

Carlos Miguel António Aldeia Lagoa

Structural iron removal from clays used in ceramic industries

Master's thesis in the scientific area of Chemical Engineering, supervised by *Professor Doctor Licinio Ferreira* and *Professor Doctor Paulo Ferreira* and submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

September 2017



UNIVERSIDADE DE COIMBRA

Carlos Miguel António Aldeia Lagoa

Structural iron removal from clays used in ceramic industries

Master's thesis submitted to the Department of Chemical Engineering, Faculty of Sciences and Technology,
University of Coimbra

Supervisors

Professor Doctor Licinio Ferreira

Professor Doctor Paulo Ferreira

Host institution

Department of Chemical Engineering, Faculty of Science and Technology of University of Coimbra

Rua Sílvio Lima, Pólo II

3030-790 Coimbra, Portugal

Coimbra

2017

I dedicate this work to my parents, without which I would not be pursuing an academic degree as they always gave me all the support I needed to succeed, even when I did not deserve it. Aside from my parents, I dedicate this work to my brother, for keeping me not too focused on my work, so I could get some rest for my brain, even when I didn't want to rest. Finally, I dedicate this to my girlfriend and soulmate, who is also an academic, for understanding the hardships involved in a work like this and always being there for me.

My advice for everyone is to make your work your number one priority, as long as it is not the only priority you have, for everything in life must have a balance.

Acknowledgments

Such work like this is never done alone and in that matter, I owe a lot to the people around me who helped me in this difficult and time-consuming task.

Firstly, I would like to thank my supervisors, Professor Doctor Paulo Ferreira and Professor Doctor Licinio Ferreira, for their invaluable help and guidance, for without them, this study would have never been conducted in a serious and believable manner.

Secondly, I would like to thank to Carolina Pinheiro and Aline Arim, for the introduction around the labs and the guidance given in almost every single task or experiment involved in this study. I would also like to thank the rest of the staff for giving me all the conditions I needed to develop this study and for letting me stay after hours so I could finish the tasks I had to complete.

Finally, I would like to thank my family and my girlfriend for all the patience they had while I had to be closed at home to complete this study. Their support has given me the strength to finish this study.

Abstract

Clays are used in many applications; however, their utility depends heavily on its composition and physical properties. Most clays harvested from dig sites, tend to have impurities that may or may not affect their uses, with iron being the impurity that most affects the properties of the clay. Iron content makes the difference between a usable clay and an unusable clay in any application. This is because of its impact in the structure and in the physical properties of any clay. The most important property in this matter is the reddish color given to the clay when fired, which may render the clay unusable for the paper industry as well as in the porcelain industry, for example. The aim of this study is to reduce the iron content in clays by acid treatment and the restoration of properties that such treatment might change, as well as understanding how the process will work when operated at a higher scale.

The clay subject to experimentation was collected from UNIPASTA, SA dig sites near Alcacer in Portugal. Its characterization was firstly done in its raw state, and later after acid and base treatment, to determine the changes in composition and physical properties. The clay was treated with hydrochloric, oxalic and citric acids, for two hours at 90°C, to find which acid was most suitable for the process, with hydrochloric being selected for the optimization phase. After acid treatment, the material was then washed thoroughly with distilled water until neutral point was achieved, to make sure no acid was present in the clay matrix.

After optimization of the acid treatment, the acid treated clays were treated with Sodium Hydroxide, Potassium Hydroxide and Aluminum Hydroxide, to find the most suitable base to restore the plastic properties of clays as well as their chemical composition. Atomic absorption spectroscopy, X-ray fluorescence spectroscopy, thermogravimetric analysis and Fourier transform infrared spectroscopy techniques were used to determine the physical and chemical properties of the raw and acid treated clays, while a mechanical strength test was used to measure the restoration of the clay's properties after base treatment. The results of the raw material indicate that the clay used in this study is comprised of mostly SiO₂, Al₂O₃, Fe₂O₃ and K₂O with traces of MgO, CaO, Na₂O, TiO₂, P₂O₅, MnO and Cr₂O₃. Iron content was reduced by half, from roughly 4% to roughly 2% in Fe₂O₃. Mechanical properties were restored and enhanced by the basic treatment, with NaOH presenting the best results in that matter.

Resumo

As argilas podem ser utilizadas em várias aplicações. Porém, a sua utilidade, depende em grande parte da sua composição e propriedades físicas. A maioria das argilas retiradas das escavações tendem a conter impurezas que podem ou não afetar a sua utilidade, sendo o ferro a impureza que mais afeta as propriedades de uma argila. A quantidade de ferro faz a diferença entre uma argila poder ou não poder ser utilizada numa aplicação específica. Isto é devido ao impacto que a presença de ferro tem nas propriedades físicas e na estrutura da argila. A propriedade mais importante que é afetada é a cor avermelhada com que o ferro fica quando cozido a altas temperaturas, o que o torna impróprio para a indústria do papel e da porcelana, por exemplo. O objetivo deste estudo será, então, a remoção do ferro da argila por tratamento ácido, a restauração das propriedades retiradas pelo tratamento e também a compreensão do processo em larga escala.

As argilas testadas foram retiradas de escavações pertencentes à UNIPASTA, SA situadas perto de Alcácer, em Portugal. A sua caracterização foi feita primeiramente na matéria-prima e mais tarde na argila tratada por ácido e base, de forma a determinar as mudanças de composição química e propriedades físicas. As argilas foram tratadas com ácido hidrocloreto, ácido oxálico e ácido cítrico, durante duas horas a 90°C, de forma a determinar qual o melhor ácido a ser utilizado no processo, tendo sido escolhido o ácido hidrocloreto para a fase de otimização. Após tratamento ácido, a argila foi lavada com água destilada até pH neutro, de forma a certificar que não existe ácido na matriz da argila.

Após otimização do tratamento ácido, as argilas tratadas com ácido foram então tratadas com hidróxido de sódio, alumínio e potássio, de forma a encontrar a melhor base para a restauração das propriedades plásticas da argila assim como a sua composição química. Espectrometria de absorção atômica, espectrometria de fluorescência de raios-X, análise termogravimétrica e espectrometria de Fourier foram utilizadas de forma a conhecer as características da matéria-prima, assim como a sua versão tratada e testes mecânicos foram feitos de forma a conhecer as propriedades plásticas das argilas tratadas com tratamento básico. Os resultados à matéria-prima indicam que a argila utilizada neste estudo contém maioritariamente SiO_2 , Al_2O_3 , Fe_2O_3 e K_2O com vestígios de MgO , CaO , Na_2O , TiO_2 , P_2O_5 , MnO e Cr_2O_3 . O conteúdo de ferro nas argilas foi reduzido por metade, de perto de 4% para perto de 2% em Fe_2O_3 . As propriedades mecânicas foram restauradas e melhoradas pelo tratamento básico, sendo o NaOH a melhor base para este efeito.

Contents

List of Figures	x
List of Tables.....	xi
Abbreviations and Acronyms	xii
1 Introduction.....	1
1.1 Motivation.....	1
1.2 Objectives.....	2
1.3 Structure of the thesis.....	3
2 Background.....	4
2.1 Clay and clay minerals.....	4
2.2 Application of clays in the ceramic industries.....	9
2.3 Chemical treatment of clays	11
3 Literature review	12
4 Materials and methods	16
4.1 Apparatus and reagents	16
4.2 Experimental procedures.....	16
4.2.1 Sampling method	16
4.2.2 Sample preparation.....	17
4.2.3 Acid treatment	17
4.2.4 Alkaline washing of acid treated clays	18
4.3 Analytical techniques	18
4.3.1 Flame absorption spectroscopy	19
4.3.2 X-ray Fluorescence Spectroscopy.....	19
4.3.3 Thermogravimetric Analysis.....	20
4.3.4 Fourier transform infrared spectroscopy.....	20
4.3.5 Plasticity analysis.....	21
4.4 Data Analysis	22
5. Results and discussion.....	23
5.1 Characterization of raw clays	23
5.1.1 Iron content analysis.....	23
5.1.2 Chemical composition analysis	24
5.1.3 Thermogravimetric Analysis.....	24
5.1.4 FTIR analysis	25
5.2 Acid treatment results.....	26
5.2 Alkaline washing results	30
5.3 Scale-up Tests.....	31

5.4 Preliminary Economical Evaluation.....	31
5.5 Preliminary Process Design	33
6 Conclusions and Recommendations	35
References.....	37
Appendices.....	41

List of Figures

Figure 1.1 - Structure of the thesis.

Figure 2.1 - Weathering processes for the origin of clay minerals.

Figure 2.2 - Tetrahedral and octahedral sheets in clay structure.

Figure 2.3 - Types of clay and its structure.

Figure 4.1 - Clay samples considered for this study.

Figure 4.2 - Jar mill used for the preparation of the powdered samples.

Figure 4.3 - Schematic representation of the acid treatment.

Figure 4.4 - Schematic representation of the washing process.

Figure 4.5 - Equipment used in the preparation of the pellets for XRF analysis.

Figure 4.6 - Bruker s8 tiger used for the XRF technique.

Figure 4.7 - Equipment used to prepare the pellets for mechanical resistance analysis.

Figure 5.1 - Thermogravimetric results for all five clays considered.

Figure 5.2 - FTIR analysis for clay samples a) A1, b) A2, c) A3, d) A4 and e) A5.

Figure 5.3 - Iron content after treatment for each acid tested.

Figure 5.4 - Pareto chart for all variables studied.

Figure 5.5 - 3D model surface for the process in study.

Figure 5.6 - Observed and expected values for the model in study.

Figure 5.7 - Plasticity results for the basic treatment tests.

Figure 5.8 - Simplified process diagram for economical evaluation.

Figure 5.9 - First process design.

List of Tables

Table 2.1 - The ceramic industry in Portugal.

Table 3.1 - Treatments, conditions, materials and results for the literature overview.

Table 4.1 - Experimental conditions based on a Box-Behnken factorial design.

Table 5.1 - Results of iron content for raw clays.

Table 5.2 - Results of the chemical analysis of raw clays in mass percentage.

Table 5.3 - Results of the chemical analysis of clay after acid treatment.

Table 5.4 - Results of the acid treatment of clay according to the experimental design.

Abbreviations and Acronyms

LNEG – Laboratório Nacional de Energia e Geologia

CEC – Cation Exchange Capacity

XRF – X-ray Fluorescence

FTIR – Fourier Transform Infrared

TGA – Thermogravimetric Analysis

AAS – Atomic Absorption Spectroscopy

CA – Citric Acid

HA – Hydrochloric Acid

OA – Oxalic Acid

S/L – Solid to liquid ratio

1 Introduction

1.1 Motivation

The motivation behind this work comes from the need to innovate in a way that a clay would be considered usable in the production of a great variety of ceramic products.

The use of clays in many industrial applications (production of paper, ceramics, plastics, paints, etc.) depends heavily on its composition and physical properties. Most clays harvested from dig sites, tend to have impurities that may or may not affect their uses, with iron being the impurity that most affects the properties of the clay. Iron content makes the difference between a usable clay and an unusable clay in any application. Since iron is one of the more abundant elements of the Earth's crust, around 6% in mass, its presence in clays comes without surprise (Stucki et al., 2005). The presence of iron in these clays is a very important factor when considering a clay for ceramic uses, as it gives the clay a reddish colour, unfit for most of its applications. Another disadvantage of having iron in the clay structure is its ability to cause swelling of the clay. Swelling of the clay may cause disruptions when used as a construction material for buildings, highways, etc., as it may cause a pressure build-up. It is known that the extent of this swelling may be altered by changing the oxidation state of iron in the clays from +3 to +2 (Stucki et al., 1984).

Innovation is very important in industry in general, but even more for ceramic industries which have been around for centuries, and everything around it seems solved. However, in this industry, some questions remain unanswered like how to use or treat clays with high structural iron. For a clay to be considered fit for production of first grade ceramics, their iron content should be below 1%, as it gives unwanted properties to the clay like high shrinkage, short vitrification range and non-plastic properties above that concentration (Grim, 1979). To achieve that standard, other researchers have tried a plethora of approaches that include, but are not limited to, froth floatation, gravity and magnetic separation, reductive roasting, size separation by hydrocyclones, selective flocculation and acid treatment (acid leaching) (Ajayi & Adefila, 2012). These treatment possibilities were studied mostly in a laboratorial scale, needing some kind of scale up studies so they can be used at an industrial scale. This work comes from the need to be competitive in this industry, as mentioned before. In order to become competitive, one must have versatile raw materials, which does not happen due to the iron content being a key factor in defining the uses of almost any type of clay. Knowing how to treat and how the treatment impacts the clay itself, is something that may be the difference between a struggling and a thriving ceramics enterprise.

1.2 Objectives

The general objective of this work is then to find the appropriate treatment to minimize iron in clays, in a way they can be used to their maximum potential. Which means, reducing their structural iron content to levels below 1%, or at least remove as much iron as possible so the clay can have some flexibility in its uses. In this context, the specific objectives of this study are:

- To determine physical and chemical parameters of raw clays:
- To find optimal conditions for iron removal based on a factorial design;
- To revert the properties of acid treated clay by washing with a selected alkaline solution;
- To perform preliminary scale-up and preliminary economic feasibility studies.

1.3 Structure of the thesis

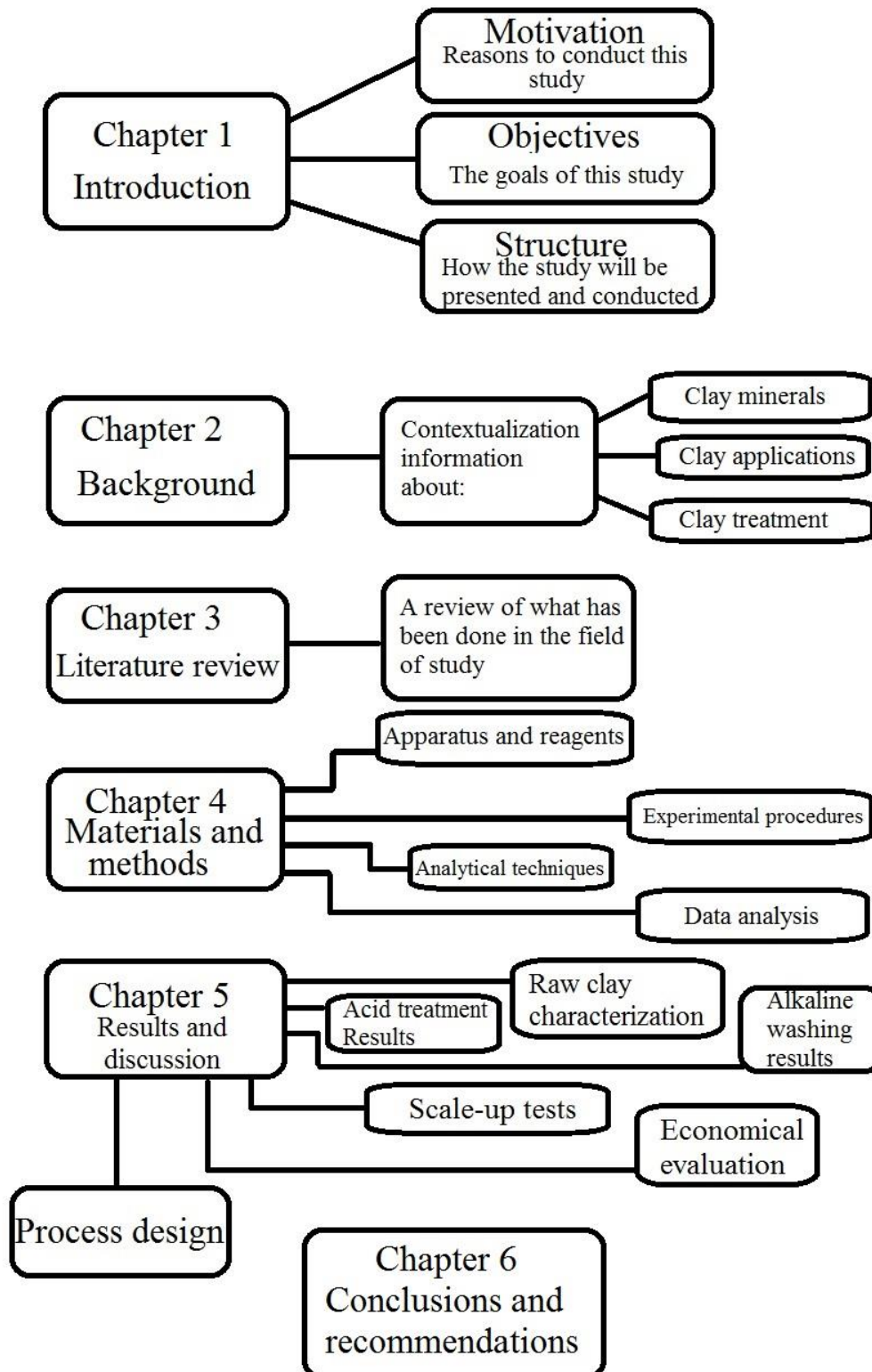


Figure 1.1 – Structure of the thesis.

2 Background

2.1 Clay and clay minerals

Although the uses of clay can be traced to ancient history, the scientific study of clays is a relatively new field of study, dating back to the mid-1930's after the emergence and general acceptance of the definition of the clay mineral concept, which will be referred to later in this study.

As there is no uniform nomenclature for clay and clay material, clays can be regarded as many different things, depending on the use it is being given. For ceramists, it is a chemically heterogeneous and complex structure of colloidal particles, including clay minerals mixed with organic matter and finely divided quartz (Stucki, 2012). Being ceramists the greatest consumers of clay worldwide, it is important to understand the structure and behavior of clays depending on their composition, which can be associated with types of clays with different structures, properties and uses.

According to geologists, the Earth was once a molten mass of material. As the Earth began to cool, those materials settled into distinct layers. The outmost layer is comprised of igneous rock, which includes mainly silica and alumina (Nigrosh, 1986). Clay deposits derive from such layer, in a process called weathering. Weathering can be called both a mechanical and a chemical process. This process occurs at or near the Earth's surface, and comes with a decrease in the particle size of the material, as the mechanical component, and a recombination of the chemical materials as the chemical phase of weathering. Clay minerals are often formed by the hydrothermal weathering of feldspar (Wachira David Maina, 2014). This is due to the hydrogen ion from carbonic acid displacing the cations from feldspar, as well as other chemical processes, as seen in Figure 2.1:

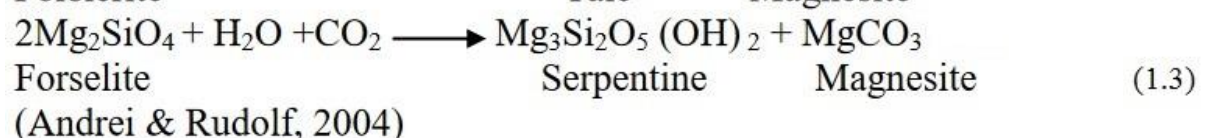
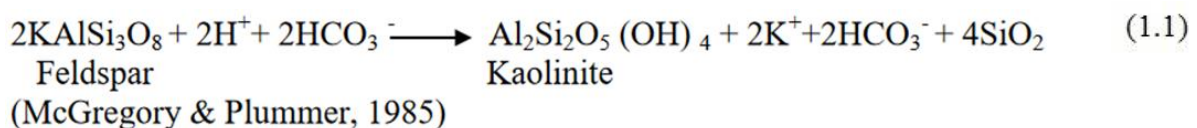


Figure 2.1 – Weathering processes for the origin of clay minerals.

Weathering of clays usually happens in temperatures from -5°C to 25°C, leading to the transformation of original minerals to clay minerals and soluble elements (Meunier, 2005).

Clays are usually, in its majority, comprised of layered silicates normally known as phyllosilicates. Although they commonly are the major constituent, it may vary its composition depending on the parent rock from which they were once formed. Clay minerals are hydrous silicates made of aluminum and or magnesium with significant amounts of other cations in their crystalline structure like iron, nickel and chromium (Rodrigues, 2003). One of the most important aspects of those clay minerals is the ability to undergo extensive isomorphic substitution of the cations not only on their surfaces but also in their structures. Isomorphic substitution usually occurs between similar sized cations like Al^{3+} and Si^{4+} , among others (Wachira David Maina, 2014). Many clays contain water as an integral part of its structure, which gives them some of their properties like its plasticity, but when in the presence of high temperatures, it loses its water, becoming a refractory material. The latter issue is really important for the ceramic industry as clays are subjected to high temperatures to become more resistant materials for a large spectrum of uses which ranges from construction to decorative purposes.

The presence of high amounts of silica in the clay (25-50%) is seen as a way to counter the clay's ability to shrink on drying and firing of ceramic products and it is a reason to use raw materials, as raw clays mostly have around 50% silica in their composition. The presence of vegetation near the clay's digsite also impacts the chemical composition of clay minerals, as it is the case of magnesium based chlorites such as amesite and chamosite (Velde and Barre, 2010).

Before going into any detail about the iron removal processes, one must understand the behavior and structure of clay minerals. Clay minerals are composed by layered sheets of silicates. Those layers can be made of tetrahedral and octahedral units. Those units are made of AlO_6 , octahedra, and SiO_4 , tetrahedra (Atkins et al., 2006). Those units may contain an array of other ions, due to the capacity to undergo extensive isomorphic substitution. Since the tetrahedral unit has a net negative on its surface, (SiO_4^-) cations will be present in the inter layer structure in order to counter balance that negative charge. Clay minerals form in the presence of water and have variable amounts of iron, magnesium, alkali metals, alkaline earth and other cations found on or near some planetary surfaces. Clays are usually comprised of several of these clay minerals as well as traces of metal oxides and organic matter. Some properties of the clays are due to the number of combinations of clay minerals in the structure (Bailey, 2004). Most common ions in the structure itself are Si^{4+} , Al^{3+} and Fe^{3+} while in the interlayer structure is usual to find Na^+ and K^+ ions (Figure 2.2).

Because the process of weathering varies from place to place and since the clay material has the ability to undergo extensive isomorphic substitution, as seen before, clay samples will

contain a lot of variance. That variance is due to subtraction and addition of elements to their structure. Just by letting time pass, the clay will constantly be morphing as it adds and subtracts different cations in the structure, so the clay that is today in certain place, might be completely different tomorrow, if the environmental conditions around it are changed (Konta, 1992). As an example, kaolinite is more likely to be formed if rainfall is high while if rainfall is at lower values, smectite is more likely to be formed. This fact makes it possible to make clays useful in palaeoclimatic reconstructions, interpretation of the tectonic history of a region, among other uses.

Before going into the overview of the structure of clays, it is important to know and understand the types of clay minerals in which iron is present. Primary iron minerals such as goethite and hematite are the most common source of iron in clay minerals (Wachira David Maina, 2014). Iron can also be found in the form of carbonates, sulphides, sulphates, phyllosilicates, agricultural soil, hydromorphic and lateritic soils (Stucki, 2006). It can also be found in the forms of Olivine, Amesite and Feldspars, among others (Anthoni, 2000).

Clay minerals tend to have high amounts of water in their structures, with that water taking the form of hydroxyls in the crystal structures or interlamellar water. The interaction between water and the clay itself is responsible for cation-exchange reactions, adsorption, catalytic properties, shrink and swell phenomena and plasticity (Schoonheydt and Johnson, 2006). The chemical mechanisms that contribute to clay mineral-water interactions include H-bonding, charge-dipole attraction, ligand-ligand repulsion and Van de Waals interactions. Apart from that, contributions can also occur through hydrolysis and redox interactions depending on the nature of the exchangeable cation (Quirk, 2003; Laird, 2006). The cation-exchange capacity refers to the quantity of exchangeable cations in a clay mineral. That capacity is both dependent and independent of the pH value in which the reactions occur, with the independent part being due to isomorphic substitutions in the octahedral and tetrahedral layers and the dependent part due to broken bonds at the crystal edges (Vaughan and Patrick, 1995).

One major characteristic that makes this study worth it is the ability of clay minerals to be dissolved by mineral acids, such as hydrochloric acid (Eze et al., 2012). Organic acids can also be used but they can only be adsorbed by the clay minerals (Calderon et al., 2005). From that, it is concluded that both mineral and organic acids could be employed, but mineral acids would present greater results.

The two types of sheets can be seen in Figure 2.2. Figure 2.2(a) shows a tetrahedral sheet structure made by oxygen sharing of two tetrahedral units, while Figure 2.2(b) shows the octahedral structure, which occurs by sharing of an edge between two octahedral units.

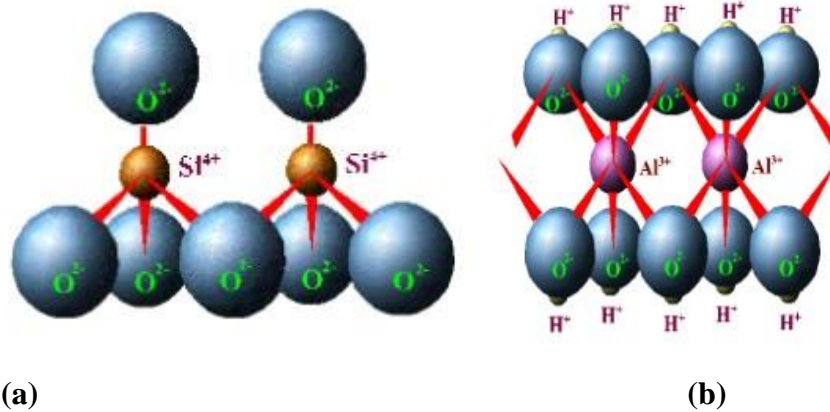


Figure 2.2 - Tetrahedral and octahedral sheets in clay structure (Wachira David Maina, 2014).

After knowing the types of structures that may be formed, it is necessary to know the naming of the various types of structure in clays. The nomenclature committee of Association Internationale Pour l'Etude des Argiles (AIPEA) in association with the International Mineral Association (IMA), has made recommendations concerning the naming and classification of clay phyllosilicates. The groups that are better documented are shown in Figure 2.3, which shows the names of some minerals based upon the number of layers of each unit as well as the basal heights and relative expansivity of the minerals.

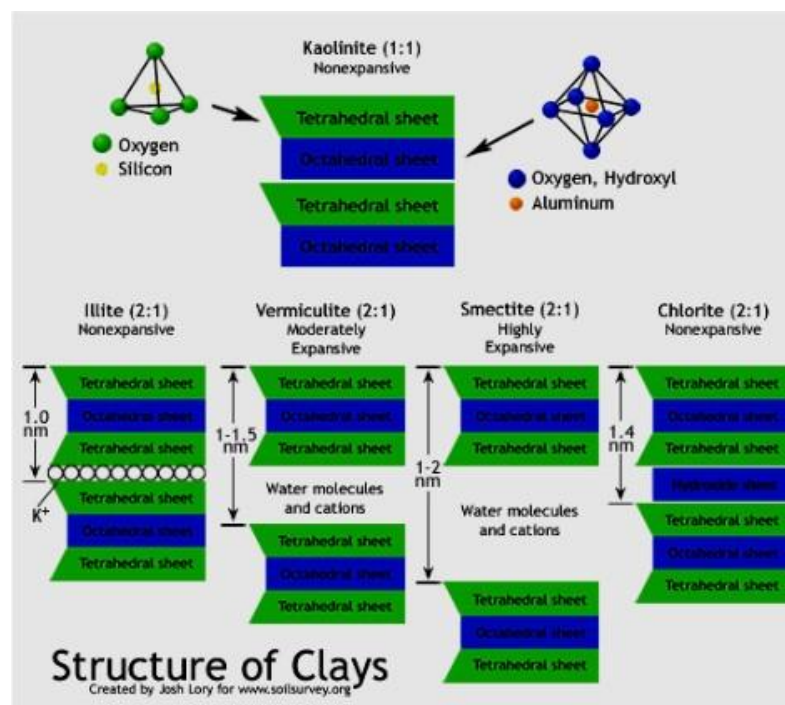


Figure 2.3 - Types of clay and its structure

(<https://pt.slideshare.net/LeahBrueggeman/phyllsilicate-clays>).

Kaolinite groups are 1:1 clay minerals which have the following general formula; $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$. This type of clay mineral is usually found in warm and moist climates. Its structure is composed of alternate silicate and gibbsite sheets (Wachira David Maina, 2014). These sheets are not tightly bonded together with only weak bonding between them. (Sarwenaj, 2008). Smectites are 2:1 clay minerals of general formula consisting of: $(\text{Ca}, \text{Na}, \text{H})(\text{Al}, \text{Mg}, \text{Fe}, \text{Zn})(\text{Si}, \text{Al})_4\text{O}_{10} \cdot x\text{H}_2\text{O}$. This clay mineral is responsible for both shrinking and swelling properties of soils and have adhesive properties that help against natural erosion. It is also responsible for landslides that occur due to the amount of water that its structure can absorb, as it reduces the strength of the soil (Sarwenaj, 2008). Their negative charge also influences their reactivity to environmental materials, making them susceptible to absorbing pesticides or herbicides. Illites/micas are classified as 2:1 layered silicates and usually possess an array of different cations in their structure to balance lattice charges (Wachira David Maina, 2014). These clay minerals show the following general formula; $\text{KHA}l_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, with potassium being the most extensive and the most important cation in this structure. These type of clay minerals are mostly found in argillaceous rocks and formed by the weathering process of feldspar. Formation of this type of clay mineral is known to be favoured by alkaline conditions and high concentrations of Al and K (Wachira David Maina, 2014). Finally, the chlorite group is known to be comprised of 2:1 silicates with general formula $\text{X}_{4-6}\text{YO}_{10}(\text{OH}, \text{O})_8$, where X can be Al, Fe, Li, Mg, Mn, Ni and Zn while Y can be Al, Si, B or Fe (Gaboriaud et al., 2005).

Iron can be found in clays in two forms: as hydrated iron oxides or incorporated into crystal structure of clay minerals. In the first form, it is usually found adsorbed to the surface of clay particles where it acts as a compensating cation pillar between silicate layers (Stucki, 2006). In this form, it is responsible for the ion exchange capacity. In both forms, it is responsible for the reddish color given to the clay when fired. The adsorbed version can be removed without chemical attack, but the structural iron is much more difficult to remove, which is why suitable leaching processes should be studied in detail. This chemical attack also damages the clay's structure, which in turn will affect its plasticity and therefore, its mechanical properties which are of utmost importance when the clay is to be used in structural engineering (Wachira David Maina, 2014).

2.2 Application of clays in the ceramic industries

The ceramic industry makes up for 70% of all clays “marketed in the crude or beneficiated form and those marketed only as finished products” (Thomas W. Smoot, 1964). Clays are used in the ceramic industry as one of three types of material: structural clay products, whitewares and refractories.

The structural clay products can be called heavy clay products, as they are the products used for building purposes which include but are not limited to building brick, sewer pipe, drain tile, conduits, structural tile, lightweight aggregate and light-weight clay block. Most of these products are shaped by an extrusion method, while others can be pressed, hand-molded or marketed unshaped to be included in other products. The most important characteristics of the clays for this kind of application are the plasticity, dryness without cracking or warping and low and wide vitrification range. As the first two requirements are easily understandable, the low and wide vitrification range ensures that there will be close to no complications to the firing part. Apart from that, the clay should have low carbonate content, for two main reasons. The first is due to the fluxing action of carbonates that tend to shorten the firing range and/or cause spots on the fired clay. The second reason is due to the formation of CaO and MgO resulting from the firing of common carbonate-bearing clays that will hydrate easily and disrupt the firing of the product. Finally, if the clay has a spread in particle size, it tends to widen the vitrification range and promote a stronger texture than those clays with a narrow range of particle sizes. The presence of other non-clay minerals will too help achieve a stabler material, as they are usually three-dimensional shapes as opposed to the two-dimensional usually found in clay minerals and the mixture between 2D and 3D will result in a more stable material (Thomas W. Smoot; 1963).

The whitewares include all kinds of porcelain, dish ware, sanitary ware, electrical porcelain, floor, wall, among others. The processes to manufacture such wares include, but are not limited to, slip casting, jiggering, extruding, power pressing and hand molding (Thomas W. Smoot; 1963). Although the raw material requirements vary a lot for each application, it is the type of materials in which the characteristics of the raw materials matter the most. Most of the material used are composed of kaolin, ball clay and ground non-clay materials like feldspar, quartz, talc among others. Beneficiated or treated clays are being used more and more in this industry, for better characteristics and therefore, a better final product.

The refractory type materials are materials which keep their mechanical properties even at high temperatures, usually the type of materials used as interior lining of industrial ovens, furnaces and even reactors. The major refractories that are based on clay are fireclay brick, high alumina brick, ladle brick and acid proof brick. Although, inside each category, there are several subcategories that describe nuances of each brick type. Most of these products are made from

clays rich in kaolinite and from high-alumina clays, while having to contain low amounts of iron, titanium or alkaline earths as they give unwanted properties for this particular use. As there are a lot of different types of brick, an array of possible materials can be found in these types of clay. The general requirements being that the major clay mineral is kaolinite in association with aluminum hydrates and quartz (Thomas W. Smoot; 1963).

In Portugal, there were a total of 605 ceramic companies (Table 2.1), but only 401 active companies, in 2010, as shown by the report on the ceramic industry in Portugal “Innovation and ecodesign in ceramic industry; situation analysis in Portugal” made by LNEG. That report also states that the capacity of development and quality of ceramic products made in Portugal has been increasing over the years. Despite that, the Portuguese ceramic industry faces some challenges like competition from the Asian market, whose prices are usually lower, the increase in restrictive environmental legislation and the lack of recognition from the Portuguese brands abroad. This report also shows that there is a lack of training and know-how on the ecodesign part, and this is why the environmental legislation is considered to impair the ceramics industry.

Table 2.1 – The ceramic industry in Portugal.

	Bricks and roof tiles	Wall and floor tiles	Table and ornamental ware	Sanitary ware	Special ceramics	Total
Total number of companies	146	60	319	19	61	605
Number of active companies	104	40	201	16	40	401

Apart from the ceramic industry, clays are also used as heterogeneous catalysts. After acid treatment and after cation exchange, those clays can be considered as solid acids that act as heterogeneous catalysts for a broad spectrum of uses in the chemical industry. These catalysts have some advantages associated with them like low cost, ease of separation, reduced waste generations and environmental friendliness (Igbokwe et al., 2011). For the clays to be used as catalysts, they cannot have iron or other metal ions, as they can poison the catalysts (Wachira David Maina, 2014). This makes the acid treatment of clays for iron removal an even more important issue since it affects not only its uses in ceramics, but also in other industries, lowering the worth of clays with iron even more. A newer and not fully developed use for clays can be in nuclear waste management, as they possess low permeability, high plasticity and good adsorption properties (Madsen, 1998; Landais, 2006)

2.3 Chemical treatment of clays

The chemical treatment of clays has always been a studied topic in the ceramic industry in order to have better and targeted properties for each of its uses. Some of those treatments include but are not limited to froth floatation, gravity and magnetic separation, reductive roasting, selective flocculation and acid treatment or leaching (Wachira David Maina, 2014).

Iron can be found in clay minerals as a part of the crystal structure or as a hydrated oxide adsorbed in the clays surface. Structural iron, if in low amounts, is usually acceptable. When in colloidal form, iron can be removed by physical methods like magnetic separation while structural iron must be removed with chemical procedures.

As reported by the literature, acid treatment, besides leaching cations from octahedral and tetrahedral sheets, dissolves impurities such as calcite and replaces the exchangeable cations with hydrogen ions (Wachira David Maina, 2014). Apart from that, it also increases the surface area of the material and pore size. There were some tests done with chlorination in extractive metallurgy to remove iron and titanium from kaolin, with excellent results (Ruiz et al., 2006). Most of such techniques are good for removing iron from the clays, but it comes with a cost of having their structure changed and degraded, some to a point where the clay becomes unusable. That is due to the loss of plasticity of the clay, which is a very important factor when evaluating a clay's application and worth. Plasticity is the property that makes a body change its shape without rupture when external force is applied and the ability to regain its' original shape when that external force is removed (Keller, 1979). Since it is believed that plasticity is related to most of the properties that are of interest to engineers (Dumbleton and West, 1966), the need to restore the properties of the clays becomes vital if treated clays are to be employed in an industrial context. Such techniques can be employed after the treatment like basic treatment to restore the structure or included in the treatment to reduce the damage done to the structure like softer process variables. The most experimented chemical treatment is acid treatment or leaching because of its higher impurity removal. The higher removal implies also a higher impact on its structure and therefore, on the final properties of the treated clay. In order to restore those properties, another treatment step will be necessary. The need for two separate reactions and the need to purify and recycle process reagents means that this process will need to be thoroughly studied in order to determine all steps' optimal conditions and the best purifying techniques for the process before it can be successfully industrialized.

3 Literature review

Over the last decades, some efforts have been done on the development of suitable treatment methods to remove iron impurities from raw clays. Chemical treatment of clays has been investigated by many researchers.

O. P. Mehra et al. (1957) studied the removal of iron with a dithionite-citrate system buffered with sodium bicarbonate, concluding that the structural iron is immune to this treatment. That work only examined the iron removal from the clay minerals themselves, and not from the clay as a whole. Some technical difficulties were also found in this work that would make industrial use near impossible. Wachira Maina et al. (2014) conducted a study to reduce the iron content of clays by acid treatment as well, including treatments to reverse the damage done by the acid treatment. The acid treatment was conducted using different acids ranging from 2 to 10 M for 2h and bases at 0.5M for 24h in order to discover the best reagents and optimize the process itself. This last study seems to be the most promising and will serve as a starting point for this work. Joseph W. Stucki et al. (1984) studied the effects of reducing the structural iron and dissolution with citrate bicarbonate. Although this study was aimed at cation exchange capacity alterations, they also tested the impact of the method on the dissolution of iron.

Lindiane Bieseki et al., (2013) tested the removal of iron from montmorillonite rich clays using a factorial design method. For that purpose, they used hydrochloric and sulphuric acid, having observed that HCl was the best to maintain the clay's structure. They also found the optimal conditions for the treatment method tested. R A Hernández Hernández et al. (2002) studied the effects of leaching kaolin to remove iron using oxalic acid. The test was made on kaolins because those were the clay minerals more resistant to acid attack. These authors determined the optimal conditions for the acid application and achieved very positive results with near 80% iron removal in that context. B. D. Mitchell et al. (1953) tested methods for free iron oxides removal from clays, using acid ammonium oxalate and aluminum-ammonium tartrate methods. They found some difficulties associated with determining the iron by sodium salicylate. Thus, they tried to use sodium hydrosulphite to find a fully inorganic procedure. The optimal conditions for those treatments were found and it was concluded that the treatment would be good in all types of clay materials although the extraction percentages were not the best.

A.K. Panda et al. (2010), studied the effects of sulphuric acid treatment on the characteristics of kaolin clay. The acid was used in a wide range of concentrations (1-10M) and was followed by calcination at 500°C. Apart from the impurity removal, the clay was also tested

for Si/Al ratio, surface area and pore volume and it was concluded that the treatment used increased all the values in the direction needed for their scope, which was using the clay as a catalyst.

Beena Tyagi et al. (2006) studied the structural modifications on acid activated montmorillonite clays using FTIR techniques. For that study, different concentrations of sulphuric acid were tested. Results show that at low concentrations, octahedral sheets are the ones more affected by the treatment while tetrahedral sheets are only affected at higher concentration values. It was also verified that magnesium ions were more likely to be leached than iron and aluminum ions, for low concentrations. The partial substitution of octahedral aluminum, magnesium and iron was clearly identified. J. Madejová et al. (1998) studied the structural modifications during acid treatment resorting to FTIR techniques as well, but on dioctahedral smectites and hectorite. Hydrochloric acid was used for that study, under different conditions. They found that hectorite is much susceptible to acid attack than the smectites. They also found that the mechanism for smectite dissolution in hydrochloric acid is independent of layer composition, but is dependent on the treatment's temperature and acid concentration. It was concluded that the rate of smectite dissolution increased with the increase of octahedral magnesium or iron.

Other studies tried to collect data for the reaction in order to understand it better, like K. Bahranowski et al. (1992) who studied the removal of non-structural iron from kaolinite-group minerals, using sulphuric acid. They studied the impact of the treatments on the composition of the clay minerals over time, in order to get some information about the kinetics involved in this kind of treatments. J.A. González et al. (2006) studied the bleaching of kaolins by chlorination of iron and titanium. Their goal was to establish reaction mechanisms, precautions and optimal conditions. The studies were carried out using chlorine gas to calcinate pellets in order to remove iron and titanium by volatilization of the respective chlorides. Although the studies had some success on the removal of the targeted compounds, removing iron which could not be removed by other techniques, the operating conditions are extreme and hard to achieve and maintain without financial losses. Thomas B. Hofstetter et al. (2002) studied the different types of iron in the clay minerals' structure and their reactivity as well as accessibility. It was discovered that Fe(II) bound by ion exchange did not show much reactivity when compared to the other types of iron in clays but it is also only a small fraction of the iron.

There are lots of different kinds of clays and they behave differently based on their properties. B. B. M. Dewu et al. (2016) studied iron removal from bentonitic clays and its effect on rheology concluding that hydrochloric acid was the reagent with lower impact on the clay's structure with acceptable results on iron removal. This study was not on the ceramic's scope,

but can be useful to understand and implement future treatments adapted to the ceramic industry.

Other authors investigated biological approaches to remove impurities from raw clays. Asfaw Zegeye et al. (2013) applied a biological procedure to remove iron from kaolin clays with iron-respiring bacteria since kaolin is one of the more resistant type of clay to acid treatments. That treatment affected the properties of the clays but not as much as the acid treatment. Chris Bonney et al. (1993) studied the mechanisms of dissolution and precipitation of iron during iron removal treatments. Those treatments included acidic and alkaline conditions, as well as biohydrometallurgical techniques for the removal of iron from solutions. These tests were meant to result in a process that could be commercialized. Vibeke Ernstsén et al. (1996) tried reducing the iron in minerals in order to increase its reduction capacity using a combination of *Pseudomonas* strains for 160d. Although this study is not related to ceramics, it shows that the structural iron can be changed in terms of oxidation state and if one type of iron is less impacting to have in the clay's structure, it can be achieved with proper treatment.

Clays are used in many more fields than the ceramic industry and A. R. Nascimento et al. (2015) studied the effects of acid treating montmorillonite clays to be used as catalysts for the esterification reactions in the production of biodiesel. They used sulphuric acid at different concentrations, then proceeded to characterize and use it in the esterification process. Optimal conditions were found, having improved the esterification process. These studies and their results are summarized in Table 3.1.

Table 3.1 – Treatments, conditions, materials and results obtained from the literature overview.

Author	Material type	Treatment	Conditions	Results
O. P Mehra et al, 1957	Hematite, Goethite and Nontronite clays.	dithionite-citrate system buffered with sodium bicarbonate.	80-90°C 20% Na ₂ S.9H ₂ O Oxalic acid until pH = 7 t = 15 to 60 min.	Highly effective at removing free iron oxides. Low removal of structural iron and low damage on structure.
Wachira Maina et al, 2014	Montmorillonite Clays	Acid treatment and basic treatment with different acids and bases.	100°C 2-10 M acids T= 2h 0.5M bases T= 24h	High iron removal and full plasticity restoration.
Joseph W. Stucki et al 1984	Montmorillonite and Nontronite clays	Citrate bicarbonate treatment.	70°C t = 30 min	Iron oxidation state independent from CEC. Moderate iron removal.
Lindiane Bieseki et al, 2013	Montmorillonite clays	Various acid treatments	HCl, HNO ₃ and H ₂ SO ₄ 4M 25-75°C t = 6h	Nitric acid inefficient for iron removal. Sulfuric and hydrochloric acid very efficient for iron removal.

Table 3.1 (continuation) - Treatments, conditions, materials and results obtained from the literature overview.

R Hernández Hernández et al, 2002	A Kaolinitic clays.	Oxalic acid leaching.	0.01 – 0.5 M t = 5-120 min 100°C	Very high iron removal and whiteness index.
B. D. Mitchell et al, 1953	Illitic, Vermiculitic and montmorillonoidal clays.	Acid ammonium oxalate, aluminum-ammonium tartrate and sodium hydrosulphite treatments.	40-45°C t = 15min	Optimal conditions found.
K. Bahranowski et al, 1992	Kaolinite, dickite halloysite	Free iron removal by acid leaching	95°C 0.5-14 h 15% H ₂ SO ₄	Good iron removal both structural and free iron oxides.
J.A. González et al, 2006	Kaolin, magnetite, hematite and limonite.	Chlorination.	700-950°C 2h	Good decrease in iron oxide content, also removed titanium.
B. B. M. Dewu et al, 2016	Bentonite.	Oxalic and hydrochloric acid treatment	70°C 1-1.8M acids 6h	Good iron removal, average 30%.
Asfaw Zegeye et al, 2013	Kaolin.	Microbial treatment	Bacteria <i>S. putrefaciens</i> 5 days 30°C	Increased whiteness index and around 50% iron removal
Chris Bonney et al, 1993	Bentonite, illite, kaolinite.	Biohydrometallurgical techniques.	Oxalic and citric acids 29-42 g/l 4h 70-100°C	30-40% iron removal
Vibeke Ernstsén et al. (1996)	Clayey till from Denmark.	Microbial treatment	<i>Pseudomonas</i> strains combination	Fe(III) to Fe(II) transformation at 24%.
Thomas B. Hofstetter et al. (2002)	Nontronite and Hectorite	Nitroaromatic Compounds	Different NACs used to probe different kinds of Fe.	Most iron in clay can be accessed and reacted with except for iron bound by ion exchange.
A. R. Nascimento et al. (2015)	Montmorillonite	Sulphuric acid treatment	Acid concentration 0.2-0.8mol L ⁻¹	Improved conversion of oleic acid (65%) in esterification processes.
A.K. Panda et al. (2010)	Kaolin	Sulphuric acid treatment	1-10M acid for 2h followed by 500°C calcination for 2h	Impurity removal, increased Si/Al ratio, increased pore size and surface area.
Beena Tyagi et al. (2006)	Montmorillonite	Sulphuric acid treatment	N.A.	Octahedral sheets affected at low concentrations. Tetrahedral sheets at high concentrations.
J. Madejová et al. (1998)	Smectite and hectorite	Hydrochloric acid treatment	N.A.	Smectite less susceptible to acid attack. Relations between parameters achieved.

4 Materials and methods

4.1 Apparatus and reagents

All the apparatus used were made of borosilicate glass or ceramic due to the acidic nature of most of the experiments and were thoroughly cleaned before and after each procedure and analysis. The cleaning phase for most apparatus included rinsing with dilute nitric acid followed by deionized water. Analytical grade reagents were used in all experiments or analysis and all the weighing was done using an analytical balance.

4.2 Experimental procedures

4.2.1 Sampling method

The samples collected for this study were harvested from excavation sites which belong to UNIPASTA SA, a ceramics enterprise based in Pombal, Portugal. The samples were collected from a depth of approximately 6 to 8 meters from 3 random locations in the excavation site. From the five clays tested, A1 was the chosen clay to work with because of its higher iron content and its blackish colour, two very important factors to be changed by this treatment. A1 is a clay gathered from Alcácer, relatively near Lisbon. A2, A4 and A5 are light orange colored clays gathered from Redinha, Anadia and Lisbon, respectively. A3 is bentonite from Mozambique and A4 is a kaolin. In Figure 4.1 are shown pictures of the 5 raw clay samples that are referred above.



Figure 4.1 – Clay samples considered for this study.

4.2.2 Sample preparation

At first, the raw clay was milled with water and sodium triphosphate to prevent agglomeration of the clay. After being water milled in a jar mill for 10 minutes, the clay was dried overnight in an oven at 105°C. After allowing the clay to dry, it was crushed with a hammer and dry milled for 6 minutes being finally sieved in a 1mm sieve.



Figure 4.2 – Jar mill used for the preparation of the powdered samples.

4.2.3 Acid treatment

Before performing the studies devoted to the clay treatment with a suitable acid, a screening step was carried out with 3 different acids (hydrochloric acid, citric acid and oxalic acid) to choose the most effective for iron removal. The screening tests were performed with the acids at 4 M and at 0.2 solid to liquid ratio.

For the acid treatment (Figure 4.3), samples were prepared as described in the sample preparation section. 20 g of a certain sample was weighed into a borosilicate glass conical flask, along with 2 M HCl. The resulting slurry was then heated at 90°C and stirred in a fume chamber, with the help of an electrically heated hot plate for 2 hours, covered to avoid mass losses. The slurry was then filtered using Filter-Lab filter paper no. 1250 in order to separate the acid from the clay matrix. Such filtration was done with the help of a vacuum pump, with the liquid being stored for iron concentration analysis. After filtration, the clay was washed thoroughly with distilled water until neutral point was obtained (Figure 4.4). The clay residue was dried in an oven at approximately 105°C overnight and then crushed and stored for chemical analysis with XRF techniques, with the calibration curves shown in appendix III. This treatment was repeated

with various concentrations and solid to liquid ratios. The concentrations used were 2 M, 4 M and 8 M while the ratios used were 0.2, 0.4 and 0.8 g/ml.



Figure 4.3- Schematic representation of the acid treatment.

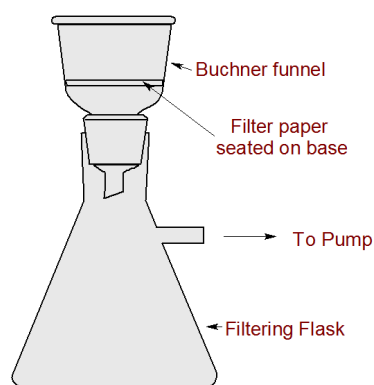


Figure 4.4 – Schematic representation of the washing process.

4.2.4 Alkaline washing of acid treated clays

As it was performed in the acid treatment, 3 selected bases were tested in order to select the best one. Those bases were NaOH, KOH and $\text{Al}(\text{OH})_3$. For the base treatment, 20 g of acid treated clay was mixed with 40 mL of the selected bases and was left for 24h, with constant stirring, at room temperature. The slurry obtained was then filtered with the help of a vacuum pump and washed with deionized water until all the black liquid formed during reaction is separated from the clay. The clay was then dried and stored for plasticity tests. All bases used were 1.5M and the solid to liquid ratio was kept constant at 0.5 g/ml. Figures 4.3 and 4.4 also show how the treatment and washing was done for the basic treatment.

4.3 Analytical techniques

For the characterization of the raw clays, atomic absorption and X-ray spectroscopy techniques were used to know the elemental composition of the clays, while FTIR and TGA

techniques were employed to know the structure and other types of matter present in the clay. All calibrations were done with standards provided by the manufacturers of the instruments.

4.3.1 Flame absorption spectroscopy

For this technique, approximately 0.1g of powdered clay sample was weighed into a 100-ml plastic bottle to which was added 1 ml of Aqua Regia, a mixture of HCl and HNO₃ in a 3:1 ratio by volume, and 3 ml of HF were also added to this mixture. The solution was then tightly covered to avoid loss of silicon. The solution was then left to stand overnight for it to become clear. After the solution becomes clear, and using an automatic dispenser, 50 ml of boric acid was added to dissolve any organic matter in the sample. The solution was then diluted with 46 ml of distilled water to make 100 ml of total solution volume. After standing for a few hours, the solution was used for the flame absorption techniques.

4.3.2 X-ray Fluorescence Spectroscopy

For the XRF techniques, carried out in a Bruker s8 tiger, pellets were prepared. Such pellets had 9 g of dried sample which were mixed with 1 g of SPEX SamplePrep PrepAid TM so the pellets were stable enough to not cause any damage to the instrument. After mixing, the resulting powder was pressed at a 15-ton force for about 20 seconds. After the pellet was made, and after analysis, the results were expressed in terms of percentage oxides and will be shown in the results section of this study. This technique was of crucial importance as it provides the oxide concentrations in the treated material.



Figure 4.5- Equipment used in the preparation of the pellets for XRF analysis.



Figure 4.6 – Bruker s8 tiger used for the XRF technique.

4.3.3 Thermogravimetric Analysis

Thermogravimetric analysis was carried out through SDT Q600 (V20.9 Build 20) instrument (Artisan Technology Group, Champaign, IL) under N₂ atmosphere. A small amount of raw material was subject to elevated temperatures around 600°C, starting at 25°C at an increased temperature of 10 °C/min. This technique was carried out in order to know what kind of materials were present in the samples.

4.3.4 Fourier transform infrared spectroscopy

For this technique, KBr pellets were produced with some raw material to produce five different spectra of five different clays. A powdered sample of 2mg in 200mh KBr was pressed in a mould and was then analyzed by the FTIR equipment (spectrometer Jasco FT/IR – 4200), at a resolution of 4cm, with the spectral data of the sample being collected between 400 and 4000 cm, in order to know what kind of clay minerals were present in the raw material, as well as its structure.

4.3.5 Plasticity analysis

The alkaline washing of the acid treated samples allows to restore the properties of clay plasticity. The usual method to measure the plasticity is based on the cone penetrometer technique. That technique requires specialized instrumentation not available at the Department of Chemical Engineering of Coimbra, so an alternative had to be found.

Since the more the clay bends, the more it will impact mechanical resistance data and the more the clay bends, the greater its plasticity, one can test the treated clays for mechanical resistance in order to see the effect of the process in the clay's plasticity. As reported by F.A. Andrade et al. 2011, a clay-water system of high plasticity requires more force to deform it and deforms to a greater extent without cracking than one of low plasticity which deforms more easily and ruptures sooner. F.P. Hall, (1923) tried to establish an equation for the plasticity parameter but did not manage to because the clay's plasticity is dependent on more variables than the ones he tried to measure and correlate. The plasticity test in this study was made by pressing the material in a rectangular shape, about 5mm thick and support it on two bars. A third bar will press the object, in the midpoint between supporting bars, until it breaks. The equipment (Crometro Machina CR4-2001) will then provide the force needed to break the object subject to the test. The formula used to calculate the mechanical resistance, MR, is as follows:

$$MR = \frac{3 * F * D}{2 * L * t} \quad (4.1)$$

where, F is the force given by the equipment, D is the distance between supporting bars, L is the width of the moulded clay and t is the thickness of the moulded clay. The results are given in force per squared centimetre.



Figure 4.7 – Equipment used to prepare the pellets for mechanical resistance analysis.

4.4 Data Analysis

In order to evaluate the consistency and possible correlations between variables, all tests were subject to statistical analysis using the Statistica 7 software. Acid treatment data were analyzed with a Box-Behnken factorial design with a supporting Pareto chart, while the base treatment was analyzed in a simpler way due to time and technical restraints.

The FTIR spectra was analysed with the Spectrum Quant software in order to get a spectrum of all the structural interactions in clays while for the TGA technique, the data gotten from the machine was handled with the help of the SigmaPlot software.

Table 4.1 refers to the Box-Behnken factorial design, with a total of nine experiments with varying solid to liquid ratios and acid concentrations, in order to determine the optimal conditions for this process. Each run had a duplicate run for consistency of the results and detection of possible flaws in the experiment. A 3D model graph was constructed from the data collected from the treatment phase and will be displayed later in this study.

Table 4.1: Experimental conditions based on a Box-Behnken factorial design.

Run	Solid to liquid ratio (g/cm ³)	Acid concentration (M)
1	0.2	2
2	0.4	2
3	0.8	2
4	0.2	4
5	0.4	4
6	0.8	4
7	0.2	8
8	0.4	8
9	0.8	8

5. Results and discussion

5.1 Characterization of raw clays

This section is devoted to the determination of relevant physical and chemical characteristics of the raw clays using different analytical techniques.

5.1.1 Iron content analysis

Five samples, with duplicate runs, were analyzed for the quantification of their iron content using AAS technique. The AAS analysis of the raw materials was cross-checked with the XRF analysis to confirm or discard values that could seem out of the ordinary. The results, presented in Table 5.1, show that the clay with the most iron in their structure is the one from the A1(1) run. It can also be seen that clays A4 and A5 have similar but slightly lower iron content.

Table 5.1: Results of iron content for raw clays.

Sample	%Fe
A1(1)	1.72
A1(2) *	0.65
A2(1)	1.21
A2(2)	1.333
A3(1) *	0.53
A3(2) *	0
A4(1)	1.66
A4(2) *	2.66
A5(1) *	2.7
A5(2)	1.57

* Values discarded by XRF comparison.

As seen in Table 5.1, different types of clay have different amounts of iron in their structure. That was expectable because of their difference in structure and the clay minerals comprised in the material. As seen before, isomorphic substitution is likely to occur in this kind of materials, which can explain the different amounts of iron since it is almost random what kind of ions will be in each clay's structure, since the clay's composition changes almost by meter of where it was dug from. The runs marked with an asterisk, were discarded because the

results were not in accordance with the results obtained by XRF analysis. The equation used for the calculations can be found in the appendices part of this document.

5.1.2 Chemical composition analysis

The results from Table 5.2 show that all clays have silica and aluminum as their major components with the minor components being potassium, iron and magnesium with trace amounts of chromium, phosphorus, manganese, titanium and calcium. The elemental analysis for A3 is off because of interactions with the SiO₂ and the Al₂O₃ curves in the calibration of the equipment, which have not been fixed by UNIPASTA yet, and was a factor to not choose A3 as the clay to be tested. From the results, A1 has a higher silica and iron content, compensated by a decrease in aluminum. No samples could be used in high grade ceramics due to the immense amount of iron in the samples. The sums of the results are not close to 100% due to the presence of other components that the analytical equipment could not measure, like organic matter.

Table 5.2: Results of the chemical analysis of raw clays in mass percentage.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃	Sum
A1	59.21	12.22	4.48	1.11	0.43	0.61	3.97	0.76	0.19	0.03	0.008	83.02
A2	51.33	22.41	3.24	0.67	0.19	0.23	2.01	0.98	0.21	0.01	0.019	81.30
A3	84.59	4.32	2.8	2.03	0.95	0.99	0.13	0.23	0.08	0.01	0	96.13
A4	49.49	21.54	3.82	0.2	0.05	0.27	3.71	0.36	0.22	0.02	0.007	79.69
A5	44.48	29.43	4.03	0.41	0.06	0.2	2.22	0.3	0.22	0.03	0.006	81.39

5.1.3 Thermogravimetric Analysis

The TGA technique shows how the raw materials loses mass with increased temperatures and it is used to know what other types of material are present in the sample. It can be seen in Figure 5.1 that A3 loses more mass in the heat period from 25 to 100°C, which is associated with free or adsorbed water losses. This likely happens due to its structure being close to a smectite. From 300°C to 600°C, is where the hydroxyl water is lost, due to the oxidation of iron from +2 to +3 (Stucki, 1984). If the test was made to higher temperatures, it would be seen a decrease in mass around 900°C due to loss of organic matter.

As previously mentioned, the A3 sample loses larger amounts of water when compared to the other clays which can be due to its structure being close to a smectite. It can also be seen that it loses almost all of its water in that phase, meaning that it has a low hydroxyl water content. All other clays have similar behaviour throughout the technique, with A5 having the most hydroxyl water and A2 the most water removed from the material.

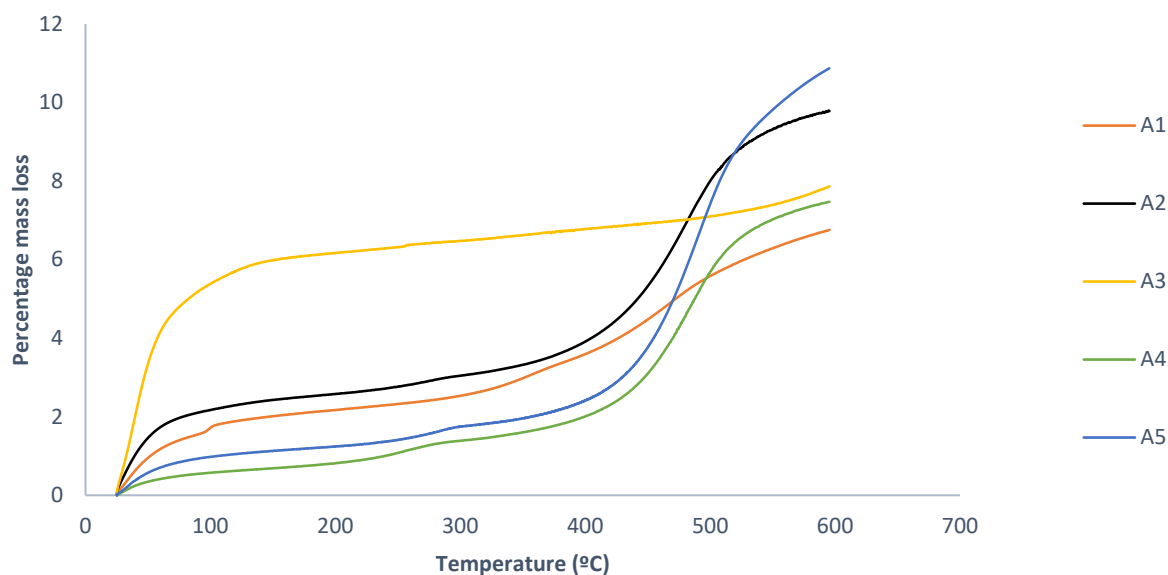


Figure 5.1 - Thermogravimetric results for all five clays considered.

5.1.4 FTIR analysis

From Figures 6a to 6e, it can be observed that all samples exhibit similar spectra with different peaks associated to mineral composition of the clays. All samples showed peaks at 3400 to 3600 cm^{-1} and at around 1600 cm^{-1} associated with hydroxyl stretches and vibrations, usually observed in clays. All samples show a shoulder at around 700 cm^{-1} , which is attributed to the presence of quartz. Samples A5, A4 and A2 showed a peak at 1007 cm^{-1} associated with the presence of the clay mineral saponite. From the increased peaks at around 3600, it is shown that samples A2, A4 and A5 will have increased alumina content, which is confirmed by the XRF analysis of the raw samples. This is explained by the fact that the peak in that area is due to the -OH stretching assigned to hydroxyl groups coordinated to octahedral cations like aluminum in this case. The three peaks at 875, 836 and 915 cm^{-1} are indicative of the presence of AlFeOH, AlMgOH and AlAlOH, respectively and can be used to compare the composition and structure of the samples (Beena Tyagi et al. 2006). A peak at 1032 cm^{-1} that can be attributed to the clay mineral montmorillonite occurs in all the samples. All samples but A1 had a peak at 1116 cm^{-1} or 1088 cm^{-1} which points towards kaolinite and/or dickite. A3 to A5 showed a peak at around 646 cm^{-1} which is a sign of the presence of hectorite in the material (Michal Ritz, 2011). The broadness of the slope at around 3600 cm^{-1} is indicative of the substitution of Al^{3+} with Fe^{2+} or Mg^{2+} cations (Beena Tyagi et al. 2006).

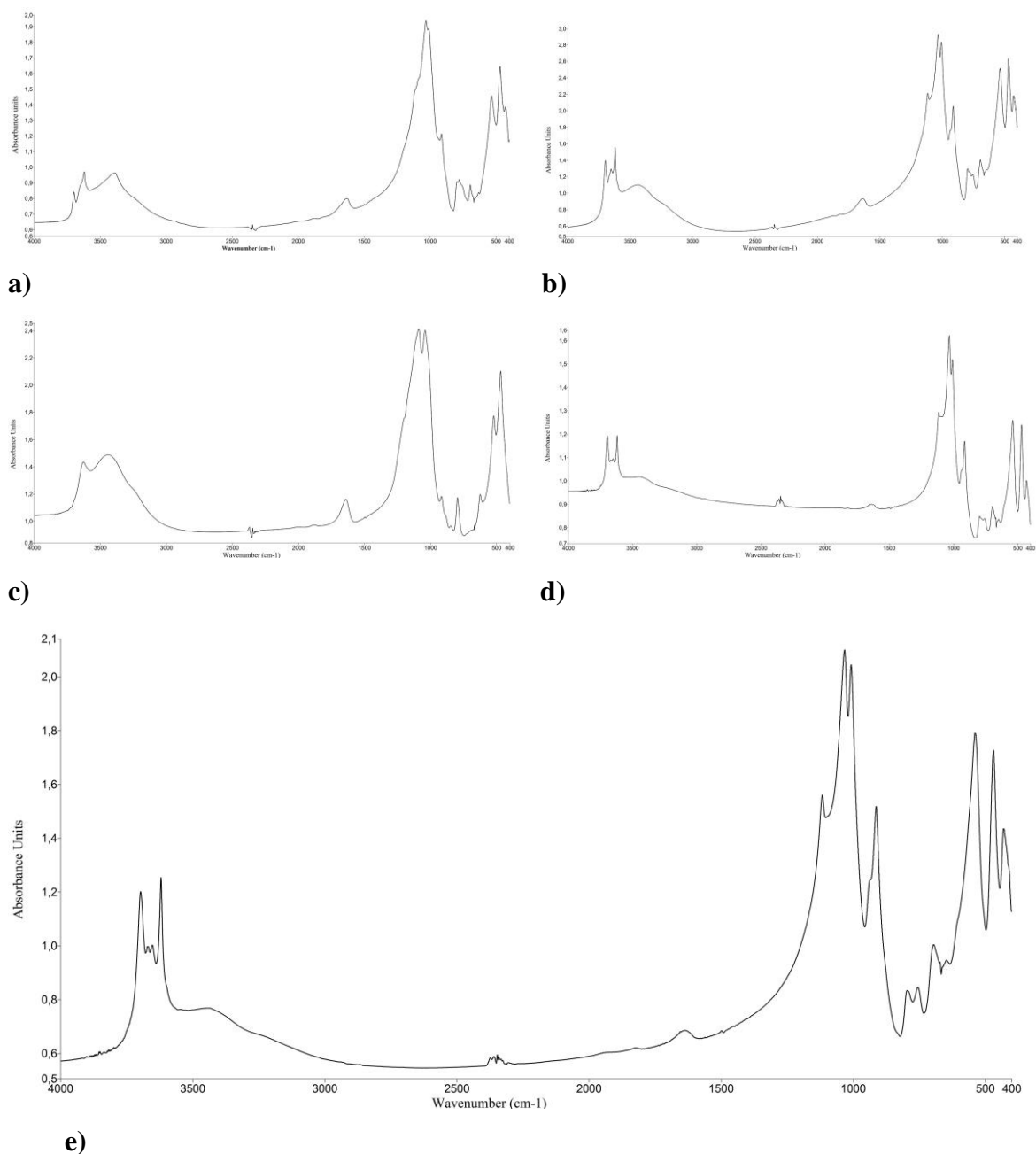


Figure 5.2 – FTIR spectra for clay samples a) A1, b) A2, c) A3, d) A4 and e) A5.

5.2 Acid treatment results

After analysis of the characterization results, the sample chosen for this study was the clay A1, due to the higher iron content as well as its blackish colour. The results from the acid screening step are shown in Table 5.3 and Figure 5.3, in which CA refers to treatment with citric acid, HA to hydrochloric acid and OA to oxalic acid. The difference between runs HA (1) and HA (2) are justified by the run HA (2) having had a problem with mass loss during the treatment and not having enough mass for analysis by XRF technique. As oxalic acid and hydrochloric acid had similar results, hydrochloric was the chosen acid due to difficulties encountered while working with oxalic acid. Those difficulties were associated with dissolving the acid in water, an arduous task at 4 M which did not happen while working with hydrochloric

acid. On the other hand, it can be seen that oxalic acid damages the structure slightly less than the hydrochloric acid, which makes it a target to be studied in later stages of this study if it is to be implemented at an industrial scale. This can be seen in the lower removal of other oxides from the material. It can also be seen that the ratio Si/Al has changed with the treatment. From the raw material chemical composition, one can see that the Si/Al ratio takes a value of 4.845 and after treatment that value changes to approximately 5.3 for the acetic acid, around 6 for hydrochloric acid and around 5.6 for the oxalic acid. The Si/Al ratio is an indicative of the destruction of the structure with higher ratios being a sign of greater structure destruction. The destruction is caused by the discharge of Al ions from the octahedral layers during the acid treatment (Wachira David Maina, 2014). All in all, the acid treatment also reduces the Al concentration, but it is greatly compensated by the decrease in iron content. The effect of this ratio on the properties of the clay will be studied in a more advanced phase of this study.

Table 5.3: Results of the chemical analysis of clay after acid treatment.

Run	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃	Sum
CA(1)	64.55	12.25	3.58	0.91	0.14	0.58	3.94	0.74	0.05	0.02	0.008	86.768
CA(2)	62.62	11.69	3.93	0.93	0.14	0.58	3.94	0.76	0.06	0.02	0.008	84.678
HA(1)	67.57	12.24	2.4	0.78	0.11	0.58	3.72	0.81	0.03	0.01	0.007	88.257
HA(2)	72.52	10.07	1.48	0.5	0.12	0.64	3.51	0.82	0.02	0.01	0.007	89.697
OA(1)	67.26	12.03	2.39	0.81	0.33	0.58	3.77	0.8	0.02	0.01	0.008	88.008
OA(2)	66.72	11.61	2.44	0.84	0.36	0.6	3.8	0.78	0.02	0.02	0.007	87.197

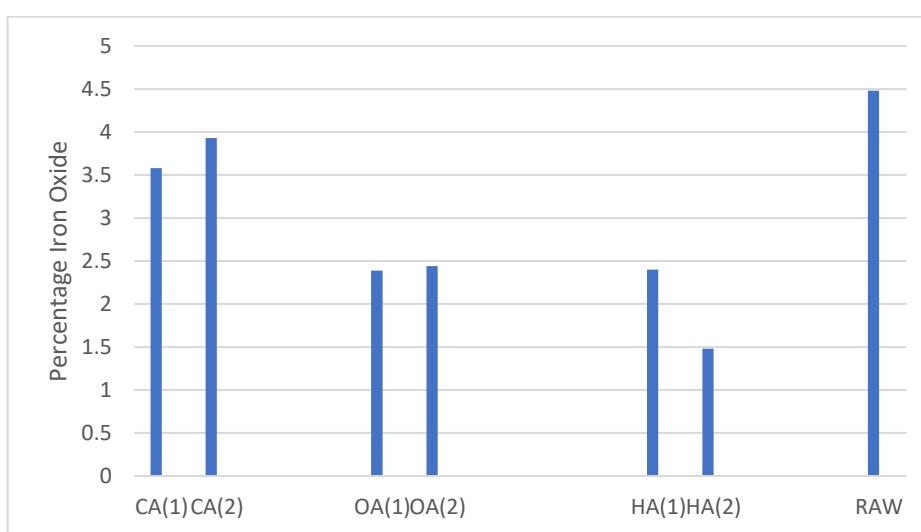


Figure 5.3 – Iron content after treatment for each acid tested.

In Table 5.4, the data relative to the Box-Behnken factorial design is presented, as well and its results. It can be seen that the best removal values are achieved with 4M HCl at 0.2 g/ml with similar results when the acid molarity is 8M. With the increase in molarity, it can be seen that the results vary less with the increased ratio, so, it can also be concluded that the more concentrated the acid, the less will the ratio influence the result.

Table 5.4: Results of the acid treatment of clay according to the experimental design.

Run	Solid to liquid ratio (g/cm ³)	Acid concentration (M)	Removal of iron (%)
1	0.2	2	27.92 ± 1.03
2	0.4	2	17.84 ± 0.55
3	0.8	2	15.96 ± 1.90
4	0.2	4	34.35 ± 2.55
5	0.4	4	23.59 ± 3.42
6	0.8	4	19.78 ± 1.81
7	0.2	8	32.85 ± 1.73
8	0.4	8	27.53 ± 0.91
9	0.8	8	23.03 ± 2.73

Figure 5.4 shows the Pareto chart from the factorial design which indicates that all variables are statistically relevant for the process and both linearly and quadratically. It can be observed the relevance from all bars from the chart being past the line located at $p=.05$, which is the condition to meet statistical relevance with a 95% confidence level. It can also be seen that, both quadratically and linearly, the ratio S/L is the most significant factor in the process. Finally, it can be concluded that the linear influence is prevalent over quadratic influences, so the model of the process should have a slight curvature with linearity prevailing.

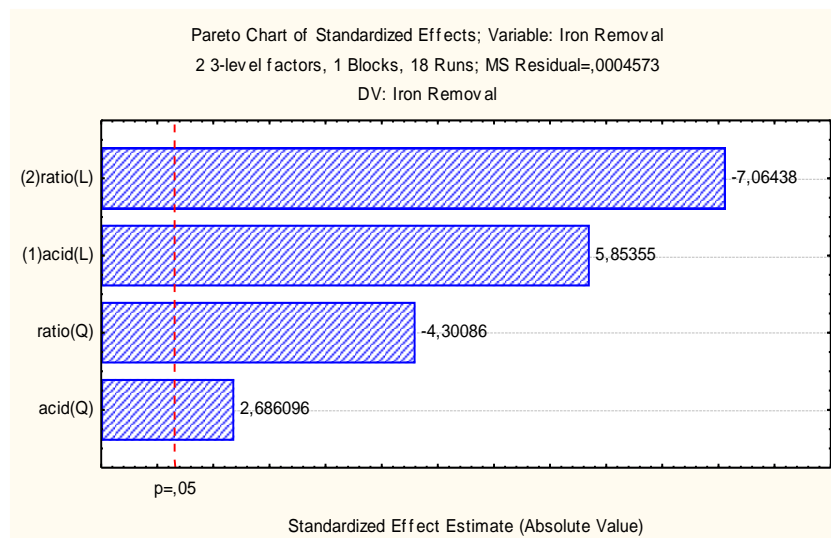


Figure 5.4 – Pareto chart for all variables studied.

Figure 5.5 shows the three-dimensional response surface relating the response variable (removal efficiency of iron) and the two independent variables (ratio S/L and acid concentration). The optimal region identified in this Figure suggests that the highest iron removal values are achieved for low S/L and high HCl concentration.

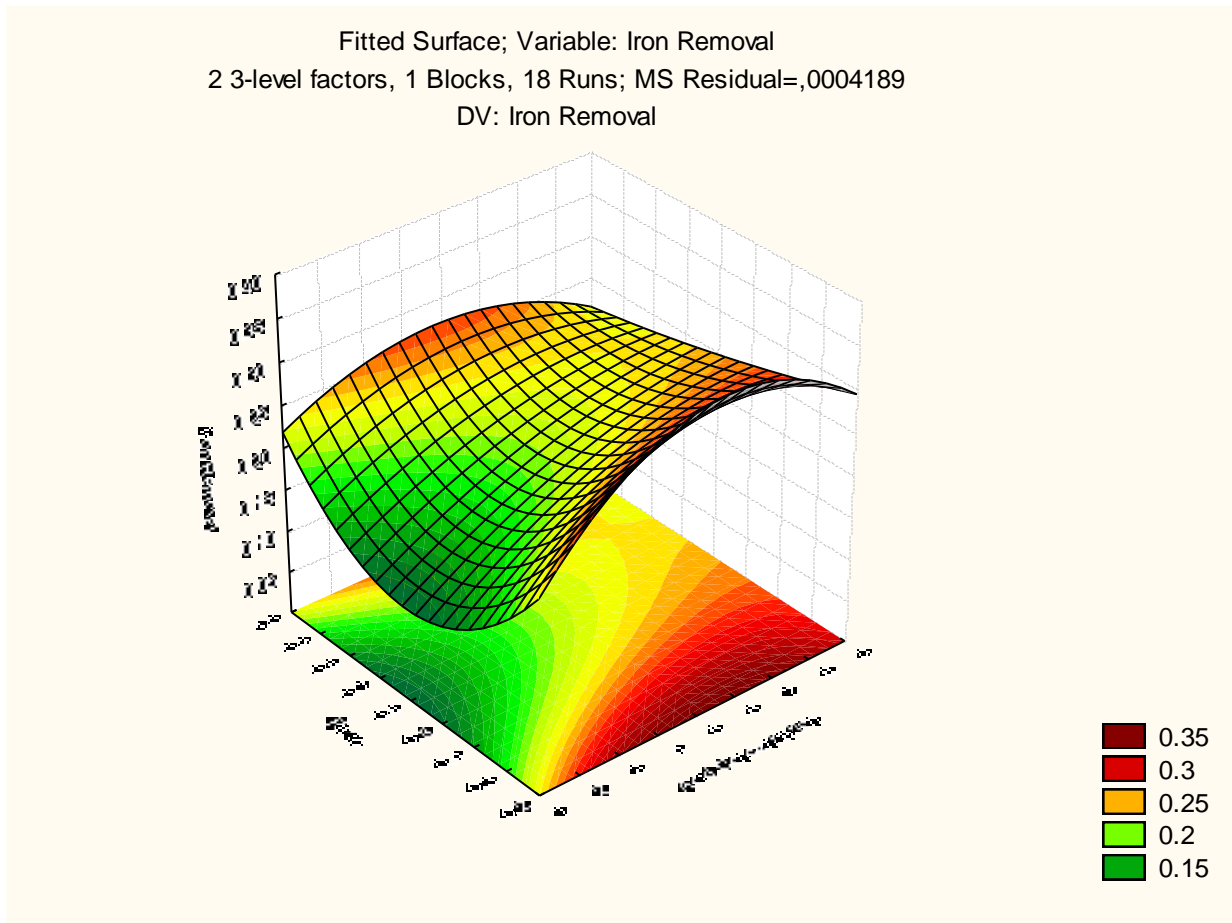


Figure 5.5 – 3D model surface for the process in study.

The comparison between the expected results provided by the regression model and the experimental values are shown in Figure 5.6. From this comparison, it can be concluded that the error is within the acceptable range of variation and thus, can be validated as the model for the process in study. From the data shown in Figure 5.6, one can conclude that the optimal conditions for the process reside in the 4-8M range for acid concentration, with a S/L ratio of 0.2 g/cm³

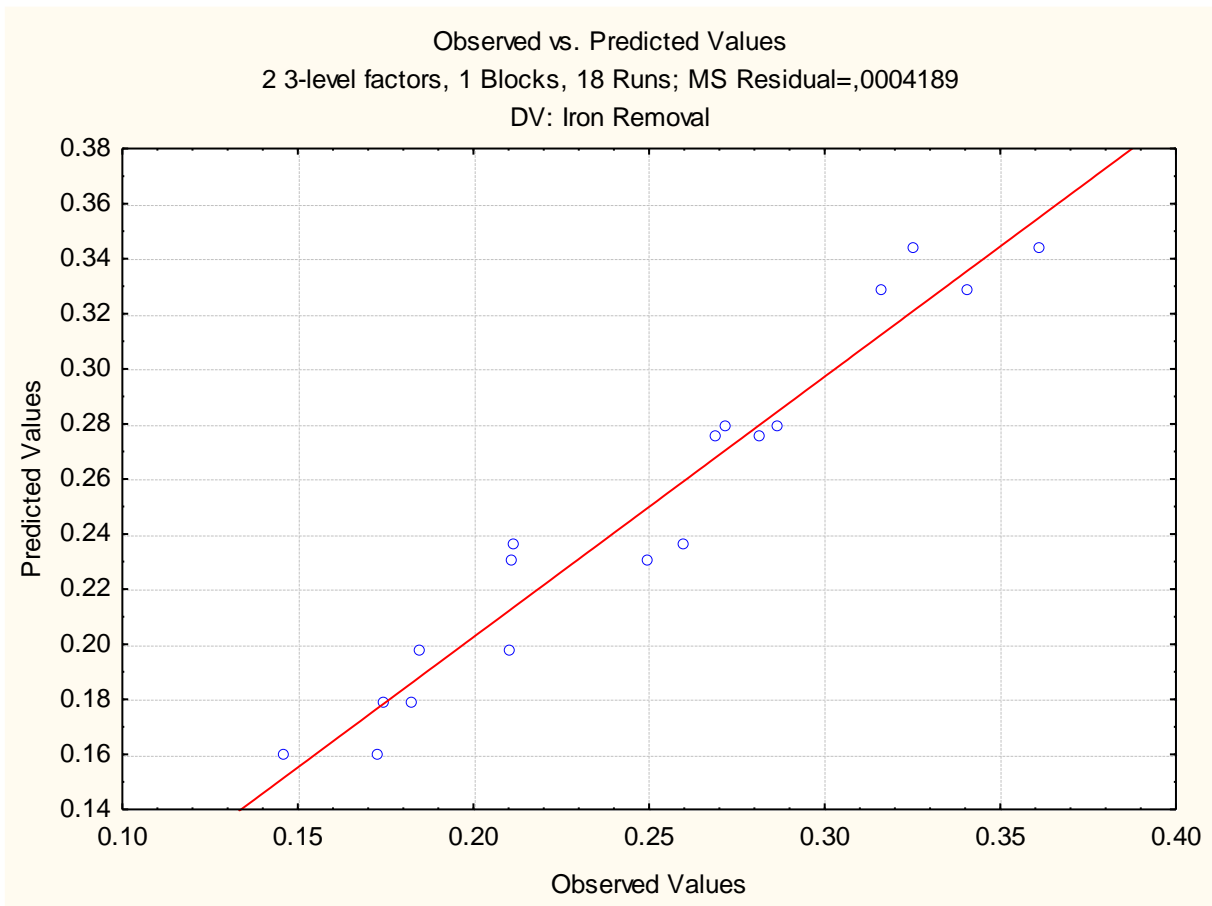


Figure 5.6 – Observed and expected values for the model in study.

5.2 Alkaline washing results

After calculating the mechanical resistance as described in the materials and methods chapter, Figure 5.7 shows that the plasticity of the clays is affected by the acid treatment, lowering the mechanical resistance to almost half. After basic treatment, the clay had its plasticity, not only restored, but also enhanced to double the resistance of the raw clay. As it can be seen, the best base from the ones tested was Sodium Hydroxide. It was also the base with which there was more difficulties in handling due to the black thick paste that is originated from the treatment, possibly due to the dissolution of organic matter by the Sodium Hydroxide. Only with further testing one can say for sure if the increase in restored plasticity is worth the cumbersome process. The second most promising base was Potassium Hydroxide, as it restores the plasticity with no enhancement of such property, but with much less difficulties due to the lesser thickness of the black liquor obtained. One of the goals was to observe if the main cation in the base was used to restore plasticity and therefore included in the composition, giving the control over the composition of the clay as a factor for custom treatment depending on the use it would be getting, but due to lack of time, it will have to be studied at a later time.

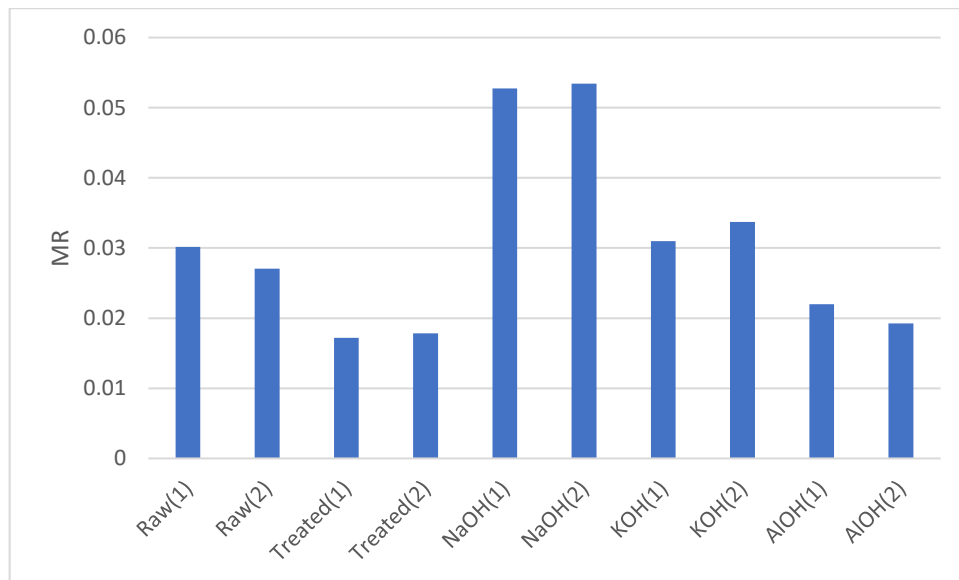


Figure 5.7 – Plasticity results for the basic treatment tests.

5.3 Scale-up Tests

After studying the acid and basic treatment, a quick study was made to evaluate the impact of scaling up the process. The conditions used were 4M hydrochloric acid and 0.2 solid to liquid ratio, with 250g of clay and 1.25 liters of acid, as those were the conditions in which the most iron was removed in the main tests. The two runs performed lead to iron removal percentages of 31.53 and 32.34%. When compared to the factorial tests, where the iron removal was of 34%, one can see that the removal was slightly affected from the scaling up, most likely due to stirring difficulties, which can be solved when applied on an industrial scale. It can then be concluded that the process could be scaled up without great impact on the results, from the data collected. These tests did not have an alkaline washing phase due to difficulties in conducting said phase, due to the difficulties in filtering the slurry obtained from the alkaline washing treatment.

5.4 Preliminary Economical Evaluation

For a process to be used in an industrial setting, economic profit must be guaranteed. For that purpose, a preliminary economic evaluation was done in order to get a first insight on the feasibility of this process at an industrial scale. For this evaluation, both processes will be treated as a single process, with no waste recycling.



Figure 5.8 – Simplified process diagram for economical evaluation.

As shown in Figure 5.8, the input variables are the hydrochloric acid, sodium hydroxide, clay, energy and labor. After the processing of the raw clay, treated clay and wastes are generated. To evaluate the economics of the process, one must know the costs of all involved parts in this process. For the price of the raw clay, it was estimated 5€/ton, as it contains a high iron content and that is a factor that will decrease the value of the clay. It was also estimated that one qualified worker would be needed to control the process, which is valued at 6.25€ per hour. Assuming that treating a ton of clay takes one work day, that would represent a cost of 50€. To treat a ton of clay, 5 thousand liters of hydrochloric acid would be needed, which have an approximate value of 831€. For the basic treatment phase, a thousand liters of 1.5M NaOH would be needed, which is expected to cost 21€. For the energy part, it was assumed that the materials would be heated from 25°C to 90°C, only for the acid treatment, and the specific heat set by the following expression:

$$CP_{mix} = m_{clay} * CP_{clay} + m_{HCl} * CP_{HCl} \quad (5.1)$$

Where m represents mass and CP the specific heat. The specific heat for clay is set at 1381 J/kg°C and for HCl is assumed to be the same as water, 4.18 J/Kg°C. With the mass of clay being 1 ton and the mass of HCl 5 tons, the specific heat of the mixture is set at 1.4MJ/°C, making for a total of 91MJ to heat a batch of 1 ton of clay, which translates to 3€, admitting that electricity would be used. The final accounting for this process lead to an overall cost of 910 € per ton of treated clay. In short, it can be concluded that the treated clay and the wastes will have to be valued at 910€ in order to make the process viable. The price of the treated clay will depend on its new characteristics but would never make up for the costs associated. This was an expectable result, as no recycling of reagents was considered. After these results, one can conclude that the way to make this process viable is having a good HCl recycle process since it makes up for most of the expenses.

5.5 Preliminary Process Design

After the first economical approach, and since the results are heavily influenced by the process design used in the process, a first process design will be explored. As this is only a prototype design, which hasn't been tested for real feasibility, no actual dimensions will be given to the equipments, nor mass flows will be calculated and should be viewed as a mere suggestion of what the process would look like if implemented in an industrial setting.

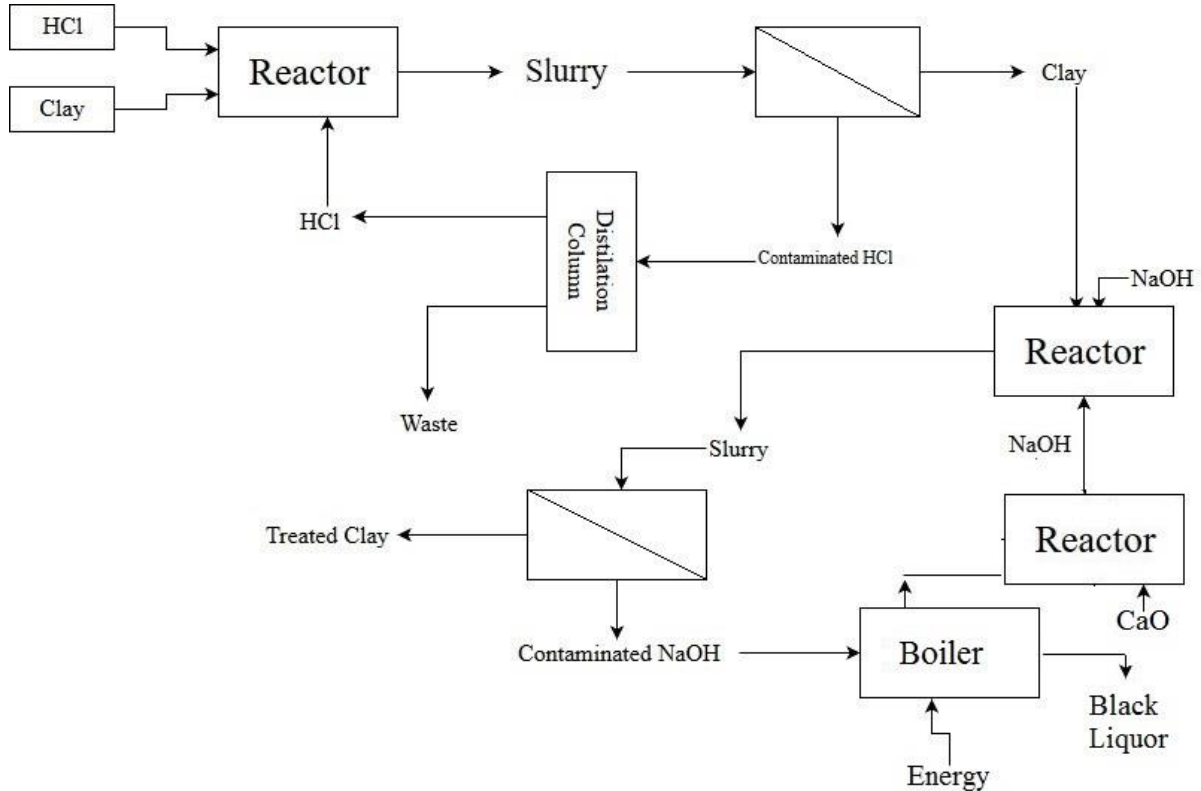


Figure 5.9 – First process design.

Firstly, hydrochloric acid and raw clay enter a reactor at 90°C. After the reaction, the slurry obtained will be filtered in order to separate the clay from the spent HCl, with the spent HCl being directed to a distillation column or other similar process to purify the HCl for the first reactor. Not enough information on what type of waste is produced to know how to treat it, further investigation will be needed in that regard. The acid treated clay will then enter a reactor with NaOH for the basic treatment. The slurry obtained from that reaction will be filtered to separate the contaminated NaOH from the final treated clay. The contaminated NaOH will then go through a boiler with Energy to recover the spent NaOH, a reaction used in the paper industry to recover NaOH after the wood cooking phase along with concentrated black liquor, which can be burned to recover some of the energy spent in the process. After the boiler, the boiled phase will go through a reaction with CaO, used in the paper industry to restore the spent NaOH.

An example of the design of a reactor would be quite simple, as no major alterations are predicted to happen in the material in the first two reactors. The volume needed for the reactor would be described by the following equation:

$$V = \frac{\rho}{m} * 1.1 \quad (5.2)$$

With V being the volume of the reactor, ρ the average density of the clay and acid mixture and m the mass of the mixture. The 1.1 factor is to take into account any gas (HCl) generation, leaving a 10% margin of the volume for security and recycling reasons. For the third reactor, suggested for the NaOH recuperation, extensive research into the paper industry would be needed to see if that process can be adapted. In the first two reactors shown, one of the critical parts in defining the results will be the type of agitation as it is most likely the cause of the decrease in iron removal shown in the scale-up tests shown earlier in this study. An example set of equations for the design of a stirrer can be found in a study conducted by Olumide Babarinsa et al., 2014 and will be shown in the appendix chapter (Appendix IV).

Further studies would be needed for the filter design, as more information about the particles present in the slurry is needed as well and their behavior when forced into pores. As the slurry generated from the reactor phases might be a not very fluid one and contain suspended particles of various characteristics, the pumps used for the movement between equipments might have to be carefully designed with some experimentation involved.

The distillation column phase of this processes was not tested and its only a suggestion on how it could work. Other possible operations include liquid/liquid separation with a solvent for Fe, in order to recuperate the HCl present in the contaminated HCl.

This process design is still very raw and will need to be tested and enhanced if this process is to be employed at an industrial scale.

6 Conclusions and Recommendations

In this study, five types of clay were considered for a series of treatments to remove iron from them and restore the properties afterwards. From the FTIR analysis, it was seen that the clay minerals present in the clays were: montmorillonite for all clays; kaolinite for all clays but A1; A5, A4 and A2 had saponite while A3 and A5 showed the presence of hectorite.

This study also showed an improvement in the properties of the clays after acid treatment with the decrease in iron content, as well as an improvement in the plasticity of the clays after base treatment. Even with good results, the targeted iron content of 1% was not achieved but could be achieved under harsher conditions of temperature or with longer reaction times.

It is also established in this study that from the acids tried, hydrochloric acid is the one with higher iron removal and the most destructive behavior in the clay structure, as seen by the final value of the Si/Al ratio.

The study has established that base treatment restores the plasticity of the acid treated clay, and even enhances it, with the base treated clays having their mechanical resistance doubled when compared to the raw material.

According to this study, the most suitable conditions for the iron dissolution are 0,2 g/ml solid to liquid ratio, 4-8M acid concentration, at 90°C for two hours. With the two last variables being fixed variables.

This study establishes that this process could be scalable, with further research being needed in that regard, as the scale-up and process designs were just preliminary and would consume an amount of time that would justify a whole new study.

It is established in this study that this process is more dependent on the solid to liquid ratio than on the concentration of the acid used. It is recommended that the time factor is also studied in order to evaluate how it will enhance the process. It can also be seen that the linear component of each variable is the most impacting which means that with an increase in those variables, an almost linear response will be expected.

Further research is necessary so the process in study can be industrialized as there are many variables that might be impactful to the process that were not taken into account like stirring and the effect of the water to acid ratio that could explain why the runs 4.3 and 8.3 of the factorial design lead to similar results.

Additional research will be required in order to evaluate other areas in which the treated clays could be used, so that custom treatments could be used depending on the destination the clay will have and while doing so, expand the target market for said clays.

It is highly recommended to test several washing techniques, as the one used in this study had some limitations regarding the speed and effectiveness of the filtering. Such difficulties arise from the formation of a black, thick sludge after basic treatment which is most likely due to the organic matter present in the clay and which is very hard to separate from the rest of the clay. It is advised to study the paper industry processes, as this sludge might be comparable with the black liquor that originates in said process.

References

- A. R. Nascimento, José A. Alves, Marcus Melo (2015) – Effect of the acid treatment of montmorillonite clay in the oleic acid esterification reaction. In *Material Research* vol.18 no.2
- A. K. Panda, B. G. Mishra, D. K. Mishra, R. K. Singh (2010) – Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay. In *Colloids and Surfaces A: Physicochemical and engineering aspects*. Vol. 363, Issues 1-3, Pages 98-104.
- Ajayi, O. A. & Adefila, S. S. (2012) – Comparative study of chemical and biological methods of beneficiation of Kankara kaolin. In *International Journal of scientific and technology research*, 1(8): 13-18.
- Anthoni J. F. (2000) – Classification of common rocks. Retrieved from <http://www.seafriends.org.nz/enviro/soil/rocktbl.htm> Retrieved 27th August 2017.
- Atkins, P., Overton, T., Rourke, J., Weller, M., and Armstrong, F. (2006). *Shriver and Atkins Inorganic chemistry* (Fourth edition). New York: Oxford University Press page 168, 338, 628.
- Asfaw Zegeye, Sani Yahaya, Claire I. Fialips, Maggie L. White, Neil D. Gray and David A. C. Manning (2013) - Refinement of industrial kaolin by microbial removal of iron-bearing impurities. In *applied clay science*, Vol.86, 47-53.
- B. D. Mitchell and R. C. Mackenzie (1953) - The removal of free iron oxide from clays. The Macauley Institute for soil research. 115-118.
- Beena Tyagi, Chintan D. Chudasama and Raksh V. Jasra (2006) – Determination of structural modification in acid activated montmorillonite clay by FT-IR spectroscopy. In *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. Vol.64, Issue 2, pages 273-278.
- Calderon, D., Martinez, M., Mendez, O. and Rodriguez, J. (2005) – Iron leaching of Mexican clay of industrial interest by Oxalic acid. *The AZO Journal of Materials online*, 1(2005) (ISSN 1833-122X) DOI: 10.2240/azojomo0168.
- Dorothy Carroll and Harry C. Starkey (1971) - Reactivity of clay minerals with acids and alkalines. In *clays and clay minerals*, 1971. Vol. 19, 321-333.
- Dumbleton, M. J & West, G. (1966). Some factors affecting the relation between the clay minerals in soils and their plasticity. In *Clay and clay minerals*, Vol.6, pages 179-193.

- Eze, K., Nwadiogbu, O. & Nwankere, T. (2012) – Effect of acid treatment on the physiochemical properties of Kaolin clay. *Archives of applied Science research*, 4(2):792-794.
- F.A. Andrade, H. A. Al-Qureshi, D. Hotza (2010) - Measuring the plasticity of clays: A review. 2010. In *applied clay science* 51 (2011) 1-7.
- F.P. Hall (1923) - Methods of measuring the plasticity of clays. In *Technologic papers of the bureau of standards*. Vol.17 346-366.
- Gabouriaud, F., Myriam, D. & Thomas, F. (2005) – Sensitivity of the acid-base properties of clays to the methods of preparation and measurement. *Journal of colloid and interface science*, 298: 139-147.
- Grim, E. (1979) – Clay uses. In Kirk, E. and Othmer, F. (Ed.), *Encyclopedia of chemical technology* (Third edition., Volume 6, pp. 207-223). New York: John Wiley and Sons.
- Hans-Rudolph Wenk and Andrei Bulakh (2004) – *Minerals, their constitution and origin* (First edition). United Kingdom: Cambridge University Press, pages 232-233.
- Igbokwe, K., Olebunne, L. & Nwakandu, S. (2011) – Effect of activation parameters on conversion. In *Clay-catalyzed Esterification of acetic acid*. *International journal of basic and applied sciences (IJBAS- IJENS)*, 11(5), pages 1-8.
- J.A. González and M. del C. Ruíz (2006) - Bleaching of kaolins and clays by chlorination of iron and titanium. In *applied clay science* Vol. 33, 219-229.
- J. Madejová, J. Bujdák, M. Janek and P. Komadel (1998) – Comparative FT-IR study of structural modifications during acid treatment of dioctahedral smectites and hectorite. In *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. Vol.54, Issue 10, pages 1397-1406.
- Joseph W. Stucki, D. C. Golden and Charles B. Roth (1984) - Effects of reduction and re-oxidation of structural iron on the surface charge dissolution of Smectites. In *clays and Clay minerals*, Vol. 32, No. 5, 350-356.
- K. Bahranowski, E. M. Serwicka, L. Stoch and P. Strycharski (1992) - On the possibility of removal of non-structural iron from kaolinite-group minerals. In *clay minerals* (1993) 28, 379-391.
- Keller, D. (1979). *Clays*. In Kirk, E. and Othmer, F. (Ed), *Encyclopedia of chemical technology* (Third Edition), Volume 6, pp.190-206. New York. John Wiley and Sons.

- Konta, J., 1992. Phyllosilicates in rivers: result of weathering, erosion, transportation and deposition. In: Galán, E., Ortega-Huertas, M. (Eds), XI Reunión Científica Sociedad Española de Arcillas. University of Granada, Spain, 23-44.
- Laird, D.A. (2006) – Influence of layer charge on swelling of smectites. *Appl. Clay Sci.* 34, 74-87.
- Landais, P. (2006) – Advances in geochemical research for the underground disposal of high-level, long-lived radioactive waste in a clay formation. *Geochem. Explor. J.* 88, 32-36.
- Lindiane Bieseki, Francine Bertell, Helen Treichel, Fabio G. Penha and Sibebe B. C. Pergher (2013) - Acid treatments of montmorillonite-rich clay for Fe removal using a factorial design method. In *Materials research* Vol.16 No.5.
- McGregory, D. and Plummer, C. (1985) – *Physical Geology*. (First edition). California State University, Sacramento: W.C.M. Publishers pages 27-30.
- M. G. F. Rodrigues (2003) - Physical and catalytic characterization of smectites from Boa-Vista, Paraíba, Brazil. In *cerâmica* vol.49, no.311.
- Madsen, F. T. (1998) – Clay mineralogical investigations related to nuclear waste disposal. *Clay Miner.* 33, 109-129.
- Meunier, A. (2005) – *Clays*. Springer, Berlin, 472 pp.
- Michal Ritz, Lenka Vaculíková and Eva Plevová (2011) – Application of infrared spectroscopy and chemometric methods to identification of selected minerals. In *acta geodyn. geomater.*, Vol. 8, 47-58.
- Nigrosh, L. (1986) – *Clay works* (Second Edition), Massachusetts, USA: Davis Publications Inc. Page 13.
- O. P. Mehra and M. L. Jackson (1957) - Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. In seventh national conference on clays and clay minerals. 318-327.
- Olumide Babarinsa, Emmanuel O. B. Ogedengbe and Marc A. Rosen (2014) – Mixing performance of a suspended stirrer for homogenizing biodegradable food waste from eatery centers. In *Sustainability* 2014, vol.6 pp 5554-5565; DOI:10.3390/su6095554.
- Quirk, J. P. (2003) – Comments on “Diffuse double layer models, long-range forces, and ordering of clay colloids” *Soil Sci. Soc. Am. J.* 67, 1960-1961.

- R. A. Hernández Hernández, F. Legorreta García, L. E. Hernández Cruz and A. Martínez Luévanos (2002) - Iron removal from a kaolinitic clay by leaching to obtain high whiteness index. In third congress on materials science and engineering 45.
- Sarwenaj, A. (2008) – Clay mineral quantification using gravimetric analysis. Master of Science in civil engineering, University of Texas, Arlington, USA pages 7-24.
- Schoonheydt, R. and Johnson, T. (2006) – Surface and Interface chemistry of clay minerals. In Lagaly, G., Theng, K., Bergaya, F., (Ed.) Handbook of clay science. Development in clay science (Vol. 1). Amsterdam: Elsevier Ltd. Chapter 3.
- Stucki, 2012. What are clays and clay minerals. Clay and Clay minerals Vol. 60, 99-199.
- Stucki, W. (2006). Properties of iron in clays. In Lagaly, G., Theng, K., Bergaya, F, (Ed.) Handbook of Clay Science. Development in Clay Science (Vol.1) AMSTERDAM, Elsevier Ltd. Page 424.
- Thomas B. Hofstetter, René P. Schwarzenbach and Stefan B. Haderlein (2002) – Reactivity of Fe(II) Species associated with clay minerals. In Environmental Science & Technology 37(3), pp. 519-528.
- Thomas W. Smoot (1964) - Clay minerals in the ceramic industry. Tenth national conference on clays and clay minerals. 310-317.
- Vaughan, J., & Patrick, D. (1995) – The mineralogy society series. Mineral surfaces. London: Chapman Hall pages 303-323.
- Velde, B. and Barre, P. (2010) – Clays developed under Sequoia gigantea and prairie soils, 150 years of soil-plant interaction in the parks French Chateaux. Clay and clay minerals, 58(6): 803-812.
- Vibeke Ernsten, Will P. Gates and Joseph W. Stucki (1996) – Microbial reduction of structural iron in clays- A renewable source of reduction capacity. In Journal of Environmental Quality Vol.27 No.4 p. 761-766.
- Wachira David Maina (2014) - Iron removal from clays by acid-treatment and reversal of the clay's plasticity. Master's thesis in Kenyatta University, Bed, Sc.

Appendices

Appendix I - further data on the AAS techniques employed.

Table I.1 – Results from the AAS techniques

Sample	mgRAW/100ml	mg Fe/L	%Fe	
A1(1)	0,128	0,022	1,72	
A1(2)	0,108	0,007	0,65	X
A2(1)	0,099	0,012	1,21	
A2(2)	0,105	0,014	1,333	
A3(1)	0,132	0,007	0,53	X
A3(2)	0,098	0	0	X
A4(1)	0,102	0,017	1,66	
A4(2)	0,124	0,033	2,66	X
A5(1)	0,1	0,027	2,7	X
A5(2)	0,102	0,016	1,57	

In table I.1, the full results for the AAS techniques are shown, with the intermediate data used for the final calculations.

Appendix II – Equation used for the percentage iron in each clay.

For the percentage iron in the raw material calculation, the following equation was used:

$$\%Fe = \frac{mg\ Fe/L}{\left(\frac{mRAW}{100ml}\right) * 10}$$

Appendix III – Calibration curves for the XRF techniques.

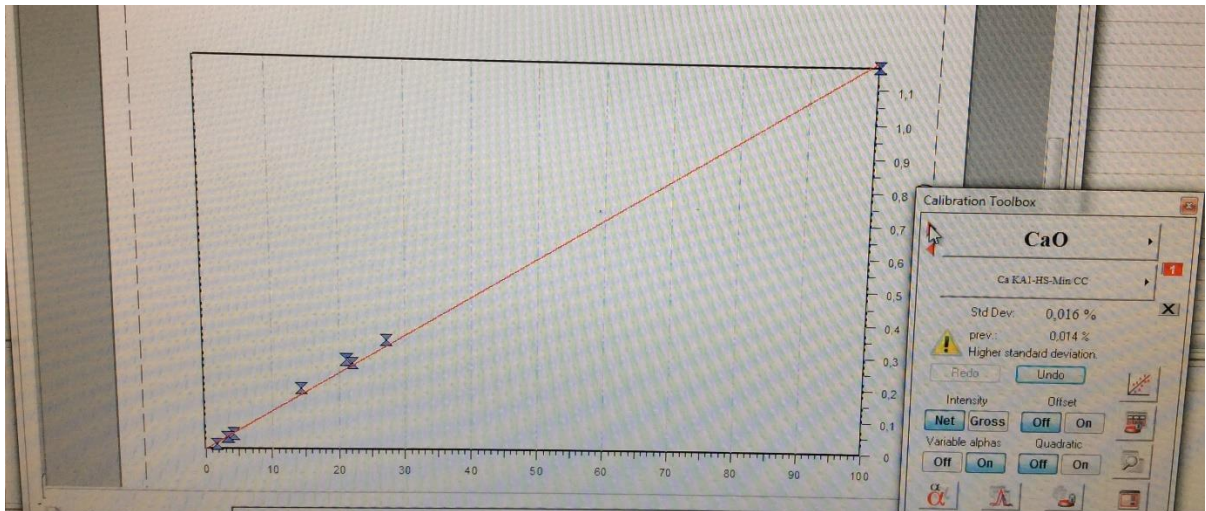


Figure III.1- XRF calibration curve for calcium oxide.

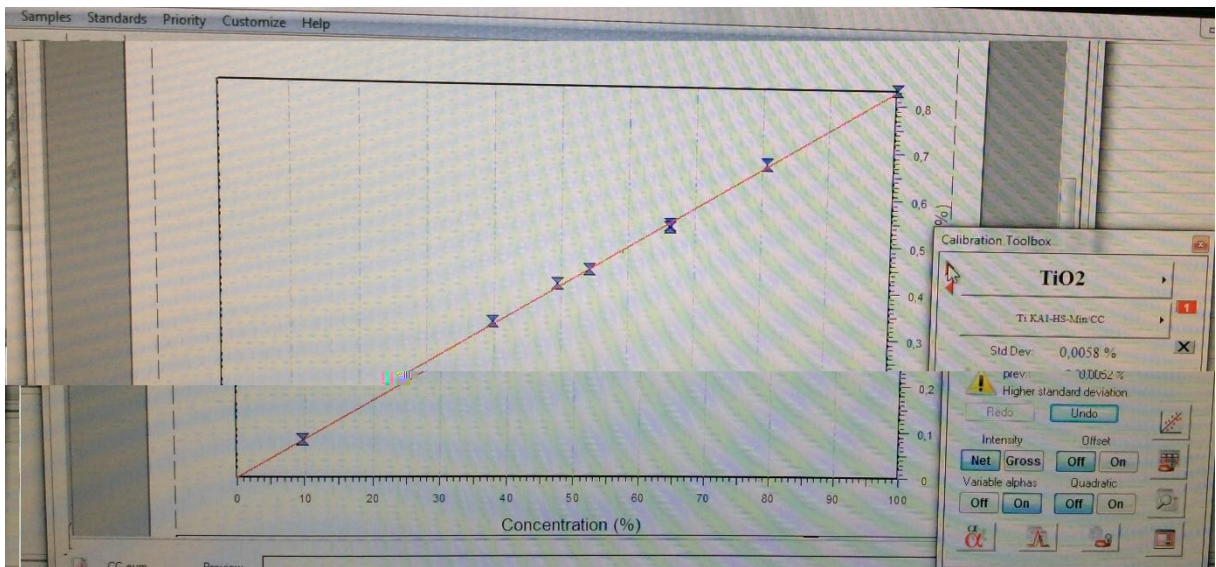


Figure III.2- XRF calibration curve for titanium oxide.

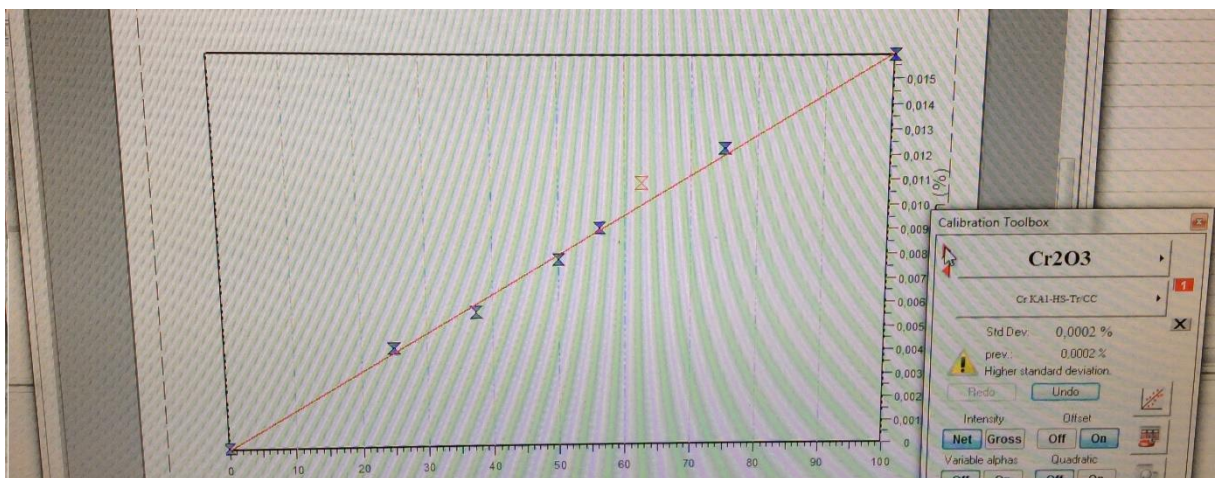


Figure III.3- XRF calibration curve for chromium oxide.

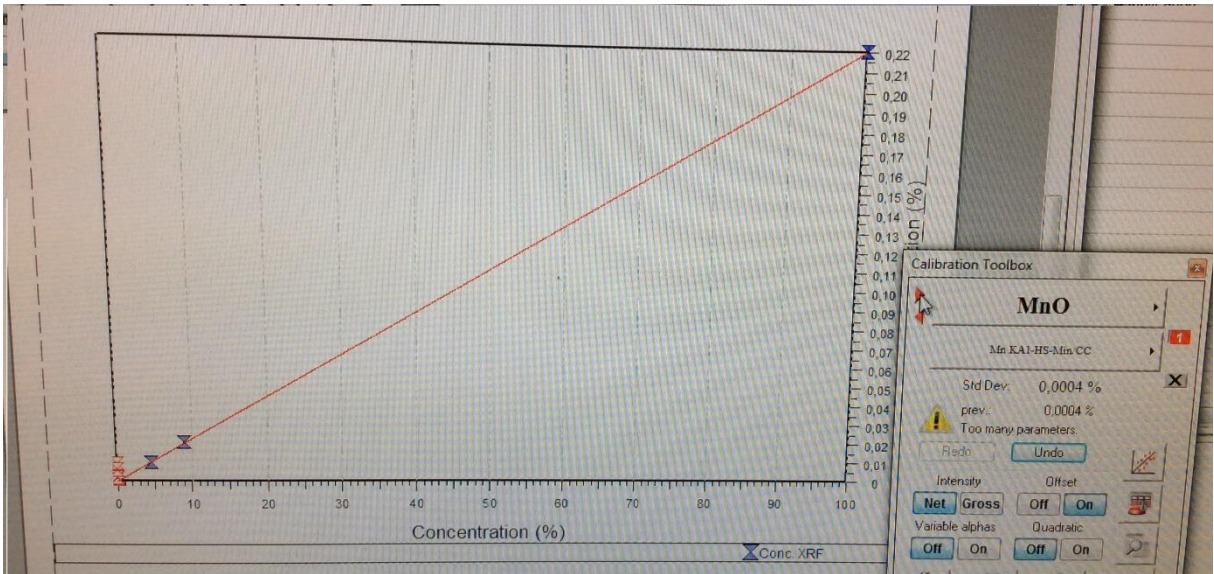


Figure III.4- XRF calibration for manganese oxide.

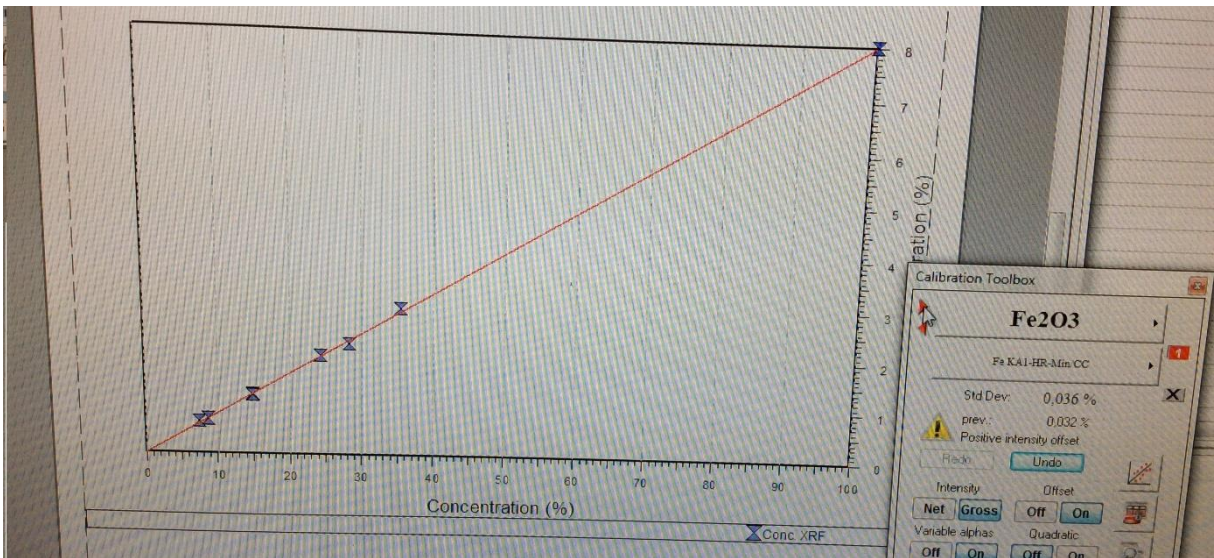


Figure III.5- XRF calibration curve for iron oxide.

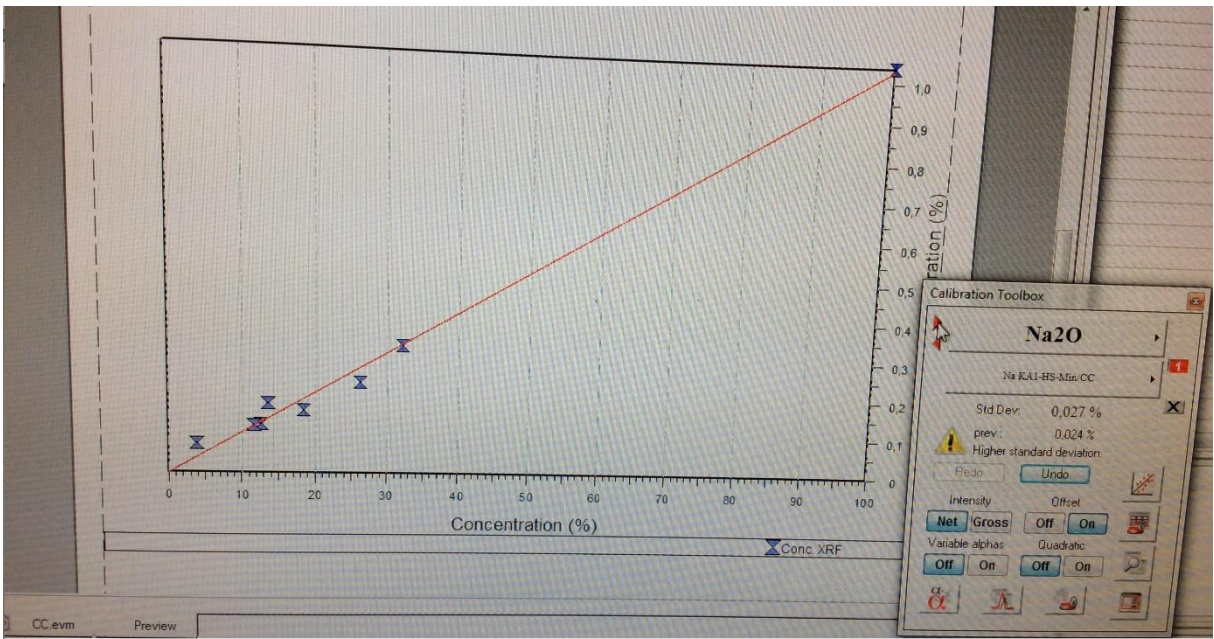


Figure III.6- XRF calibration curve for sodium oxide.

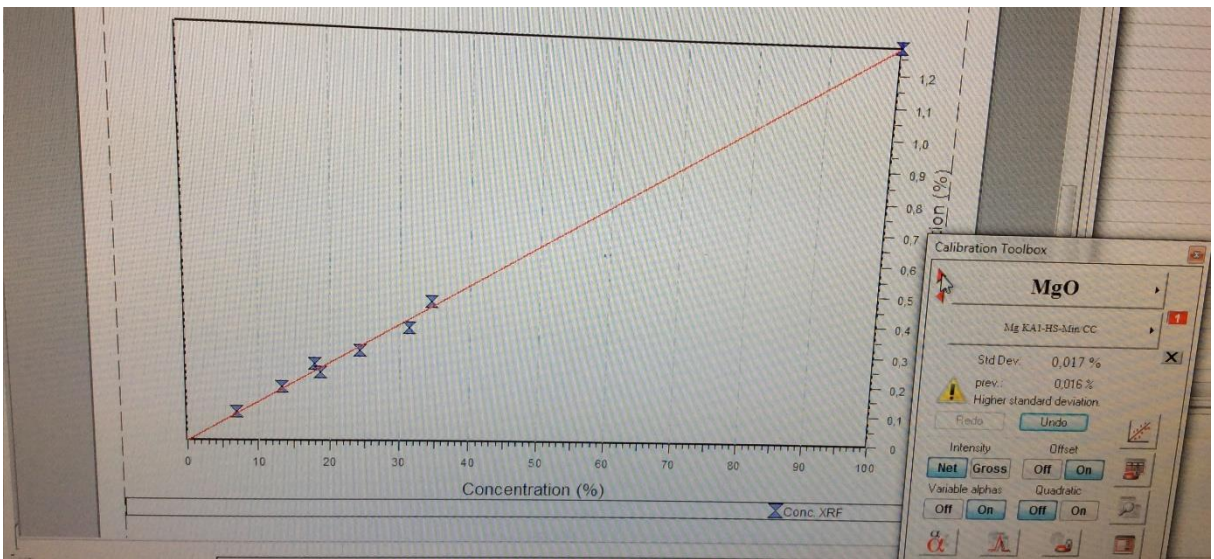


Figure III.7- XRF calibration curve for magnesium oxide.

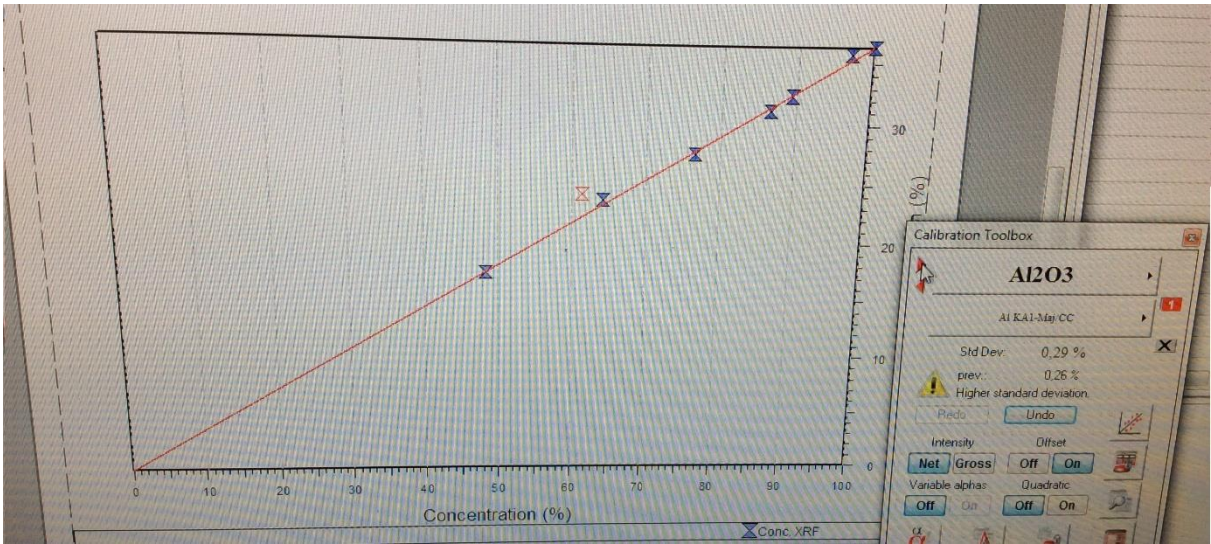


Figure III.8- XRF calibration curve for aluminium oxide.

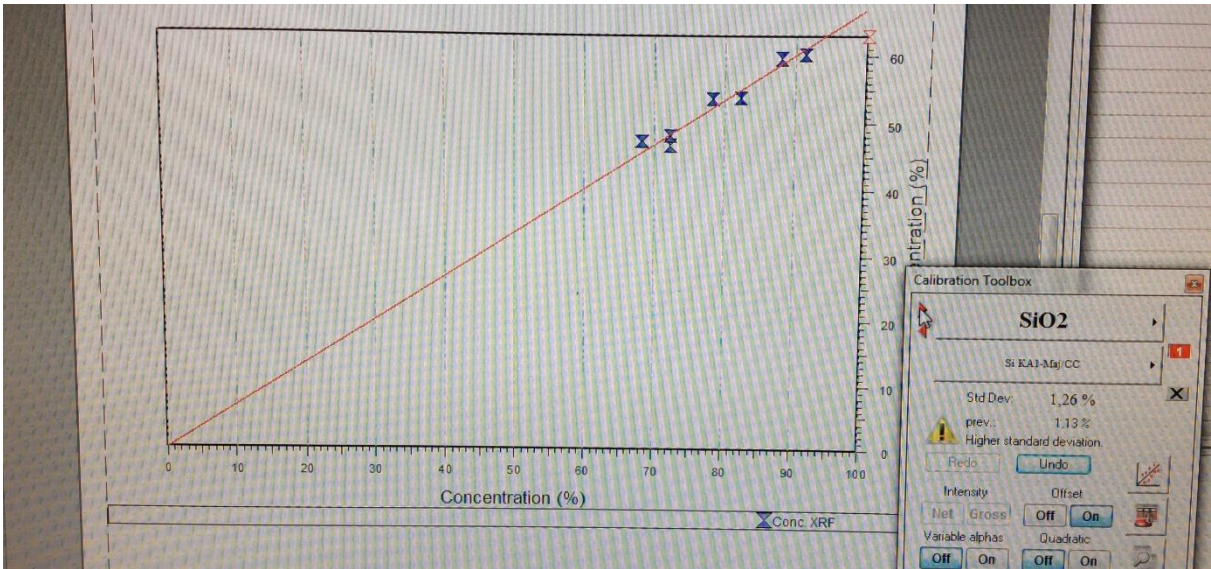


Figure III.9- XRF calibration curve for silicon dioxide.

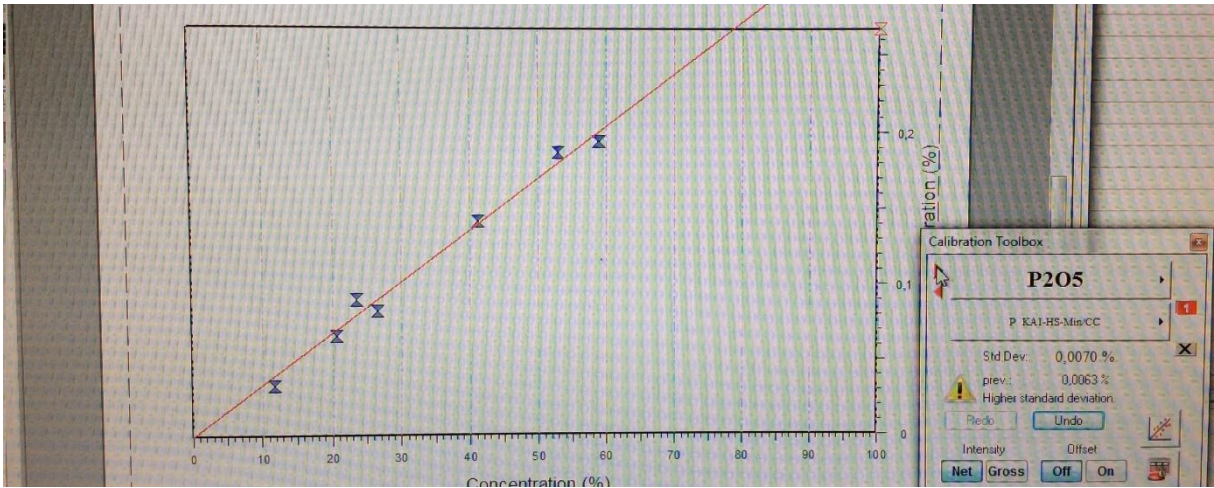


Figure III.10- XRF calibration curve for phosphorus oxide.

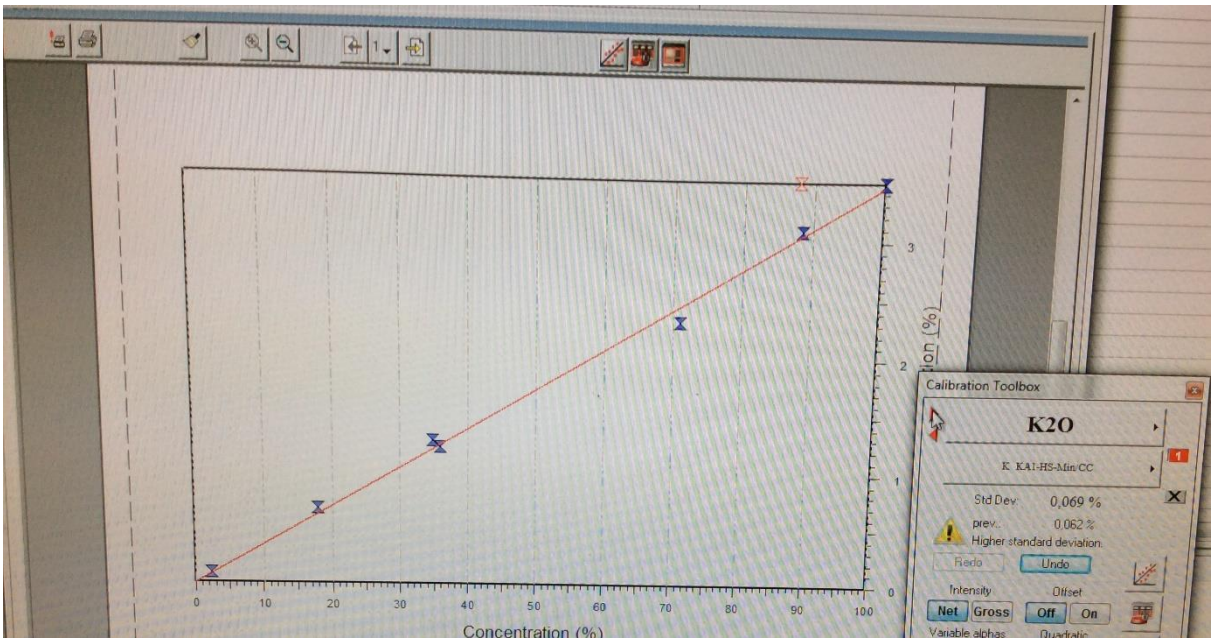


Figure III.11- XRF calibration curve for potassium oxide.

Appendix IV – Set of equations for the design of a reactor stirrer.

Continuity Equation:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0$$

Momentum Equations:

$$\rho \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = - \frac{\partial p}{\partial x} + \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) + F$$

$$\rho \left(\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) = - \frac{\partial p}{\partial y} + \frac{\partial}{\partial x} \left(\mu \frac{\partial v}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial v}{\partial y} \right) + \rho g + F$$

Energy Equation:

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{k}{\rho c} \left[\frac{\partial}{\partial x} \left(\frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{\partial T}{\partial y} \right) \right]$$

Where t stands for time, k stands for the thermal conductivity of the fluid, g denotes acceleration due to gravity, ρ is the density of the fluid being stirred and c the specific heat capacity of the fluid. Finally, u and v stand for fluid velocity components. For the F value, it is derived from the force impact of the propeller on the fluid and is described by the following set of equations:

$$F = \rho V^2 A$$

where:

$$V^2 = (wr)^2 - u^2$$

In this equation, w will stand for the rotational speed for the impeller in radians per second, r stands for the radius of the impeller and A the blade surface area. All these equations assume no frictional force between the impeller action and the fluid.