43	40.23	0.05	0.04	0.00	20.18	0.08	0.99	1.44	9.04
2.2NaOH	15.20	0.20	26.71	47.40	0.05	0.05	0.00	1.14	0.10	0.86	1.23	6.97
3.1H2O	0.20	0.25	21.41	71.91	0.03	0.04	0.06	1.65	0.09	0.16	0.59	3.57
3.1KOH	0.22	0.17	19.43	60.94	0.03	0.05	0.02	11.93	0.08	0.16	0.72	6.18
3.1NaOH	10.70	0.19	20.71	56.20	0.03	0.04	0.06	1.57	0.08	0.15	0.59	9.62
3.2H2O	0.22	0.30	30.52	60.09	0.03	0.04	0.01	1.91	0.09	0.19	0.89	3.16
3.2KOH	0.23	0.25	24.59	51.75	0.03	0.03	0.01	13.09	0.09	0.18	0.95	4.58
3.2NaOH	7.79	0.32	26.52	55.43	0.03	0.03	0.01	1.71	0.09	0.16	0.78	3.91
4.1H2O	0.16	0.31	19.20	73.38	0.08	0.21	0.01	1.77	0.14	0.43	1.23	2.57
4.1KOH	0.20	0.34	17.20	60.27	0.07	0.22	0.01	14.65	0.14	0.48	1.37	4.01
4.1NaOH	13.62	0.30	20.03	56.25	0.08	0.26	0.01	1.87	0.15	0.49	1.39	4.27
4.2H2O	0.20	0.28	17.38	74.35	0.07	0.23	0.01	1.85	0.13	0.22	1.14	3.25
4.2KOH	0.21	0.27	16.22	63.76	0.06	0.23	0.01	11.94	0.15	0.22	1.26	4.32
4.2NaOH	11.20	0.33	16.45	62.79	0.06	0.23	0.01	1.74	0.13	0.21	1.12	4.34
4.3H2O	0.17	0.47	24.66	59.85	0.10	0.26	0.02	4.48	0.19	0.72	2.02	6.96
4.3KOH	0.20	0.42	22.06	53.18	0.09	0.24	0.01	14.22	0.17	0.72	2.05	6.53
4.3NaOH	13.69	0.44	23.01	51.29	0.10	0.29	0.01	1.97	0.19	0.71	1.94	6.28
4.4H2O	0.23	0.53	23.06	64.27	0.08	0.50	0.01	2.23	0.18	0.30	1.79	6.71
4.4KOH	0.25	0.45	19.48	52.32	0.08	0.44	0.01	15.79	0.20	0.30	1.90	8.68
4.4NaOH	14.36	0.42	19.21	52.82	0.06	0.44	0.01	1.91	0.17	0.26	1.63	8.59

*Loi – lost on ignition; +++ major quantities; + less quantities

Mineralogical composition

Mineralogical analysis was carried at different curing times on non-oriented powders and on oriented aggregates. The results from non-oriented powders are in Table 4.1.4. The formulations are composed essentially by quartz, phyllosilicates and feldspars (K- feldspar and plagioclase). Formulations 1 present some traces of anhydrite, siderite, pyroxenes and opal c/ct, as on the used mud. Some formulations show traces of anhydrite (2.2, 3.1, 4.2 and 4.3), and anatase (2.2 and 3.1). The formulations 4.2 and 4.4, NaOH activated, show some salt formation (thermonatrite), observed in some blocks of NaOH activated formulations, but just on the surface of the material. The salt formation can damage the material along time, so a solution for this can be to decrease the concentration of NaOH solution which is an advantage in terms of the reduction of costs with the production of this material and decrease the ecological footprint (Elert *et al*., 2015).

The formation of zeolites was an expectation; however only in formulation 3.2, with NaOH are these minerals clearly observed. However, in the KOH activated formulations there is evidence of the formation of a hydrated K alumino-silicate that could be a zeolite.

The differences between the formulations are clearer when oriented aggregates are studied, particularly regarding the phyllosilicates content. The formulations made with water present kaolinite and illite (Figure 4.1.6). In the KOH formulations, halloysite was detected. The presence of halloysite in the kaolin deposits of São Vicente de Pereira (Portugal) was described by Bobos *et al*., (2001). This kaolin was used in formulations 3.1, 3.2, 4.2 and 4.4; however, other formulations without this kaolin show also halloysite formation. The emergence of halloysite seems to be related with KOH-activation, suggesting an increase of the amorphous phase and structure disorder, as a consequence of KOH activation (Iglesia *et al*., 1975; Singh *et al*., 1996) (Figure 4.1.7). In the activated sodium formulations kaolinite and illite are the predominant minerals (Figure 4.1.8). However, in formulation 4.1, the formation of allophane is observed, which is once again indicative of a more disordered, hydrated and amorphous structure (Wang *et al*., 2018).

The mineralogical results evidenced the alkaline activation, the main changes being in the phyllosilicates structure. These results show that the activation with KOH seems to cause more changes in the structure of the minerals, especially in clay minerals than the activation with NaOH, in opposition with the results obtained in similar studies by Elert *et al.* (2015, 2019).

The mineralogical results favor the formulations activated with KOH due to non-detection of salts during the analyses performed along different curing times. In samples with NaOH thermonatrite ($Na_2CO_3 \cdot H_2O$) formation was always observed, even if only on the surface of the adobe cubes. According to various authors (Elert *et al*., 2015, 2019; Goudie *et al*., 1997) the salt efflorescence formation damages the materials.

Table 4.1.4 – Mineralogical composition

	Quartz	Phyllosilicates	K-feldspar	Plagioclase	Anhydrite	Siderite	Opal C/CT	Anatase	Zeolites	Thermonatrite
1.1 H2O	++++	+++	++	++	+	+	+			
1.1KOH	++++	+++	++	++	+	+	+			
1.1NaOH	++++	+++	++	++	+	+	+			
2.1H2O	++++	+	+							
2.1KOH	++++	+	+							
2.1NaOH	++++	+	+							
2.2H2O	++++	++	+		+			+		
2.2KOH	++++	++	+		+			+		
2.2NaOH	++++	++	+		+			+		
3.1H2O	++++	+	+		+			+		
3.1KOH	++++	+	+		+			+		
3.1NaOH	++++	+	+		+			+		
3.2H2O	++++	+++	++							
3.2KOH	++++	+++	++							
3.2NaOH	++++	+++	++						+	
4.1H2O	++++	+	+							
4.1KOH	++++	+	+							
4.1NaOH	++++	+	+							
4.2H2O	++++	+	++							
4.2KOH	++++	+	++		+					
4.2NaOH	++++	+	++							+
4.3H2O	++++	++	+		+					
4.3KOH	++++	++	+		+					
4.3NaOH	++++	++	+		+					
4.4H2O	++++	++	++	+						
4.4KOH	++++	++	++	+						
4.4NaOH	++++	++	++	+						+

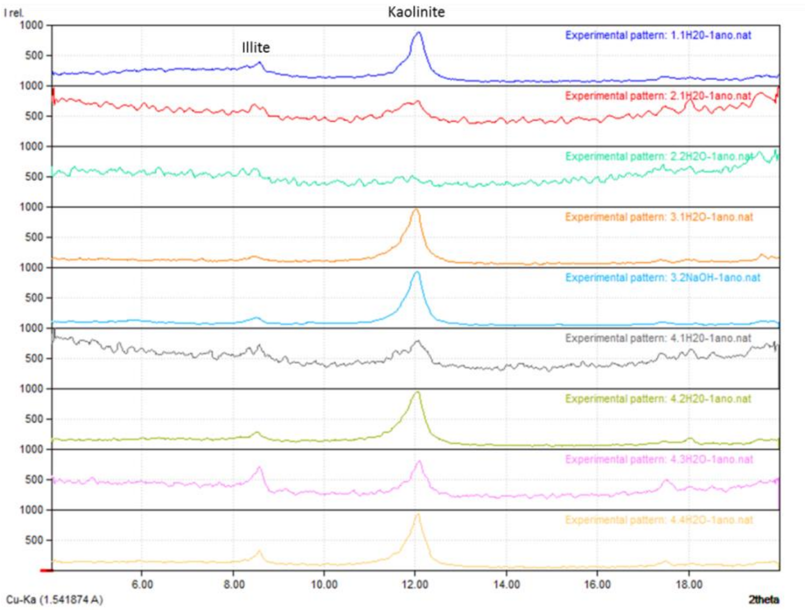


Figure 4.1.6 – XRD patterns from oriented slides of water formulations.

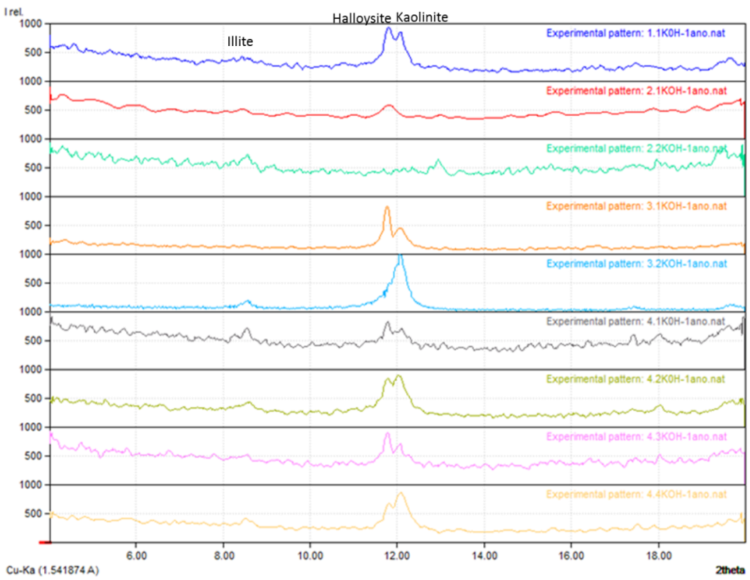


Figure 4.1.7 – XRD patterns from oriented slides of potassium activated formulations.

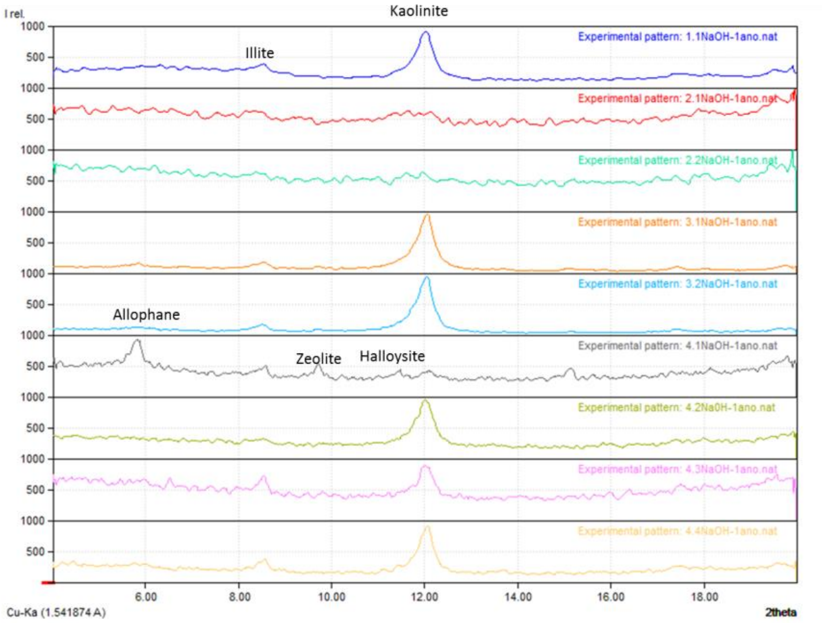


Figure 4.1.8 – XRD patterns from oriented slides of sodium activated formulations.

Specific surface area (BET)

The specific surface area results are shown in Figure 4.1.9. The specific surface area results increases slightly in the formulations activated with NaOH, being probably related with a slight expansion of the clay minerals present in formulations. However, this increase does not seem to have repercussions on the mechanical strength of materials as discussed further on.

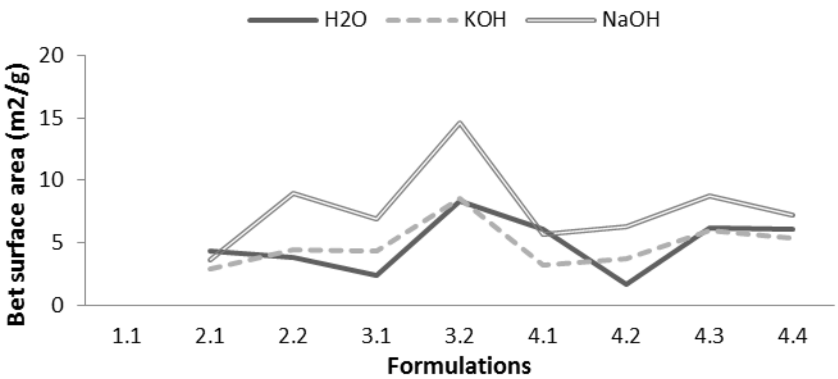
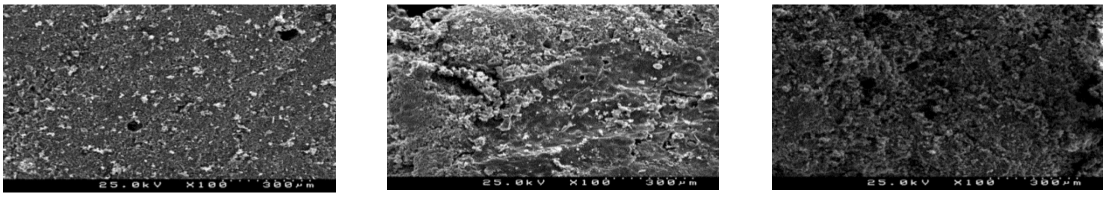


Figure 4.1.9 – BET results for 28 days of curing.

Microstructural composition (SEM-EDX)

The results of the SEM analyses allowed the comparison of the microstructure of formulations with different activators at different curing times. Figure 4.1.10 shows a representative example of all formulations which evidences that the treatments with KOH and NaOH induce the formation of amorphous material, with the characteristic "cloud" type being more visible in NaOH samples. The presence of pores was observed in all formulations and may be related to the production of the adobe cubes.

SEM analyzes allowed the observation of the formation of salts in the pores of some NaOH-activated samples (Figure 4.1.11), situation which was not observed in the KOH-activated formulations. As already noted, the formation of salts is a negative aspect of alkaline activation with NaOH, because these salts can damage the material. Other changes caused by this activator were observed in the microstructure of the materials (Figure 4.1.12).



a) b) c)

Figure 4.1.10 – SEM images of a) formulation 1.1 H_2O (180 days), b) formulation 1.1 KOH (180 days) and c) formulation 1.1 NaOH (180 days).

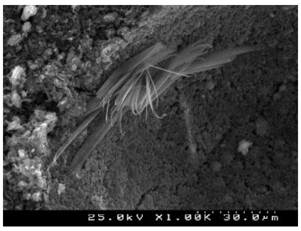


Figure 4.1.11 - SEM image with the efflorescences formation evidence (2.1 NaOH, 180 days of cure).

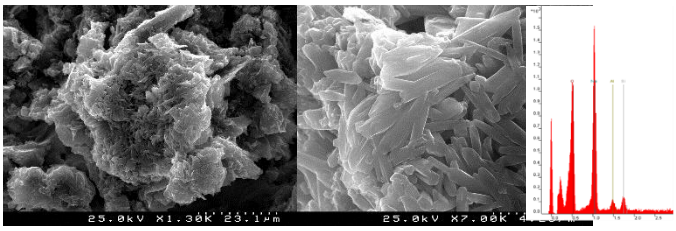


Figure 4.1.12 – SEM images showing microstructure changes caused by NaOH (4.4 NaOH, 180 days of cure).

Mechanical strength

Mechanical strength was evaluated for the non-activated (water) (Figure 4.1.13), KOH activated (Figure 4.1.14) and NaOH activated (Figure 4.1.15) formulations, at curing ages of 28, 60, 90 and 180 days. Regarding formulations without activation, the strength values varied between 0.1 and 0.9 MPa. Considering that the most frequent old adobe strengths range between 0.8 to 3.5MPa (Costa *et al*., 2019a), and taking into account the principle of materials compatibility, the formulations 1.1, 3.2, 4.1, 4.2, 4.3 and 4.4 can be used even without activation, in the filling of old adobe gaps. Alkaline activation with NaOH is the one that gives the most resistance to the formulations and the values obtained are between 0.5 and 3.5 MPa. However, in general, the KOH-activated formulation also show positive effects on mechanical strengths. The effect of KOH activation is more pronounced in formulations 2.1, 2.2, 3.2 and 4.3. These formulations with the exception of 3.2 have metakaolin in their constitution, which may indicate a favourable effect of KOH on this raw material. Formulation 1.1 behaves equally well with both used activations.

For comparative proposes, Figure 4.1.16 shows the results of the mechanical resistance mean values at the curing times of each formulation, evidencing that in the formulations activated with NaOH the highest strengths are obtained. However, activation with KOH also promotes increased strength of these materials. The results show that samples 2.1 and 2.2 have the lowest values, as a consequence of the low percentage of clay components added as raw material (kaolin and metakaolin), only 20%. Replacement of half of these components by mud is sufficient to give rise to an increase in mechanical strength (formulations 4.1 and 4.2).

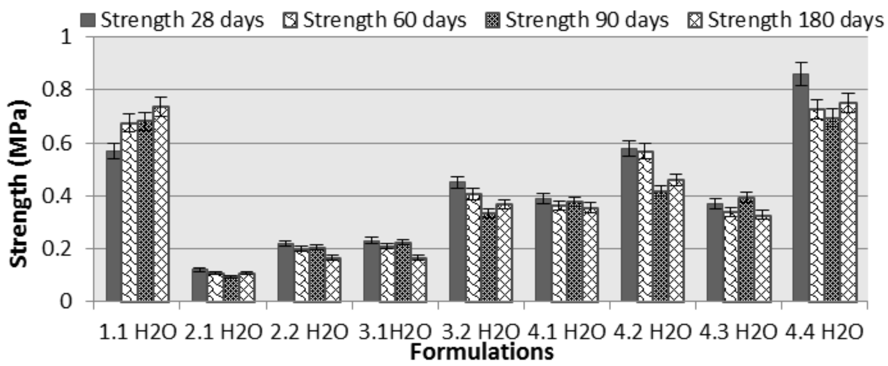


Figure 4.1.13 **– Mechanical strength for formulations without activation, in different curing times.**

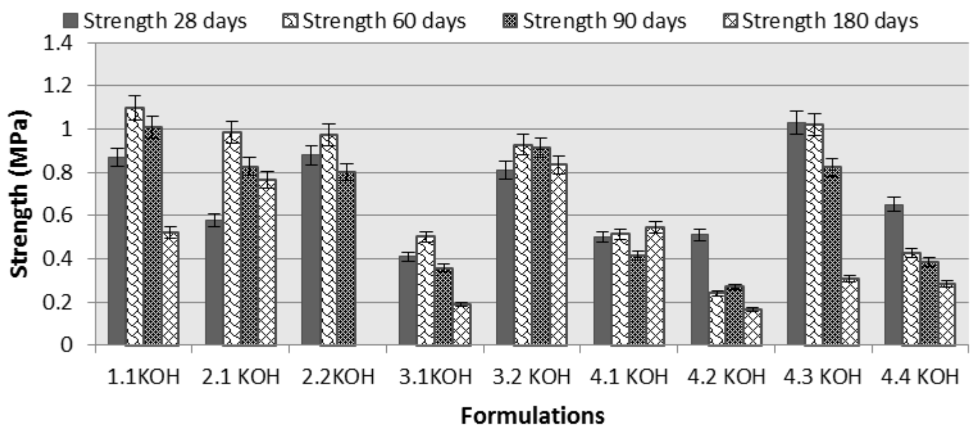


Figure 4.1.14 **– Mechanical strength for formulations KOH activated, in different curing times.**

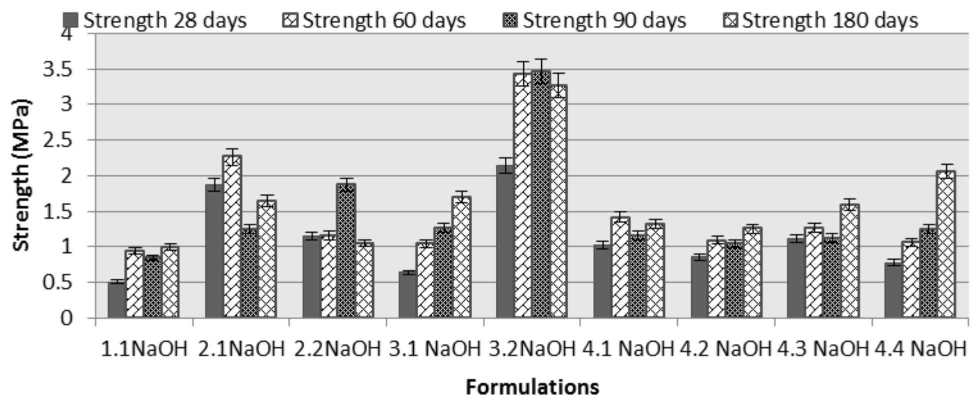


Figure 4.1.15 **– Mechanical strength for formulations NaOH activated, in different curing times.**

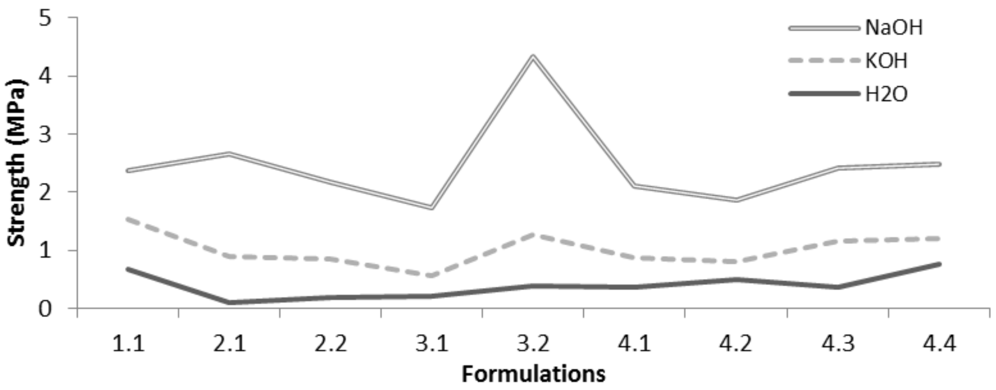


Figure 4.1.16 **– Mean of 28, 60, 90 and 180 days of cure for different activators.**

4.1.4 Conclusions

The results obtained in this research show that the mechanical strength of the adobe formulations studied can be improved by alkaline activation. Adobe blocks with NaOH (6M) and KOH (6M) activation improved strength after 28 days of cure at room temperature. The strength improvements are mainly due to the dissolution of the phyllosilicates as well as to their transformation into amorphous phases with cementitious properties (Elert *et al*., 2015).

Although NaOH activation allows for greater gains in terms of mechanical strength, the formation of efflorescence is a problem that arises from this type of activation and can lead to the damage of the material over time. According to Abdullah *et al.* (2018) concentrations of 4 M NaOH are sufficient to improve strength at 28 days of curing; thus, reducing the NaOH concentrations will avoid/reduce salt formation being a possible solution to the salt efflorescence formation. The reduction of concentration also reduces the environmental impact as well the production costs of the material.

However, since adobes do not require high mechanical strengths the solution can be activation with KOH-solution because it is sufficient to promote the demanded increase of this property.

In terms of chemical and mineralogical composition, and compressive strength, the formulations developed are highly compatible with the old adobes already studied (Costa *el al*., 2013, 2016, 2019). The durability of these materials is being evaluated over time.

These materials are being tested in the field in order to verify their compatibility with the old adobes, as well as to check if their behaviour towards the external exposure is very different from a laboratory environment.

4.2 DIATOMITE BASED GEOPOLYMERS AS RESTORATION MATERIALS

Abstract The adobe construction was a technique quite used in the past mainly in the Central Coast of Portugal, where the available geological materials potentiate this type of construction. Nowadays, adobe buildings are in a high state of degradation and must be rehabilitated in order to conserve the built heritage of this region. The ongoing research is focused on the development and testing of new materials to improve the performance of this type of construction and also to guarantee the sustainability characteristic of the adobe materials. In this context, geopolymers, which are alkaline activated aluminosilicates, arise as potential materials, having more controlled costs and environmental footprint and improving the chemical and physical characteristics of the adobes. The geopolymers under development are made from national geomaterials, kaolins, metakaolin and diatomite. It was intended to evaluate the influence of the diatomite as an additive in these materials, and it is verified that about 10% of the addition is ideal for obtaining an increase in mechanical strength. With this type of materials we can guarantee the sustainability of the adobes.

4.2.1 Introduction

The adobe masonry based construction is one of oldest technique and it was once the most used by mankind due to easily accessible geological resources. The rehabilitation of these ancient buildings must be increasingly taken into account for the memory preservation in the face of modern construction.

In Portugal, several buildings with cultural heritage are constructed with adobe mainly located in the central and southern coastal regions (Varum *et al.*, 2008); some examples are the Art Nouveau Museum (in Aveiro city centre), or the Gandareza House (in Vagos) (Costa *et al.*, 2019a).The adobe construction is a very simple technique that justifies its application in the older constructions. The word adobe comes from the Arabic "attob" meaning dry brick in the sun (Quaglianini *et al.*, 2010).

The rock/soil characteristics used in adobe construction, excluding organic component (roots, leaf), is composed by the first soil layers, which are generally rich clays, silts and sands.

The adobe construction is mainly used in the central Portugal coast where the conditions and resources are available (Costa *et al.*, 2019b). In order to better understand these materials, samples of old adobe blocks from Aveiro district and Figueira da Foz were collected (Costa *et al.*, 2019b). As first impression, the analyzed adobe presented mainly differences in color and texture (Figure 4.2.1).

Figure 4.2.1 – Studied adobes constructions.

Concerning chemical and mineralogical compositions, it was found a relative homogeneity (Table 4.2.2), as already noticed in previous studies (Costa *et al*., 2013; Costa *et al*., 2016, Costa *et al*., 2019b). Mineralogically, these samples are composed mainly of tectosilicates (quartz and feldspars), carbonates (calcite and sometimes dolomite) and phyllosilicates (kaolinite> illite, sometimes discrete smectite and chlorite). As accessory minerals, iron oxides and hydroxides have been identified, sometimes salts (mainly halite) and sulfates (gypsum). In terms of chemical composition (Table 4.2.2), these samples are mainly characterized by the significant presence of SiO_2> Al_2O_3> CaO> Fe_2O_3 loss and in smaller quantities: Na_2O, MgO, P_2O_5, SO_3, Cl, K_2O, TiO_2 and MnO. The chemical and mineralogical compositions of the samples and their low heterogeneity reflect the regional (monotonous, siliciclastic) geology control.

Concerning grain-size distribution, the amount of sand fraction in all samples varies from 83 to 98%, silt from 1 to 17% and clays from 0.1 to 0.8%; thus, there is some heterogeneity among samples regarding this classification. These values are reflected both in the water absorption capacity and in the mechanical strength of these materials. The ideal formulation for an increase in mechanical strength would be a percentage of clay at around 5% as described in (Lourenço, 2002). Through the acid attack tests it was possible to estimate the aggregate / binder ratio of the samples, approximately 9/1.

Table 4.2.2 – General properties of characterized adobes.

Mineralogy	Chemistry	Physical properties
• **Tectosilicates** (Quartz and feldspars) • **Carbonates** (Calcite and dolomite) • **Phyilosilicates** (Kaolinite e illite) • **Accessory minerals** (Iron oxides and hydroxides and salts like halite, sulphates like gypsum)	• SiO_2 • Al_2O_3 • CaO • Lost on ignition • Fe_2O_3 • Minores: Na_2O, MgO, P_2O_5, SO_3, Cl, K_2O, TiO_2, MnO	• **MB** (g MB/kg fraction <2mm) – 0.2 to 0.8 • **Capillarity Absorption coefficient** (g/dm3.m1/2) – 3 to 13 • Average water penetration (cm) - **Geelong test** – 1.5 a 3 • **Compressive strength** (MPa) – 0.3 to 4

The results obtained by the Geelong test demonstrated that the samples with the highest percentage of phyllosilicates are more resistant to the acid rainwater deterioration with a water penetration depth ranging from 1.5 cm to 3.5 cm. In terms of mechanical strength, the results obtained vary between 0.3 and 4 MPa. Lower values correspond to the older more degraded adobes. Generally, adobe has a limited mechanical strength 1 to 3.5 MPa, (Coroado *et al.*, 2010, Vega *et al.*, 2011; Illampas *et al.*, 2014).

Through this characterization, it was possible to identify the adobes' properties and define compatible new materials for the restoration and rehabilitation of adobe buildings. Along with well-preserved adobe buildings, many others are at highly degradation state.

This state is correlated with the adobe fragility against water and the related degradation that occurs hence (Costa *et al.*, 2019b).Being aware of the importance to conserve and rehabilitate national heritage, new adobe-based materials were investigated. Success of this study will mark the beginning of a large-scale restauration program supported by state and non/statal organization.

Recent works extended the properties of geopolymer in this kind of action. Geopolymers will contribute decisively to increase the sustainability of the construction because, compared to traditional cement, they have the advantage of reducing CO_2 emissions, as well as the high energy consumed during the production of clinker in a traditional cement.

In chemical terms, geopolymers are similar to synthetic zeolites, since they form through an alkaline reaction between aluminum and silicon initially available in the solution, forming complexes of polyhydroxyaluminosilicates (Bondar, 2016). Geopolymers are synthetic alkaline aluminosilicates that are formed by a reaction of a solid aluminosilicate with a highly concentrated aqueous solution of a hydroxide and / or alkali silicate (Duxson *et al*., 2007). The ongoing investigations mainly use as raw materials in geopolymers production metakaolin, fly ash, blast furnace slag, mixtures of ash and slag, mixtures of ash / slag and metakaolin, mixtures of slag and red sludge, mixtures of ash and non-calcined materials, such as kaolin (Gonçalves, 2014).

Recent studies poiting diatomite as a good additive to geopolymers (Costa *et al*., 2018).

In this work, new formulations were intended to evaluate the potential of diatomite as the source of silica in the final properties of the geopolymers. Previous studies have shown that the diatomite used as an additive in construction materials may increase the mechanical strength (Costa *et al*., 2019a). Other raw materials have been used namely metakaolin and kaolin; these were chosen because there are already several studies that recommend them for the production of geopolymers (Andrejkovičová *et al*., 2013; Hajjaji *et al*., 2013).

4.2.2 Experimental details

The chemical composition was assessed by X-ray fluorescence (XRF) using an XRF Panalytical AXIOS PW4400/40. Loss-on-Ignition (LOI) was determined by heating 1 g of the sample at 1000 ºC for 1 h in furnace.

The mineralogical composition was determined on un-oriented (random) powder mounts for raw materials and for geopolymers specimens. XRD measurements were performed using Philips PW 3050 and X' Pert PW 3040/60 equipment using Cu Kα radiation. The microstructural characterization was carried out by scanning electron microscopy (SEM – Hitachi, SU 70) and energy dispersive X-ray spectrometry (EDS – EDAX with detector Bruker AXS, software: Quantax) operated at 3–30 kV.

The cubical specimens were submitted to compressive strength tests, using a universal mechanical compression testing machine (Shimadzu Autograph AG 25 TA). The testing procedure was carried out with a maximum force of 5 kN at the speed of 50 N/s as per the standard EN 1015-11 (Moutinho *et al*., 2019).

Water absorption of the immersed specimens was calculated for each series according to Eq. (1), where W% is the adsorption of water expressed as percentage; Ww and Wd are the weights of the immersed specimen and of specimen after drying (g), respectively (Yousef *et al*., 2009 in Andrejkovičová *et al*., 2016).

$$\text{Eq. 1} \qquad W\,\% = (Ww-Wd)/Wd*100$$

Geopolymers were designed by using metakaolin 1200S, kaolin and diatomite as describe before. In water medium, alkaline activators NaOH (ACS AR Analytical Reagent Grade Pellets) and hydrated sodium silicate (Merck, Germany; 8.5 wt.% Na2O, 28.5 wt.% SiO2, 63 wt.% H2O) were used to dissolve aluminosilicate and avoid residual sodium (Barbosa, 2003). The target was the following molar oxide ratios: SiO_2/Al_2O_3 = 3, 3.5 and 4.5 depending of the formulation (Duxson *et al*., 2007; De Silva, 2008).

The mixing of the blends was carried out by Heidolph ST-1 Laboratory stirrer at two different speeds; 100 rpm for 2 min and 200 rpm for 4 min, to insure their homogeneity and avoid bubbles and agglomeration into the sample. The pastes were immediately poured into 20 x 20 x 20 mm cubic molds and placed in oven at 50 ºC for 24 h and after left at room temperature for 1 day. Curing was carried out by keeping the geopolymer cubic specimens stored in sealed plastic bags at room temperature; the specimens was tested at 1, 7, 14, 21 and 28 days of cure.

Geopolymers were prepared using Portuguese kaolin, provided by a Portuguese company Motamineral – Minerais Industriais SA. Kaolin was chosen based on the location of the deposits (short distance from adobe buildings) and the availability of kaolin of insufficient quality for its usual applications (and therefore low-cost) but adequate for these less demanding uses. In addition, the kaolin composition is similar to that of the kaolinite sands used in the original adobe formulations, thus ensuring the compatibility of the new materials with the original ones. The kaolin was used as precursor of aluminum. In order to compare the behaviour of the Portuguese kaolin it was used using metakaolin 1200S (MK) (AGS Mineraux, France), that there are already published studies with their effectiveness in the production of geopolymers (Hajjaji *et al.,* 2013).

A Portuguese diatomite it was used as a raw material, as an additive was decided because is available at acceptable costs (like the used kaolin) and belongs to a typology of materials whose use was detected in ancient buildings of the region. The diatomite used (AM) was previously characterized in an article already published (Costa *et al*., 2018), it was used as a silicon source.

For the development of the geopolymers formulations it was used the hydrated sodium silicate (Merck, Germany Merck, Germany; 8.5 wt.% Na_2O, 28.5wt.%, SiO_2,63wt., %H_2O) and sodium hydroxide (6M) (ACS AR Analytical Reagent Grade Pellets). Sodium silicate was used as a source of silicon and sodium hydroxide as an alkaline activator for dissolution of aluminosilicate. Water was the reaction medium. It was developed different types of geopolymers according the raw materials (Table 4.2.1).

Table 4.2.1. Studied formulations.

Metakaolin & diatomite					
	MKP	**MKI**		**MKD**	
Ratio SiO_2/Al_2O_3	3.5:1	3.5:1	3:1	3.5:1	4.5:1
Na_2SiO_3	25	25	20	20	25
NaOH	6	6	13	6	6
MKP	27	-	-	-	-
MKI	-	27	44	22	27
D	-	-	10	10	10
Water	13	20	50	25	25

Kaolin & diatomite calcined at 550ºC							
		A (40+20)			**B** (40+10)		**C** (40+5)
Ratio SiO_2/Al_2O_3	3:1	3.5:1	4.5:1	3:1	3.5:1	4.5:1	4.5:1
Na_2SiO_3	20	20	25	20	20	25	25
NaOH	13	6	6	13	6	6	6
MKP	-	-	-	-	-	-	-
MKI	-	-	-	-	-	-	-
K+D	54	32	37	54	32	37	37
Water	30	18	23	30	20	13	18

***MKP** – Portuguese metakaolin, calcined at 750ºC, 4 hours; **MKI** – Industrial metakaolin (1200s); **MKD** (MKP plus diatomite); **A** – 40 % of Portuguese kaolin + 20% of diatomite calcined at 550ºC, 4 hours. **B** – 40 % of Portuguese kaolin + 10% of diatomite calcined at 550ºC, 4 hours. **C** – 40 % of Portuguese kaolin + 5% of diatomite calcined at 550ºC, 4 hours.

4.2.3 Results

4.2.3.1 Diatomite, kaolin and metakaolin materials

The chemical composition of raw materials is reported in Table 4.2.3.

The mineralogical composition of Portuguese kaolin is quartz, kaolinite and illite, and in minor quantities k –feldspars, iron oxides and hydroxides, calcite and dolomite traces (Figure 4.2.2). Metakaolin shows a broad reflection centered at 2θ = 24º due to the amorphous metakaolinite along with residual quartz, illite and anatase. The Portuguese diatomite used as a raw material is composed by quartz, amorphous opal, k-feldspars, plagioclase and phyllosilicates. These silica rich materials present an amorphous structure related with the presence of around 50% of diatoms shells (Velho *et al.*, 1998).

Table 4.2.3 – Chemical composition of raw materials used in geopolymers development.

Oxides (%)	Kaolin	Metakaolin	Diatomite
Al_2O_3	36.11	40.22	6.37
SiO_2	49.2	51.64	85.86
K_2O	2.06	1.26	0.95
Fe_2O_3	1.92	2.11	1.02
TiO_2	0.14	1.52	0.25
LOI	9.87	2.5	4.96

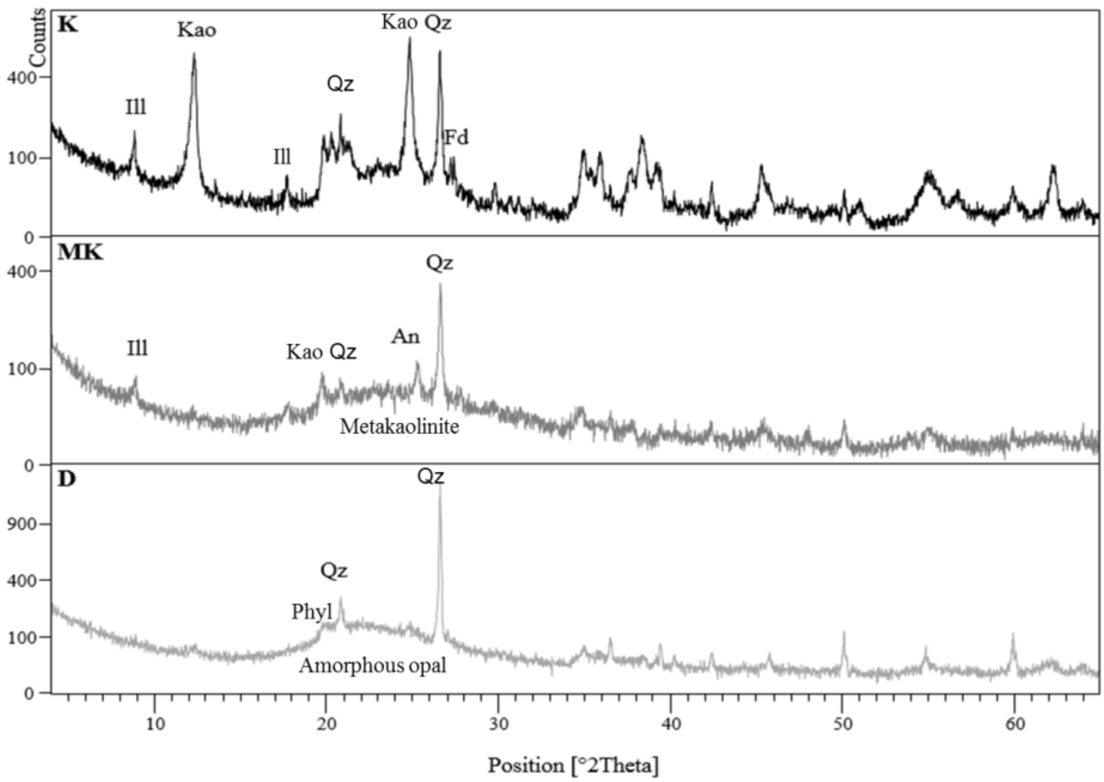


Figure 4.2.2 – XRD patterns of K - Portuguese Kaolin , MK - metakaolin 1200S and D – diatomite (Ill – illite, Kao – kaolinite, Qz – quartz, Fd – feldspars, An – anatase, Phyl – phyllosilicates).

Figure 4.2.3 shows the SEM images of the three raw materials. It´s possible to see the amorphous structures of diatomite and metakaolin.

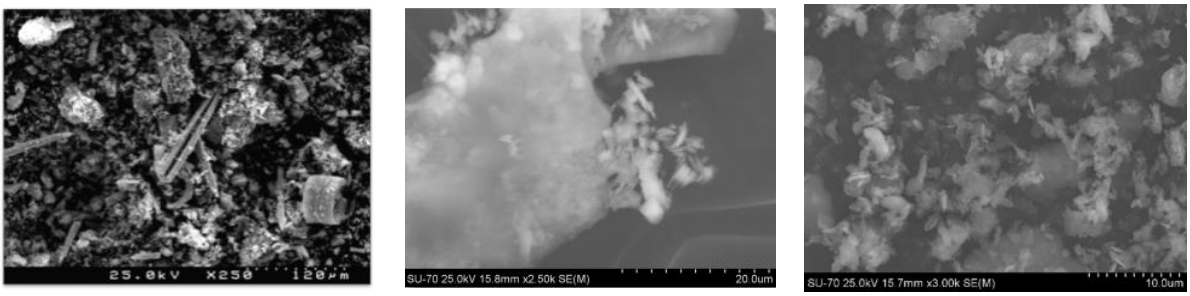


Figure 4.2.3 – SEM images of diatomite (left side), Portuguse kaolin (middle) and metakaolin (right side).

The particle size distribution of raw materials is presented on Figure 4.2.4. The diatomite presented higher aggregates compared with kaolin and metakaolin. The mean particle diameter is around 2 µm for metakaolin and kaolin, and around 20 µm for diatomite.

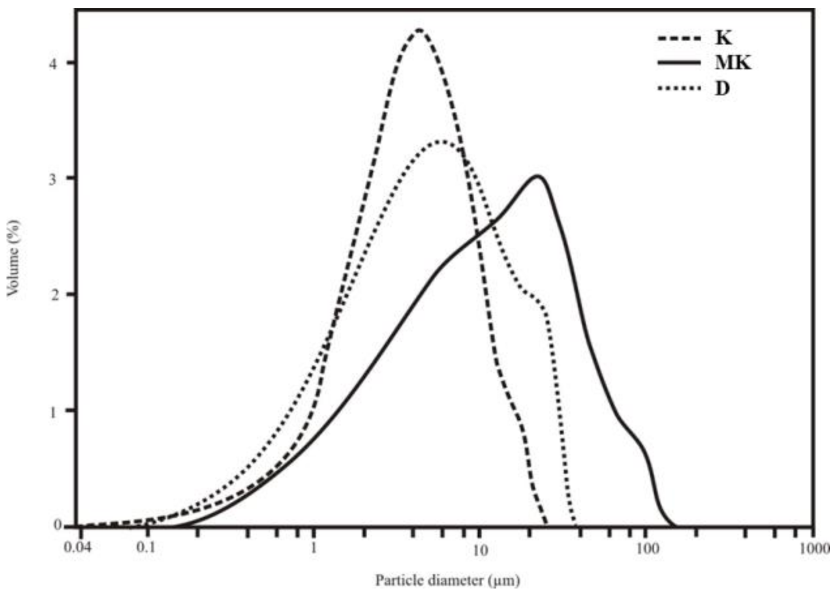


Figure 4.2.4 – Particle size distribution of K – kaolin, MK – metakaolin and D – diatomite.

4.2.3.2 Geopolymer formulations and properties

The mineralogical results are shown in Figure 4.2.5. The geopolymers formulations are composed essentially by quartz, phyllosilicates (illite and kaolinite), and in minor percentages k-feldspar, plagioclase and anatase. In the formulations with metakaolin is evident a broad reflection centered at 2θ = 24º due to the amorphous metakaolinite.

However, the others formulations show the presence of amorphous phase to relate with the diatomaceous earth, which contain amorphous silica in their composition, (in the same position but not so evident). The phyllosilicates peak around 2θ= 34º, it´s higher in formulations A, B and C, because the kaolinite quantities are higher in these formulations; in the other (MK and MKD) kaolinite are in amorphous phase (metakaolinite).
Figure 4.2.6 confirms the advanced stage of geopolymerization samples. The amorphous matrix is mainly composed by Si, Al and Na. In crystallochemical terms it is verified that the structure of the samples is cohesive and homogeneous.

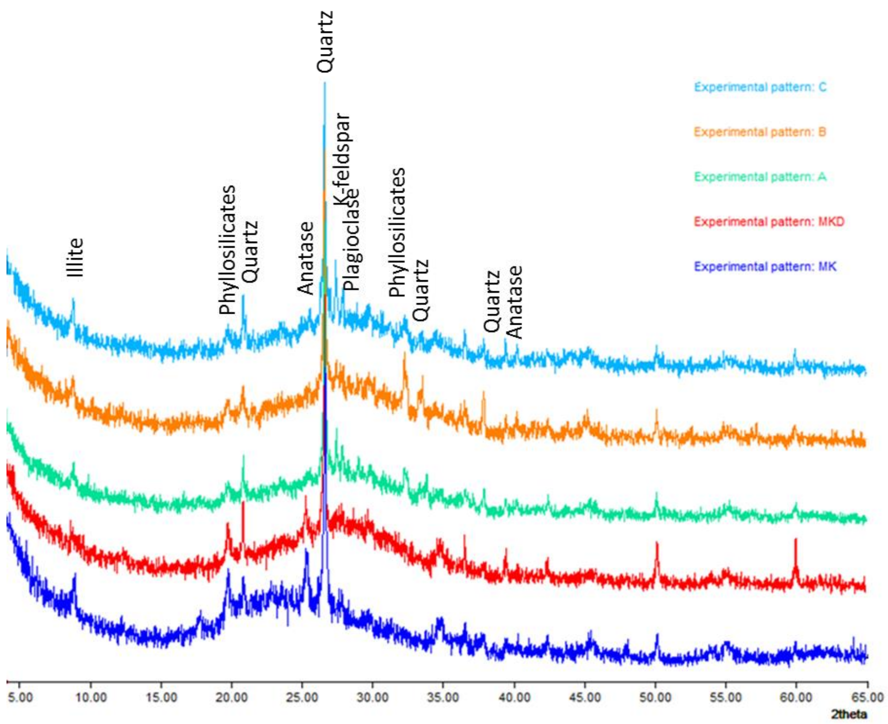
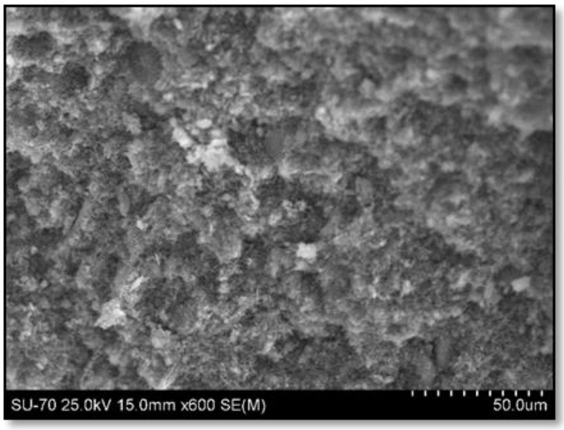


Figure 4.2.5 – XRD patterns example of the geopolymers formulations carried out.



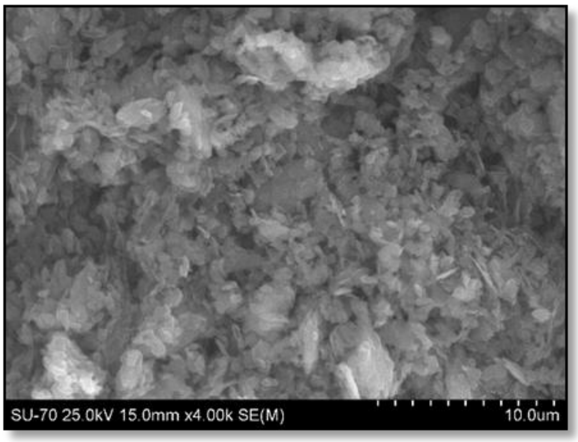


Figure 4.2.6 – SEM images of formulation MKD after 28 days of cure.

The results obtained for mechanical resistances are presented in Figure 4.2.7. The compressive strength gave values between 1 (MKD 3.5:1) to 14 MPa (C 4.5:1). As expected, the lower compressive strength values are observed in samples formulated with raw diatomite and kaolin. The reactivity of both materials should be positively affected when calcination is applied, and consequently the resistance of the geopolymer should increases (Narmatha & Felixkala, 2016).

In terms of compressive strength, the formulations C 4.5:1, that corresponds 90% of Portuguese kaolin plus 10% of diatomite calcined at 550ºC, gave good mechanical properties (close to 9 MPa after 21 days of curing). As applied in earthen based materials such as adobe, whose resistance values are considered as sufficient (Illampas *et al*., 2014, Coroado *et al*., 2010). 10% of diatomite should be the optimum addition. Above this quantity, the geopolymer samples lose their cohesion and are easily crashed.

The results of water absorption are shown in Figure 4.2.8. Most samples have a high absorptive capacity; around than 30% after 21 days of curing. Generally, water adsorption decreases when mechanical strength increases. In this case, the absorption remains high. These results are good since with it is a solution for salt lixiviation and retention problem found in the studied adobe.

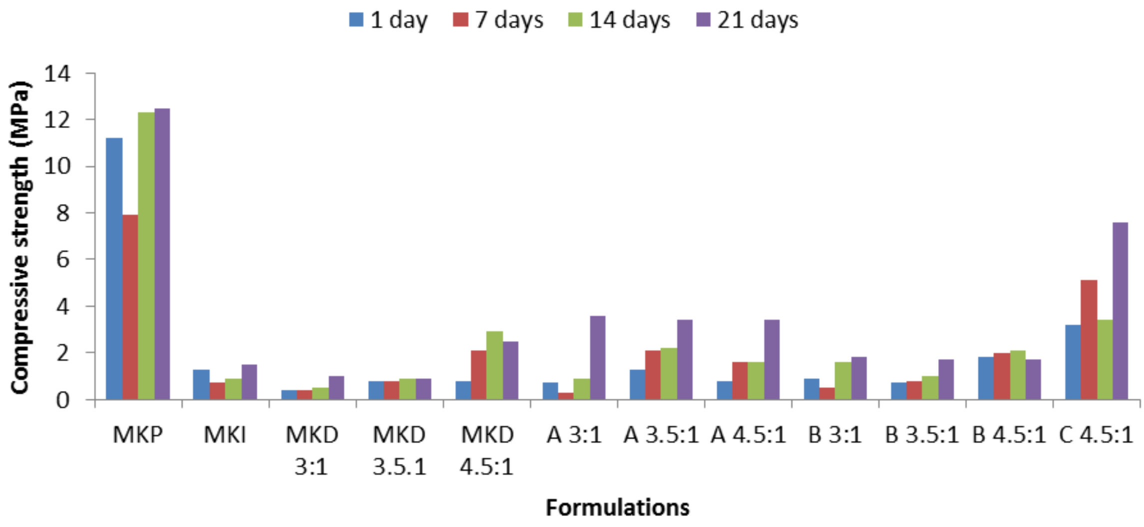


Figure 4.2.7 - Mechanical strength of the formulations tested 1, 7, 14 and 21 days of curing.

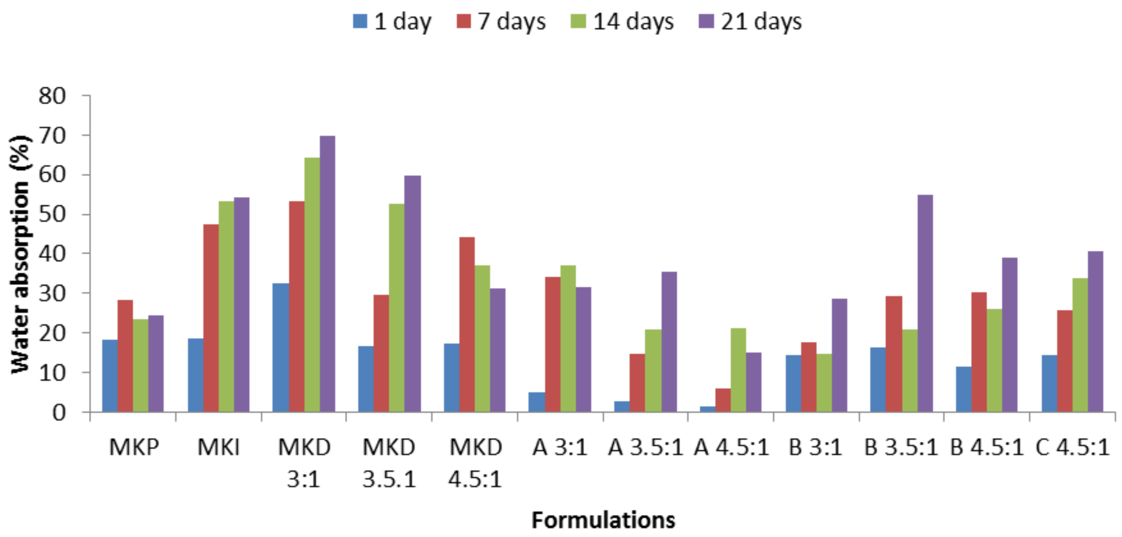


Figure 4.2.8 - Water absorption of the formulations tested 1, 7, 14 and 21 days of curing.

4.2.6 Conclusions

Mineralogically, adobes are essentially composed by tectosilicates (quartz and feldspars), which are mainly part of the aggregate, carbonates and phyllosilicates (mainly kaolinite and illite), which are the major constituents of the binders, sometimes occurring oxides and hydroxides of iron, halite and gypsum. The chemical composition reflects the mineralogical composition of the samples.

Following the characterization of the adobes, it was possible to focus into the aim of this work in developing materials keeping sustainability and compatibility but also solving/reducing drawbacks, namely presenting some capacity of absorption and retention of salts, in order to guarantee the reduction of saline efflorescence.

To assure the primary objectives of this research work, several geopolymers have been developed in order to arrive at the formulations that best ensure the proposed goals. The choice of geopolymer compared to other materials is justified mainly by the sustainability they can guarantee, as well as because the raw materials (other than activators) they require are primarily geomaterials locally available.

The geopolymers that have already been made have Portuguese industrial metakaolin, kaolin and diatomite, and Portuguese kaolin and diatomite calcined at 550ºC.

It is concluded that the addition of diatomaceous earth benefits these construction materials, as has already been found in other studies. It has been found that the addition of 10% diatomite with calcination benefits these geopolymers, obtaining the best mechanical resistance.

In terms of water absorption capacity these materials shows absorptions equal or higher than 30%, some formulations absorption capacities are higher than 50%. The geopolymers with the greatest capacity for water absorption are mainly those that incorporate diatomite and Portuguese kaolin without calcination. The amorphous structure of the diatomite, as well as the lower crystallinity of the kaolin (before calcination) allows its structures to be in the right conditions for absorption to occur.

4.3 DEVELOPMENT OF GEOPOLYMERS FORMULATIONS BASED ON LOW-GRADE KAOLINS AS A POTENTIAL CONSTRUCTION MATERIAL

Abstract Sustainability, particularly in construction materials, has been a subject of growing interest. Civil construction is one of the industries where more materials are consumed, which leads to high energy consumption and CO_2 emissions. The production of cement, especially clinker is largely responsible for these problems. As a solution, new materials emerge, which do not require much energy for their production, which are the alkaline cements, specifically the geopolymers. Geopolymers are inorganic polymers obtained by the alkaline activation of aluminosilicate precursors. In the present study geopolymers were developed with low grade kaolin (as a precursor) from a Portuguese company. The development of these geopolymers will be, due to their properties, a good solution for rehabilitation of earth buildings, especially in adobe. The development of these geopolymers is also a contribution to the sustainability of kaolin exploitations as it opens new markets for the low grade kaolins, presently not easily commercialized.

4.3.1 Introduction

In construction industry, the growing concerns about the exhausting natural resources and consequent energy consumption are increasing during the last decade, mainly due to the production of cement that, in addition to consuming different materials, entails high energy expenditure with a release of CO_2 corresponding to at least 5 to 7% of global emissions (McLellan *et al*., 2011). In order to minimize these effects, other materials arise trying to substitute OPC cements and also to fill shortages in supply. Previous investigations for new more sustainable building materials aiming cement substitution by geomaterials submitted to alkaline activation or geopolymers (Costa *et al*., 2019a).

A geopolymer is an inorganic polymer obtained by the alkaline activation of an aluminosilicate under certain temperature and pressure conditions (Davidovits, 2015). According to several authors (Costa *et al*., 2019a; Habert *et al*., 2014; Lodeiro *et al*., 2013; Petrillo *et al*., 2016), the geopolymers can be a great solution to use as construction material, especially in earth construction to rehabilitation and restoration works.

Their properties depend mainly on the chemical structure. In addition to replacing the cements, these materials can also be applied to other products, such as composites with fire-resistant fibers, anti-fire protection, in the ceramic industry (bricks and others), encapsulation of toxic and radioactive waste, among others (Davidovits, 2002).

The main advance is that sludge can be also used in the composition with fly ash (Habert, 2011). In general all aluminosilicates in which the atomic ratio Si: Al varies between 1 and

3 are considered the best fit (Pinto, 2004). The geopolymers can be produced from naturally high-strength natural phyllosilicates cured at room temperature; thus, they have good physic and chemical characteristics, such as: high workability, quick hardening, surface finishing, rapid development of mechanical strength, surface hardness, good resistance to chemical attack, heat and fire (Davidovits, 2015).

As interest in these products increases, research is starting in Portugal aiming to produce geopolymers from abundant Portuguese low-grade kaolin deposits.

4.3.2 Materials and Methods

4.3.2.1 Materials and reagents

Geopolymers were prepared using two Portuguese low grade kaolins (MIB-A and MIB-C), provided by a Portuguese company (Mibal – Minas de Barqueiros SA) with a grain size less than 30 µm (Figure 4.3.1). The main constituent of kaolin is kaolinite ($Al_2Si_2O_5(OH)_4$), which undergoes successive structural and microstructural transformations during its firing (Andrini *et al.*, 2016). The decomposition of kaolinite in metakaolinite occurs between 400 and 630ºC. The calcination (up to 400ºC) breaks down the structure of kaolin (alumina and silica layers become puckered and disorder) resulting in a metakaolin. Metakaolin is a highly reactive transition phase, an amorphous material with pozzolanic and latent hydraulic reactivity, suitable for use in cementing applications (Rashad *et al.*, 2013). Both kaolins were used in their natural state and calcined at temperatures of 300, 500 and 750ºC during 4 hours, to evaluate the effect of the temperature calcination on final products (Figure 4.3.2).

Hydrated sodium silicate (Merck, Germany Merck, Germany; 8.5 wt.% Na_2O, 28.5wt.%, SiO_2,63wt., %H_2O) and sodium hydroxide (6M) (ACS AR Analytical Reagent Grade Pellets) were used as alkaline activators. Deionized water was the reaction medium.

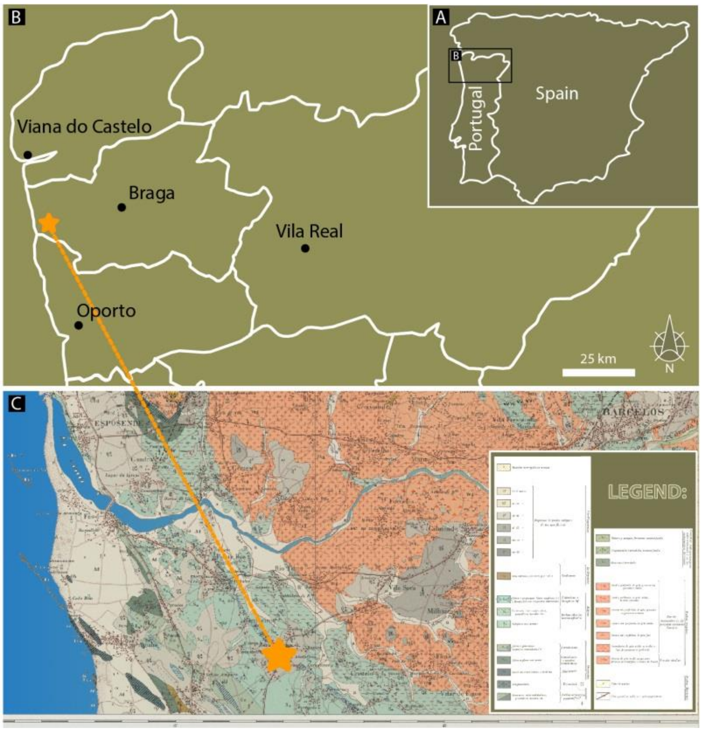


Figure 4.3.1 – Kaolin deposits location, and geological map 1:50 000 adapted, 1-C sheet Barcelos (Teixeira & Medeiros, 1969).

Figure 4.3.2 – Portuguese kaolins MIB-C A and MIB-A as natural and in different calcination temperatures.

4.3.2.2 Preparation of geopolymers specimens

The following 8 compositions (Figure 4.3.3) were prepared: GeoMIB-A and C (natural kaolin), GeoMIB-A and C 300 (kaolin calcined at 300ºC), GeoMib-A and C 500 (kaolin calcined at 500ºC) and GeoMIB-A and C 750 (kaolin calcined at 750ºC). The mixing of the blends was carried out by a laboratory stirrer (200 rpm for 2 min) to ensure their homogeneity and avoid bubbles and agglomeration into the sample. The pastes were immediately placed in cubical molds (20mm x20mm x 20mm) and put on an oven at 50ºC for 24h. During the curing time, the geopolymers specimens were stored in sealed plastic bags at room temperature (Andrejkovičová *et al.*, 2016). The assays were performed in 3 specimens of each formulation at 7, 14 and 28 days of cure.

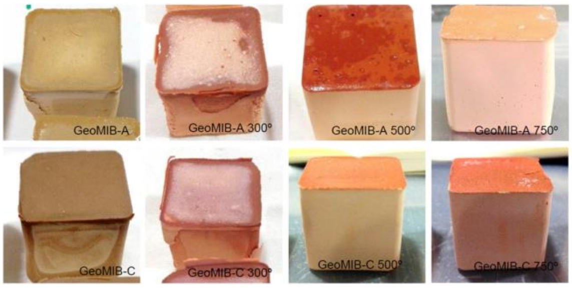


Figure 4.3.3 - Geopolymer specimens performed.

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4.3.2.3 Methods

The chemical composition of natural and calcined kaolins was assessed by X-ray fluorescence (XRF) using an XRF Panalytical AXIOS PW4400/40. Loss-on-Ignition (LOI) was determined by heating 1 g of the sample at 1000 ºC for 1 h in furnace.

The mineralogical composition was determined both on un-oriented (random) powder mounts for < 30 µm fraction analyses and on oriented aggregates for the clay fraction ones, for kaolin, and in the bulk samples of geopolymers specimens. The clay fractions were obtained by sedimentation according to Stokes law, using 1% sodium hexametaphosphate solution to avoid flocculation. For the preparation of preferentially oriented clay mounts, the suspension was placed on a thin glass plate and air-dried. XRD measurements were performed using Philips PW 3050 and X' Pert PW 3040/60 equipment using Cu Kα radiation. Scans were run between 2º and 60º (unoriented powder mounts) and between 2º and 20º 2Θ (oriented clay mounts) in air-dry state, after a previous glycerol saturation, and heat treatment (500°C). Qualitative mineralogical analyses followed the criteria recommended by Schultz (1964), Thorez (1976) and Mellinger (1979). The degree of crystallinity was estimated from XRD determination of the Hinckley crystallinity index. The Hinckley crystallinity index consists in the ratio of the height above background of the 110 and 111 peaks above the band of overlapping peaks occurring between 2θ = 20 to 23º compared to the total height of the 110 above background (Aparicio *et al*., 1999).

The microstructural characterization was carried out by scanning electron microscopy (SEM – Hitachi, SU 70) and energy dispersive X-ray spectrometry (EDS – EDAX with detector Bruker AXS, software: Quantax) operated at 3–30 kV.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out as simultaneous thermal analysis (STA) on a Setaram TGA 92 balance, under argon between ~20^0C and 1000^0C,with a heating rate of 10ºC min^{-1}.

The cubical specimens were submitted to compressive strength tests, using a universal mechanical compression testing machine (Shimadzu Autograph AG 25 TA). The testing procedure was carried out with a maximum force of 5 kN at the speed of 50 N/s as per the standard EN 1015-11 (Moutinho *et al.*, 2019).

Water absorption of the immersed specimens was calculated for each series according to Eq. (1), where W% is the adsorption of water expressed as percentage; Ww and Wd are the weights of the immersed specimen and of specimen after drying (g), respectively (Yousef *et al.*, 2009 in Andrejkovičová *et al.*, 2016).

$$W\ \% = \frac{Ww - Wd}{Wd} * 100$$

4.3.3 Results and discussion

4.3.3.1 Kaolin characterization

The textural behavior of both kaolins is presented in Table 4.3.1. Through these results it´s verified that MIB-C kaolin is finer, which means that it has better reactivity. However, both kaolins are very fine, presenting more than 85% of particles less than 25µm.

Table 4.3.1 – Texture of MIB-A and MIB-C kaolins.

	Texture (µm)									
	<100	<75	<50	<25	<10	<5	<2	<1.5	<1	<0.5
MIB-A	98.9%	98.8%	97.1%	84.1%	70.9%	51.5%	44.1%	33.2%	13.7%	3.4%
MIB-C	98.2%	98.7%	96.1%	85.8%	75.9%	68.8%	55.7%	48.5%	32.4%	7.7%

MIB-A and MIB-C samples (present similar mineralogical composition), being composed, according to the semi-quantification by 65% and 69% of kaolinite, 24% and 23% of quartz and 11% and 8 % of illite, respectively. Above 500ºC, kaolinite was destructed and a broad reflection centered at 2θ = 20º to 25º attributable to the amorphous metakaolinite appeared. MIB-C kaolin shows the presence of gibbsite in small amounts.

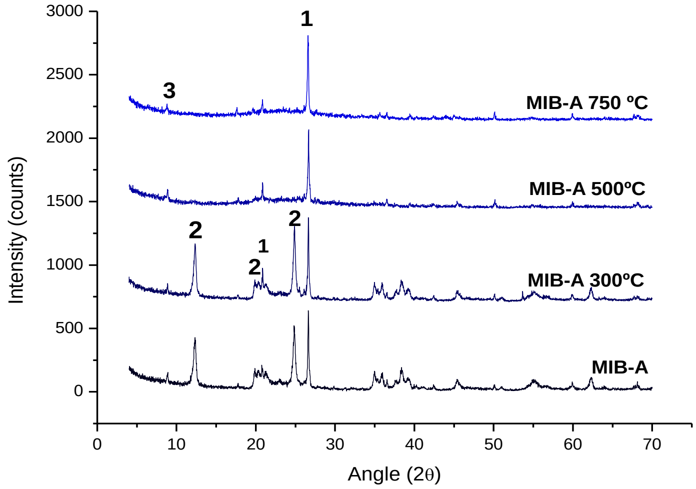


Figure 4.3.4 – XRD patterns of MIB-A samples (1 – quartz, 2 – kaolinite, 3 – illite).

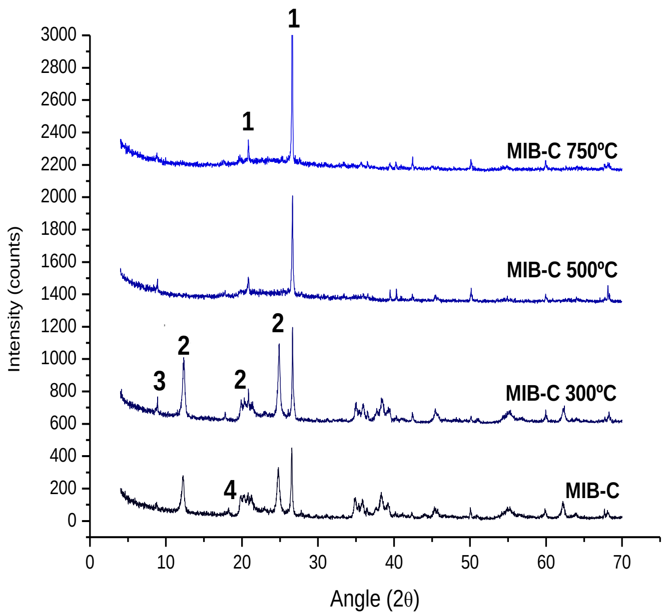


Figure 4.3.5 - XRD patterns of MIB-C samples (1 – quartz, 2 – kaolinite, 3 – illite, 4 - gibbsite).

XRD patterns of fractions under 2 µm show that Hinckley crystallinity index of kaolinite increases with calcination at 300ºC; at 500 and 750ºC calcination temperature these kaolins lose their crystallinity (Figures 4.3.6 and 4.3.7), becoming amorphous.

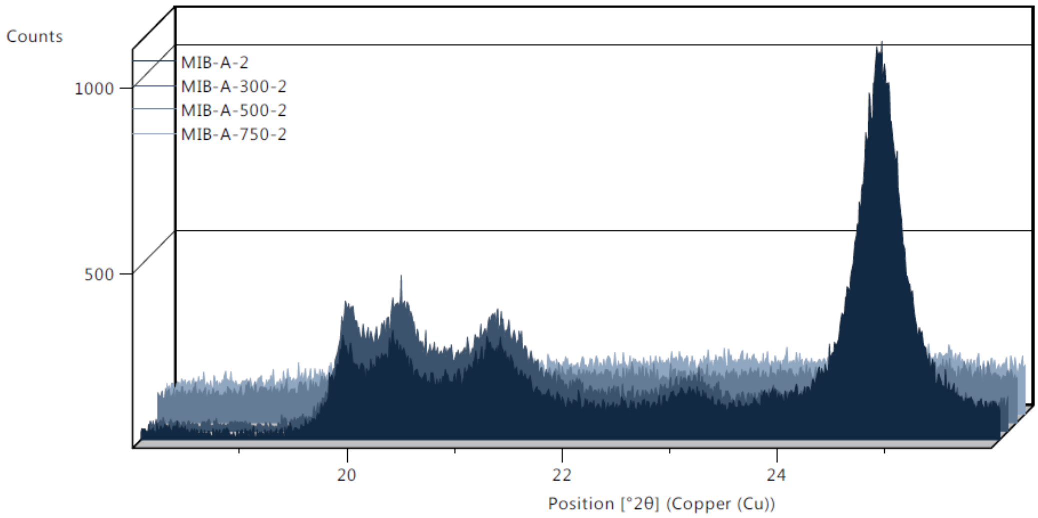


Figure 4.3.6 - XRD patterns of MIB-A samples (fraction <2µm).

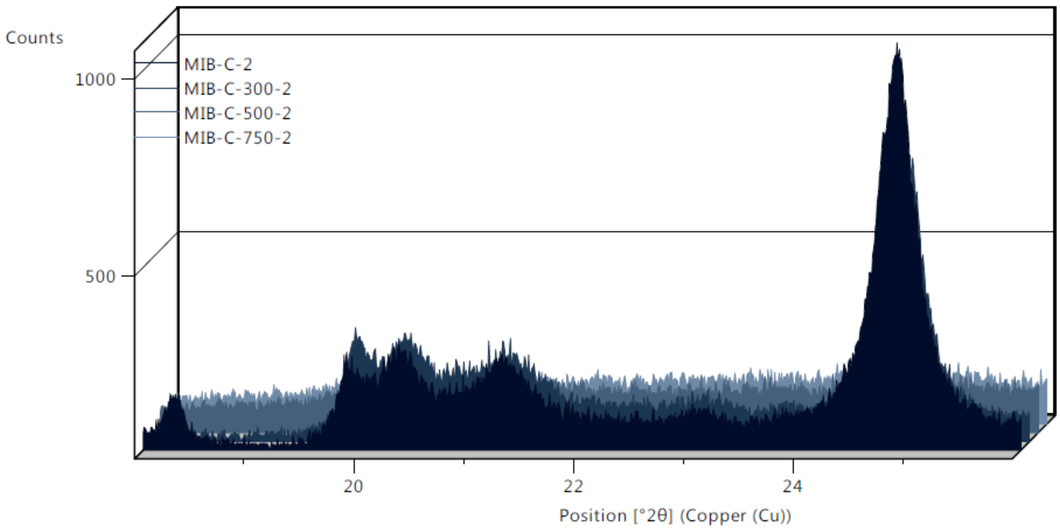
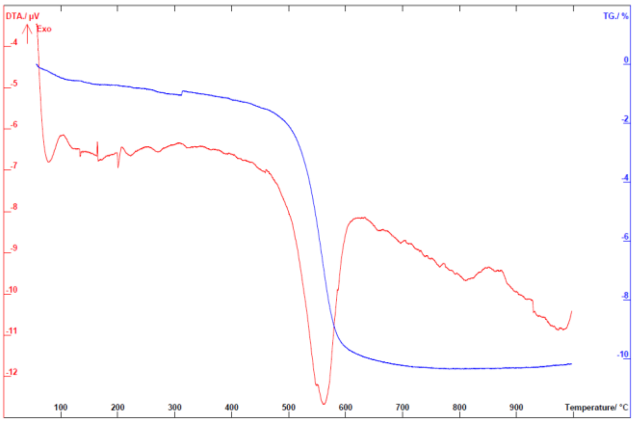
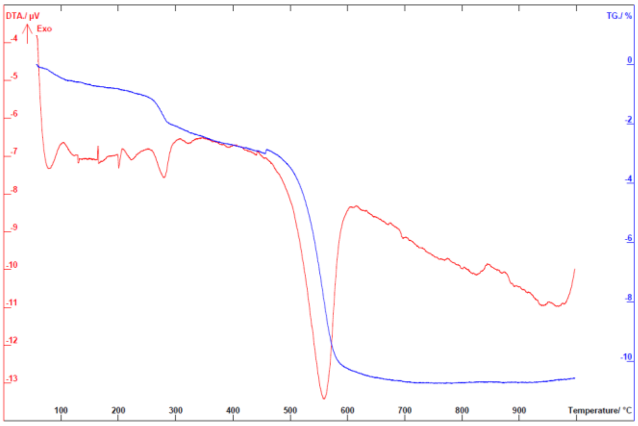


Figure 4.3.7 - XRD patterns of MIB-A samples (fraction <2µm).

Thermal behavior of kaolin samples was assessed by DTA/TG (Figure 4.3.8). Both samples MIB-A and MIB-C have a similar thermal behavior, showing no significant differences between them. DTA/TG curves of both kaolins show the presence of two endothermic peaks. The first one is less intense located around 80ºC, reflecting the losing of the surface water. The second one appeared around 560ºC, being related to the losing of structural water (dehydration of kaolin to form metakaolin) and associated to a mass loss of (close to 13% for both kaolins), between 450ºC and 600ºC. Furthermore, DTA curves of MIB-C present an endothermic peak located between 280ºC and 300ºC associated to a mass loss around 1%; corresponding to the dehydroxylation of gibbsite and formation of alumina (Haddar *et al*., 2018).



MIB-A



MIB-C

Figure 4.3.8 – ATG/TG of kaolins MIB-A and MIB-C.

Table 4.3.2 – Chemical analyses of kaolins.

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	LOI (%)
MIB-A	47.34	35.81	2.11	0.13	0.26	0.06	0.89	0.50	12.51
MIB-A300	47.52	35.21	2.13	0.05	0.27	0.06	0.94	0.50	13.05
MIB-A500	52.10	40.39	2.39	0.08	0.29	0.07	1.01	0.55	2.81
MIB-A750	53.21	41.08	2.39	0.06	0.31	0.07	0.96	0.56	0.94
MIB-C	44.92	36.11	3.42	0.03	0.24	0.06	0.90	0.47	13.54
MIB-C300	45.90	36.71	3.45	0.03	0.26	0.06	0.96	0.49	11.85
MIB-C500	50.02	41.00	3.84	0.03	0.28	0.07	0.97	0.54	2.88
MIB-C750	50.43	42.15	4.02	0.05	0.28	0.06	1.03	0.57	1.01

The chemical composition of kaolins used on geopolymers design is presented on Table 4.3.2. It is clear that in kaolin calcined at low temperatures (300°C) the Al_2O_3 content is maintained, whereas on kaolins calcined at higher temperatures (500^0C and 750^0C) the aluminum content increases slightly due to the changes on the structure of these materials. Other important aspect to mention is the loss-on-ignition (LOI), decreasing with temperature, due to the dihydroxylation related to the transition from crystalline to amorphous state. This aspect is very important, showing that with the increases in temperature we can obtain a more resistant material, in particular, to fire.

4.3.3.2 Geopolymers characterization

Si:Al, Na/Al, Na:Si and water:Si ratios

The Si:Al ratio determine the degree of polymerization (Pimraksa *et al*., 2011). The ratio was calculated according to the chemical analysis of precursors and the alkaline solutions used (Table 4.3.3). According to Duxson *et al.* (2005), higher mechanical forces are obtained for higher SiO_2: Al_2O_3 ratios, and higher porosities for lower SiO_2: Al_2O_3 ratios; they also found that for ratios between 1.4 and 1.65 there is a change of structure, changing from a porous structure to a more homogeneous one. The same authors also conclude that the porosity increases on higher H_2O: SiO_2 ratios. Accordingly, the formulations are all within the range between 1.4 to 1.65. Developed geopolymers have very similar chemical compositions and as such, the differences in values between the results of either mechanical strength or water absorption are mainly attributed to the presence of amorphous material.

Table 4.3.3 – Studied ratios of geopolymers formulations produced.

Geopolymers	SiO_3:Al_2O_3	Na_2O:Al_2O_3	Na_2O:SiO_3	H_2O:SiO_3
GEOMIB-A	1.63	0.35	0.22	1.31
GEOMIB-A300	1.66	0.36	0.22	1.31
GEOMIB-A500	1.56	0.31	0.20	1.21
GEOMIB-A750	1.56	031	0.20	1.19
GEOMIB-C	1.55	0.35	0.23	1.37
GEOMIB-C300	1.55	0.34	0.22	1.34
GEOMIB-C500	1.49	0.31	0.21	1.25
GEOMIB-C750	1.46	0.30	0.21	1.24

Mineralogical composition and SEM analysis

The mineralogical characterization of the studied geopolymers was carried out on the specimens after 28 days of cure. XRD patterns are closely similar to the used kaolins. However, a slight shift in the amorphous phase broad band is observed. The amorphous material undergoes a clear evolution from 2θ between 20º to 27º, at the raw material, to 23º to 30º on geopolymers (Saidi *et al.*, 2013) (Figures 4.3.9, 4.3.10 and 4.3.11). These changes allow us to conclude that the polymerization process is occurring in all geopolymers developed. Produced geopolymers are composed essentially by quartz, kaolinite, amorphous phases (metakaolinite) and discrete illite traces (Figure 4.3.12).

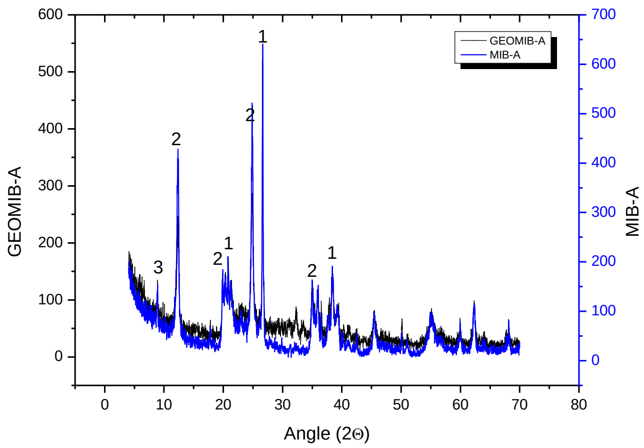


Figure 4.3.9 –XRD patterns of geopolymer GEOMIB-A and kaolin MIB-A (1 – quartz, 2 – kaolinite, 3 – illite).

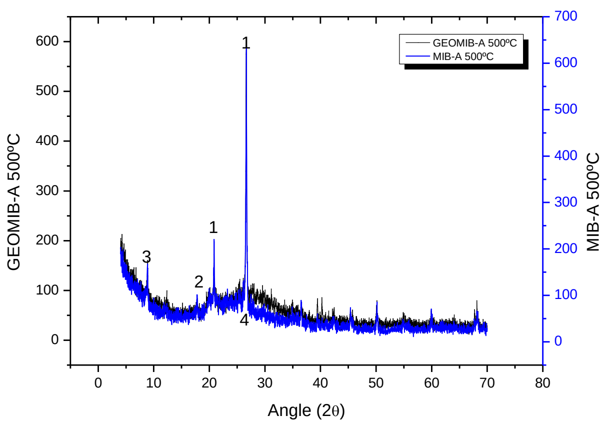


Figure 4.3.10 –XRD patterns of geopolymer GEOMIB-A 500ºC and kaolin calcined at 500ºC (1 – quartz, 2 – kaolinite, 3 – illite, 4 amorphous areas).

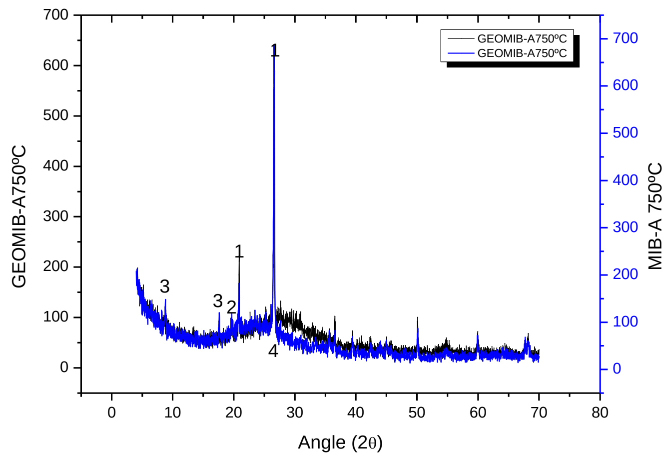


Figure 4.3.11 –XRD patterns of geopolymer GEOMIB-A 750ºC and kaolin calcined at 750ºC 500ºC (1 – quartz, 2 – kaolinite, 3 – illite, 4 amorphous area).

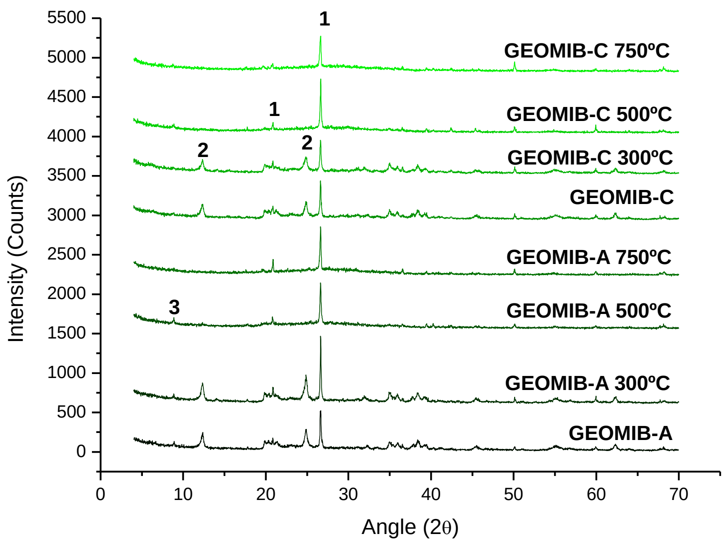


Figure 4.3.12 –XRD patterns of geopolymeric formulations (1 – quartz, 2 – kaolinite, 3 – illite).

Figures 4.3.13 and 4.3.14 show SEM images for geopolymers made with kaolins calcined at higher temperatures, displaying the amorphous structure obtained after 28 days of curing time.

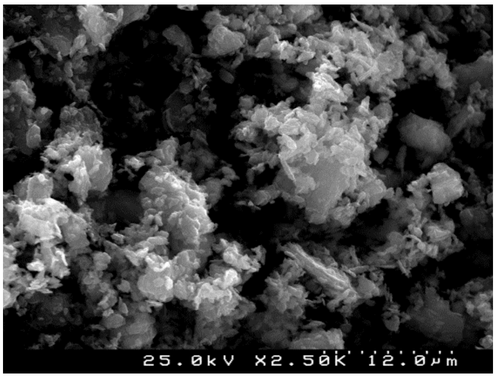


Figure 4.3.13 – SEM images of GEOMIB-A 500ºC formulations.

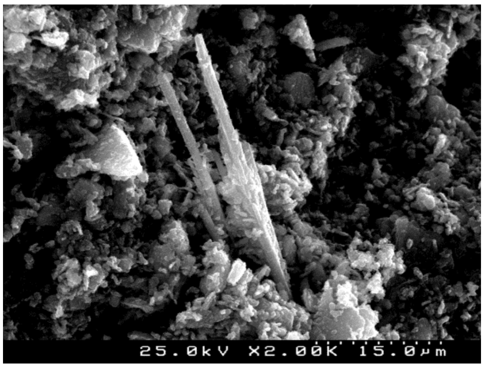


Figure 4.3.14 - SEM images of GEOMIB-C 750ºC formulations

Compressive strength

The compressive strength studied for different curing times is presented in Figure 4.3.15. The GEOMIB-C 300ºC geopolymers presents higher values in term of mechanical resistance(~10MPa). This result can be related with the presence of gibbsite and its dihydroxylation.

When kaolins A and C were calcined at higher temperatures, the compressive strength decreased considerably in comparison of raw kaolin and calcined at 300ºC. Moreover, it is observed that with larger curing period the strength decreased. This means that the consolidated material is losing its cohesion in function of time. For the GEOMIB-A and GEOMIB-A 300ºC, the opposite behavior it is verified as mechanical strength increases during the curing time. The decrease of mechanical strength on raw materials calcined at higher temperatures means that the reactivity of kaolins decreased with calcination. Thus, the desired pozzolanic effect, which confers resistance to geopolymers, is compromised. This may be related to the crystallinity of the original kaolin. According to Kakali *et al.* (2001), the degree of crystallinity of the kaolinite precursor can affect pozzolanic reactivity of metakaolinite. In this case, the pozzolanic effect of kaolinite could improve the mechanical strength of these consolidated materials, instead of metakaolinite (Tironi *et al*., 2012).

The low Na/Al ratios (Table 4.3.1) are compromising the mechanical strength of the geopolymers. According to Khan *et al*. (2014), Na/Al ratios <1 mean that the alkaline activator used was insufficient. This means that higher concentrations of NaOH solution 3 should be used. These authors also report that Na/Al ratios <1.2 can also lead to a decrease in mechanical resistance. The best ratios Na / Al should be between 1 and 1.2.

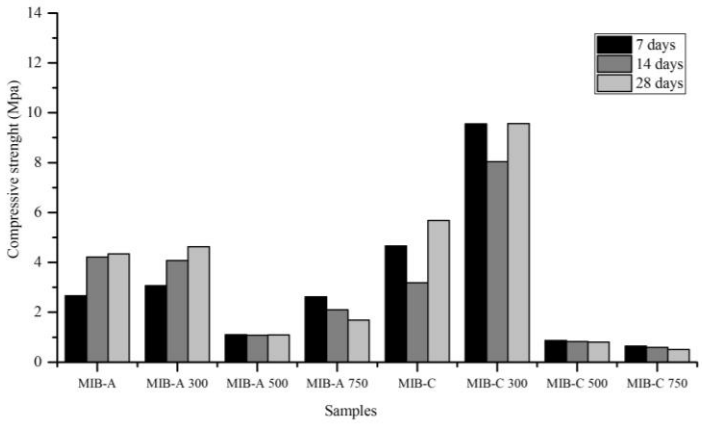


Figure 4.3.15 – Compressive strength of geopolymers at different curing times (7, 14 and 28 days).

<u>*Water absorption*</u>

Figure 4.3.16 shows the percentage of water uptake as a function of square root of time of geopolymer samples with low grade kaolins without heat treatment and calcined at 300ºC, 500ºC and 750ºC. It can be seen that the water absorption increase in the heat kaolins at 500ºC and 750ºC.

The results obtained in the compressive strength are reflected in the water absorption capacity analysis results.

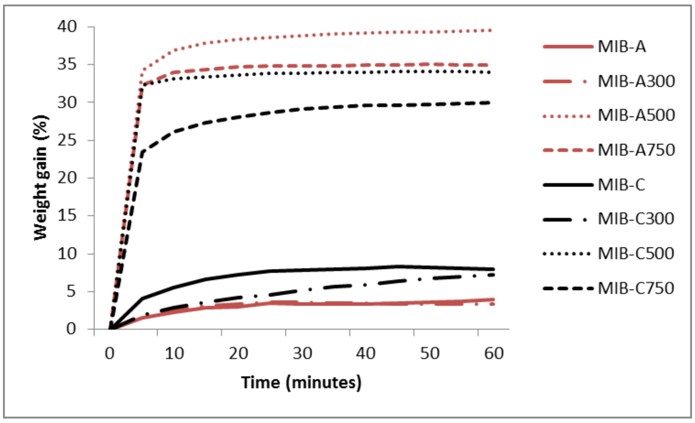


Figure 4.3.16 - Water absorption (%) of geopolymers for 28 days of cure.

The lower the value of the mechanical resistance higher is the absorption. It means that in the case of better cohesion of the consolidated products, the porosity decrease. Also, the materials obtained with raw and calcined at 300°C kaolins presented values around 5 to 10%, 3 to 4 times lower than the other ones. Geopolymers with kaolin without calcination and with calcination at 300°C exhibit similar behaviour; after around 20 minutes they are saturated.

The large difference in water absorption values relates to the change in the structure of the raw materials with heating. The dehydroxylation of kaolinite resulting an amorphous material metakaolinite with a high reactivity pozzolana. The increase of amorphous content in the raw materials facilitates water absorption capacity.

4.3.4 Conclusions

Mineralogically, the geopolymers are essentially composed by quartz, kaolinite, and aluminum and silicon rich amorphous material. The increase of amorphous material in all geopolymers comparing to precursors reveals that polymerization is occurring.

The mechanical strength shows that the natural kaolins (MIB-A and MIB-C) produce geopolymers with good results for compressive strength. These results are related to the reduced particle size of the kaolins, and the reduction of the reactivity of the calcination at higher temperatures. The development of these geopolymers is also a contribution to the sustainability of kaolin exploitations as it opens new markets for the low grade kaolins, presently being not easily commercialized.

According to Costa *et al.* 2019a, after studying several adobe construction buildings it was found that there is a need to develop sustainable materials. The developed materials need to be compatible with the old adobe materials to carry out intervention, conservation and rehabilitation works. The development of these geopolymers will be, due to their properties, a good solution for rehabilitation of earth buildings, especially in adobe. The better geopolymers developed for these propose are: GEOMIB-A, GEOMIB-C, GEOMIB-A300^{0}C, GEOMIB-C300^{0}C and GEOMIB-A750^{0}C; taking into account that the mechanical strength of adobe materials ranges in literature from 0.6 to 8.3 MPa (Illampas *et al*., 2014), the values obtained for these geopolymers (between ~2 to 10 MPa) can be considered as totally adequate. However, it is suggested that preference must be given to the geopolymers not demanding heating in the process, in order to obtain a more sustainable product, that is, more environmentally friendly, as it will cause much less CO_2 emissions.

4.4 CHAPTER SYNTHESIS

The developed materials are summarized in Table 4.4.1. 48 formulations were developed (27 of adobes alkaline activated and 21 of geopolymers). In green the materials that were selected according to the values obtained of mechanical strength, mineralogical and chemical composition and water absorption capacity and considered compatible with the old adobes are specified. 23 formulations was selected as appropriated (4 adobes alkaline activated and 19 of geopolymers). 8 formulations of adobes alkaline activated presented efflorescence's formation that needs to be better studied to assess their potential contributions to future degradation of materials. The mechanical strength of old studied adobe materials ranging 0.3 to 4 MPa. However, the selected materials present strength ranges between 0.8 to 8 MPa. Because according to the literature it´s can be find old adobes with strain values range between 0.6 to 8.3 MPa can be found (Illampas *et al*., 2014). The minimum value was a little bit increased, because it´s considered that the values under 0.8 MPa are extremely low and may affect the effectiveness of restoration actions.

It is concluded that materials developed by alkaline activation have benefits both in terms of increase of mechanical strength and also in the decreasing of water absorption. However, in the developed adobes it was concluded that activation with NaOH improves the formation of efflorescence (thermonatrite) which create damage to these materials and potentiate their degradation over time (Elert *et al*., 2019), (Table 4.4.1 yellow colour). Thus, NaOH activated adobes are not recommended at present stage, needing further studies evaluating the impact of the salts formation.

Table 4.4.1 – Formulations of geomaterials developed (○ – rejected; √ - under study, salts evaluation; √ - appropriated materials).

Adobes		Geopolymers	
1.1 H_2O	○	MKP	√
1.1KOH	√	MKI	√
1.1NaOH	√	MKD 3:1	√
2.1 H_2O	○	MKD 3.5.1	√
2.1 KOH	√	MKD 4.5:1	√
2.1NaOH	√	A 3:1	√
2.2 H_2O	○	A 3.5:1	√
2.2KOH	○	A 4.5:1	√
2.2NaOH	√	B 3:1	√
3.1H_2O	○	B 3.5:1	√
3.1KOH	○	B 4.5:1	√
3.1 NaOH	√	C 4.5:1	√
3.2 H_2O	○	C 4.5:1	○
3.2 KOH	√	MIB-A	√
3.2NaOH	√	MIB-A 300ºC	√
4.1 H_2O	○	MIB-A 500ºC	√
4.1 KOH	○	MIB-A 750ºC	√
4.1 NaOH	√	MIB-C	√
4.2 H_2O	○	MIB-C 300ºC	○
4.2 KOH	○	MIB-C 500ºC	√
4.2 NaOH	√	MIB-C 750ºC	√
4.3 H_2O	○		
4.3 KOH	√		
4.3 NaOH	√		
4.4 H_2O	○		
4.4 KOH	○		
4.4 NaOH	√		

CHAPTER 5

FINAL REMARKS, ONGOING AND FUTURE WORK

5.1 FINAL REMARKS

The first stage of the research focused on the research, collection and characterization of adobes in two main territorial sectors, Aveiro and Figueira da Foz, with a major focus on Aveiro as the region where adobe construction has a higher incidence in Portugal.

During the adobe sampling several problems were found:

- The majority of allowed samplings were buildings under demolition. Thus, most of the times it was not possible to collect enough samples to carry out all the tests initially planned.
- Initially it was planned to study interior adobe walls and exterior adobe walls with different sun exposure, which was not possible because of the previous point.
- Often the original state of degradation of the adobe samples may have influenced some results, mainly mechanical strength and water absorption by capillarity.

However, after researching and visiting several adobe buildings it's possible to conclude that the performed sampling is quite representative of the adobes in the studied regions.

In fact, there is not so much heterogeneity in the adobe blocks; only in terms of color they vary from gray to yellow, orange-yellow and brown. These colors are directly related to their mineralogical composition. Adobes done from more clayey soils (more phyllosilicates rich) show, in general, to be brownish colors, whereas those richer in iron minerals (such as iron oxides and hydroxides, like hematite or goethite) show yellow-orange colors. The greyish adobes are usually rich in lime (calcite).

Mechanical and water absorption properties of the studied adobes are influenced by their mineralogical and textural compositions. However, as already mentioned above, the mechanical strength of the studied adobes was affected by their state of degradation.

Next stage was focused on the development of new formulations of geomaterials for application in rehabilitation and restoration actions of adobe buildings.

For the development of the new materials two main assumptions were taken into account: design materials compatible with the old/original adobes; ensure the sustainability of the adobe technology and cultural tradition with the new materials produced.

The sustainability of materials is a subject of significant importance due to growing concerns about the environment. The choice of products that are either effective for the purpose and environmentally friendly throughout their life cycle are key issues to consider when studying materials. Concerns about the consumption of materials and consequent energy expenditure have increased over time due to the scarcity of some materials. In construction this concern increased due to the excessive consumption of materials, mainly due to the production of cement which, in addition to consuming huge amounts of different materials, entails a high energy expenditure as well as a release of CO_2 corresponding to at least 5 to 7% of global emissions (McLellan *et al*., 2011). Thus, cement production process, particularly during clinker production, is the main source of environmental pollution in the construction sector. In order to solve these problems, other materials arise aiming to replace cements in their applications and at the same time to fill their problems. During our investigations of new and more sustainable building materials, geopolymers and traditional earth materials alkaline activated were developed and assessed.

Heritage rehabilitation actions are specified in terms of the materials to use, requiring compatible materials depending on the building to be intervened. However, if rehabilitation and repair actions are well done, they are in themselves sustainable by increasing the longevity of existing materials.

Two types of materials were developed in present research: alkaline activated adobes and geopolymers. The development of these materials occurred successfully; although, some aspects need further study, namely water absorption, active aging and salt efflorescence formation.

The main properties of old/original adobes studied and the new materials developed are presented in Table 5.1. Through the analysis of Table 5.1 it's possible to conclude that the developed materials present similar composition and physical properties. However, water absorption behavior, especially of the alkaline activated adobes, is still being under study.

Table 5.1 – Synthesis of the main properties of old adobes and new materials developed.

	Mineralogy	Chemistry	Physical properties
Old adobes	**Tectosilicates** (Quartz and feldspars); **Carbonates** (Calcite and dolomite); **Phyllosilicates** (Kaolinite and illite); **Accessory minerals** (Iron oxides and hydroxides and salts like halite, sulphates like gypsum).	SiO_2,Al_2O_3, CaO,Fe_2O_3 Lost on ignition Minores: Na_2O, MgO, P_2O_5, SO_3, Cl, K_2O, TiO_2, MnO	**Capillarity Absorption coefficient** (g/dm^3.m$^{1/2}$) – 3 to 13; **Compressive strength** (MPa) – 0.3 to 4
Adobe alkaline activated – paper 4.1	**Tectosilicates** (Quartz and feldspars); **Phyllosilicates** (Kaolinite, halloysite and illite); **Amorphous phases**(like metakaolinite); **Accessory minerals** (Anhydrite, siderite, opal c/ct, anatase, zeolites and thermonatrite).	SiO_2,Al_2O_3,Na_2O, K_2O, Fe_2O_3 Lost on ignition Minores: CaO, MgO, P_2O_5, SO_3, Cl, TiO_2	**Capillarity Absorption coefficient** - under testing; **Compressive strength** (MPa) – 0.8 to 3
Geopolymers - paper 4.2	**Tectosilicates** (quartz and feldspars); P**hyllosilicates** (illite and kaolinite); **Amorphous phases** (metakaolinite) **Accessory minerals** (anatase).	SiO_2, Al_2O_3, Fe_2O_3,TiO_2, Na_2O Lost on ignition Minores:K_2O, TiO_2	**Water Absorption** (%) - 20 to 60% **Compressive strength** (MPa) – 1 to 14
Geopolymers - paper 4.3	**Tectosilicates** (quartz); P**hyllosilicates** (illite and kaolinite); **Amorphous phases** (metakaolinite).	SiO_2, Al_2O_3, Fe_2O_3,TiO_2, Na_2O, Lost on ignition Minores: K_2O, TiO_2	**Water Absorption** (%) - 5 to 40% **Compressive strength** (MPa) – 1 to 10

5.2 ONGOING AND FUTURE WORK

Ongoing and future works are mainly related with Chapter 4. Thus, they will be described related to the 3 papers presented in this chapter:

5.2.1 Adobe innovative formulations alkaline activated for rehabilitation of old adobe buildings.

- The water absorption capillary tests should be repeated to test the behaviour of the developed materials with water.
- Mineralogical and scanning electron microscopy analysis are being carried out in a more focused way on the clay minerals, in order to better understand the mineral transformations. New amorphous phases are being studied; these may explain better some obtained results.
- The selected formulations will be produced at larger scale and other parameters will be studied (active aging, salt efflorescence).
- The selected formulations will be tested in order to evaluate the compatibility (adhesion and other tests focused on durability should be made during longer periods, 1 to 5 years).

5.2.2 Development of geopolymers to repair traditional adobes: a way to preserve and ensure the sustainability.

- The selected formulations will be produced at larger scale and other parameters will be studied (active aging, salt efflorescence).
- The selected formulations will be tested in order to evaluate the compatibility (adhesion and others test will be made during longer periods, 1 to 5 years).

5.2.3 Development of geopolymers formulations based on low-grade kaolins as a potential construction material.

- Hinckley crystallinity indexes of kaolins should be computed in order to better understand its influence on pozzolanic activity at different temperatures.
- Specific surface area analysis (by BET) and particle size (by Sedigraph) are being studied more deeply in order to better understand the final properties of the developed geopolymers.
- The selected formulations should be produced at larger scale and other parameters will be studied (active aging, salt efflorescence).
- The selected formulations should be tested in the fill to evaluate the compatibility (adhesion and others test should be made during a longer periods, 1 to 5 years).

5.3 FULFILLMENT AND VISION

The objectives of the present PhD thesis were fulfilled. Adobes the central region of Portugal were characterized from and materials with appropriate characteristics were developed for future applications in conservation and restoration interventions in adobe architectural buildings.

In the course of the research it was possible to successfully overcome the majority of the setbacks. The development of new materials were the main purpose, starting with basic and essential characterization of materials and evolving to applied research on prototypes of new materials. In future developments of the selected materials new methods/protocols will need to be applied.

Actually, there is still much work to be done. Fragilities, including pathologies, of the developed materials must be studied and their applications in adobe buildings are crucial points that will be researched on near future.

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