CHARACTERISATION AND BENEFICIATION
OF NARSINGDI CLAY

by

Ummul Khair Sultana

A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE IN
MATERIALS AND METALLURGICAL ENGINEERING

Department of Materials and Metallurgical Engineering
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY
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CANDIDATE’S DECLARATION

This is to certify that the work presented in this thesis is original and this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

__________________________
Ummul Khair Sultana
CERTIFICATE OF RESEARCH

This is to certify that the work presented in this thesis is carried out by the author under the supervision of Professor ASW Kurny, Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering & Technology, Dhaka.

__________________________  __________________________
ASW Kurny                          Ummul Khair Sultana
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Dedicated to my parents…
A sample of clay was collected from Narsingdi, near Dhaka for the purpose of this study. The sample of clay was characterized by its moisture content, bulk density, organic matter content, pH, alkalinity, liquid limit, plastic limit, firing properties etc. X-ray fluorescence analysis, X-ray diffraction analysis, Thermogravimetric analysis and Differential thermal analysis were also done for the characterization of the sample. The average moisture content (%m) in the clay was 3.27 % which is rather low. Bulk density of the clay, as measured by pycnometer method, was found to be 2.28 g/cc. The organic matter content in the clay was about 6.31% and the pH of the clay was 5.16 which means that the clay is acidic in nature. The alkalinity of the clay was found about 4.5 (wt.%). The average liquid limit is 45.27, the plastic limit is 33.81 and the plasticity index is 11.46. The x-ray diffraction analysis showed that the clay contained mostly quartz and a small amount of kaolinite. X-ray fluorescence analysis showed that the clay sample contained 8.15% iron oxide, 27.49% alumina and 59.45 % of silica and minor amounts of other elements. The thermogravimetric analysis curves showed a mass loss till 500°C due to loss of moisture and organic matter. Subsequently a gain in mass was noted and the reasons for this gain in mass could not be identified.

Four sets of bricks were prepared and fired at four different temperatures. The bricks fired at highest temperature (i.e., 1100°C) showed maximum bulk density (2.25 gm/cm³), lowest water absorption (4.64%) and maximum shrinkage (23.3% ). It also showed the maximum cold crushing strength which was 40.724 N/mm².

The clay was leached in oxalic acid and in hydrochloric acid. Process variables, effects of concentration of acids, time and temperature and effect of stirring speed on the rate of dissolution of iron, contained in the clay sample was investigated. Temperatures studied in this investigation were in the range of 40°C to 100°C, concentrations of both acids were in the range of 0.2M to 2M and the stirring speed was in the range of 0 rpm to 1000 rpm. While finding out the kinetic models that fit the leaching reactions, the Mixed controlled process i.e., $t/\tau = [(1-2X/3)-(1-X)^{2/3}] + b[ 1-(1-X)^{1/3}]$ seemed to be the most appropriate one to fit the kinetic data of leaching of clay in oxalic acid and the diffusion controlled reaction model i.e., $t/\tau = (1-2X/3)-(1-X)^{2/3}$ seemed to be the most appropriate while leaching in hydrochloric acid. The Arrhenius activation energy for leaching in oxalic acid was found to be 41.03 kJ/mole and for hydrochloric acid was 50.82 kJ/mole. Alumina content was found to be affected by
leaching in both the acids. The x-ray diffraction analysis showed that leaching did not cause any change in phases.

The beneficiated clay was again characterized by the Atterberg limit, organic matter content, cold crushing strength, thermogravimetric analysis and X-ray diffraction analysis. The average liquid limit for the clay leached in oxalic acid was 41.72 and the plastic limit was 28.37. The plasticity index was 13.35. On the other hand the liquid limit for the clay leached in hydrochloric was 40.46 and the plastic limit was 29.1. The plasticity index was 11.36. The sample leached in oxalic acid contained 4.58% of organic matter and the sample leached in hydrochloric acid contained 3.1% of organic matter. Bricks were made by using the beneficiated clay. These bricks were fired at 1100°C and then crushed. The cold crushing strength of these bricks was found 37.26 N/mm² (i.e., clay leached in hydrochloric acid) and 40.9 N/mm² (i.e., clay leached in oxalic acid).
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<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential thermal analysis</td>
</tr>
<tr>
<td>k</td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>E</td>
<td>Activation energy</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>A</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin, unit of temperature</td>
</tr>
<tr>
<td>X</td>
<td>Fraction of reacted particle</td>
</tr>
<tr>
<td>b</td>
<td>Function of chemical reaction</td>
</tr>
<tr>
<td>A</td>
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<td>Temperature</td>
</tr>
<tr>
<td>t</td>
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Chapter 1

Introduction

1.1 Purpose of the study

Clay is a common name for a number of fine-grained, earthy materials that become plastic when wet. Chemically, clays are hydrous aluminum silicates, ordinarily containing small amounts impurities like iron, potassium, sodium, calcium, magnesium, etc.

From prehistoric times, clay has been indispensable in architecture, in industry, and in agriculture. As a building material, it is used in the form of brick, either sun-dried or fired. Clays are also of great industrial importance, e.g., in the manufacture of tiles for wall and floor coverings, of porcelain, china, and earthenware, and of pipe for drainage and sewage. Highly absorbent, bentonite is much used in foundry work for facing the molds and preparing the molding sands for casting metals. The less absorbent bentonites are used chiefly in the oil industry, e.g., as filtering and deodorizing agents in the refining of petroleum and, mixed with other materials, as drilling muds to protect the cutting bit while drilling. Other uses are in the making of fillers, sizings, and dressings in construction, in clarifying water and wine, in purifying sewage, and in the paper, ceramics, plastics, and rubber industries. Generally, in ceramic industries ceramics clay articles are made by moistening a mixture of clays, casting it into desired shapes and then firing it to a high temperature. This makes the clay hardened and the process is known as vitrification.

Clays have been used for various purposes in ceramic industries for several unique properties. Among these properties plasticity is worth mentioning. When an external pressure is applied to an object and it keeps that shape, then that object is called as plastic. Clay possesses this property, which makes it possible to give it a permanent shape. Another property of clay is that it shrinks when it is fired in kilns. This is a setting process, which allows the clay to become hard and retain the shape that is given to it. Another important thing is that clay molecules can remain attached to each other. This process is called as cohesion. Also, clay molecules stick very close to each other without leaving many pores, due to which clay is an ideal material to make ceramic vessels.
When clay is totally dried, then its surface can be painted. This makes it possible to decorate the
surface in several ways.

The sample of clay used in these investigations was collected form Narsingdi (near Dhaka). This
sample of clay contains about 27% of alumina which is rather high and provides a possibility to
be used in ceramic industries. But the clay contains rather high amount of iron as impurities. Iron
bearing impurities are harmful for various applications [23]. The major objective of this study
was to characterize the clay to determine its suitability for industrial applications and to find out
an effective route to make it iron free.

The hydrometallurgical route was investigated for the removal of iron as it is cost effective and is
not hazardous for the environment.

Two types of acids were used for the beneficiation of clay for iron removal; one was an organic
acid (oxalic acid) and the other was an inorganic acid (hydrochloric acid). Both these acids have
been used for removal of iron from clays. One of the objectives of this study was to see which
acid was more effective for the removal of iron from the clay.

The academic interest of the study included the optimisation of the leaching parameters in both
the acids. The reaction models were identified and the activation energies were calculated.

1.2 Outline of the work

The objectives of this work can be summarized as follows:

- Chemical, mineralogical and thermal characterization of the clay.

- Establishment of an effective route for removing iron bearing impurities.

- The academic interest of this study was to investigate the kinetic behavior while the clay
  was treated hydrometallurgically (i.e. through leaching operation).

The outline of the work is mentioned bellow:

- The clay was collected from a local area named Narsingdi (near Dhaka).
- It was ground to fine very fine particles (powdered form).

- The chemical composition and the phases were determined by X-ray fluorescence and X-ray diffraction analysis and also the thermogravimetric analysis was done for the clay sample.

- The clay was characterized by its moisture content, bulk density, organic matter content, pH, alkalinity, Atterberg limit etc.

- For the investigation of fired properties of the clay, four sets of bricks were made and fired at four different temperatures for the same interval of time and the temperature profile for firing was also same for all sets of bricks.

- After firing the dry weight, suspended weight and the saturation weight were determined to find out the exterior volume, open pore and impervious pore, water absorption, bulk density and specific gravity of the bricks.

- Cold crushing strength of the bricks was also determined.

- The clay was then treated by hydrometallurgical route in which it was leached in two types of acids; an organic acid (i.e., oxalic acid) and an inorganic acid (i.e., hydrochloric acid) were used.

- The kinetic behaviors for both the leaching operations were studied.

- The effects of process parameters such as acid concentration, time, temperature and stirring speed for both the leaching operations were investigated for finding out the optimum condition of leaching.
Chapter 2

Literature Review

2.1 Clay

The term clay refers to a naturally occurring material composed primarily of fine-grained minerals which is generally plastic at appropriate water contents and will harden when dried or fired. Clay usually contains phyllosilicates. It may contain materials that impart plasticity and hardness when dried or fired. Associated phases in clay may also include materials that do not impart plasticity and organic matter [1].

Clay minerals are typically formed over long periods of time by the gradual chemical weathering of rocks, usually silicate-bearing, by low concentrations of carbonic acid and other diluted solvents. These solvents, usually acidic, migrate through the weathering rock after leaching through upper weathered layers. In addition to the weathering process, some clay minerals are formed by hydrothermal activity. Thick deposits are usually formed as a result of a secondary sedimentary deposition process after they have been eroded and transported from their original location of formation.

Primary clays, also known as kaolins, are located at the site of formation. Secondary clay deposits have been moved by erosion and water from their primary location [2].

2.2 Clay minerals

Clay minerals are hydrous aluminium phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations. Clay minerals are products of weathering and low temperature hydrothermal alteration. From an academic point of view, clay minerals may be divided into the following groups:

1) Kaolinite

Kaolinite, chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, is a group of industrial minerals. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral [3]. Rocks that are rich in kaolinite are known as kaolin or china clay [4].
It is a soft, earthy, usually white mineral (dioctahedral phyllosilicate clay), produced by the chemical weathering of aluminium silicate minerals like feldspar. In many parts of the world, it is colored pink-orange-red by iron oxide, giving it a distinct rust hue.

Kaolin-type clays undergo a series of phase transformations upon thermal treatment in air at atmospheric pressure. Endothermic dehydroxylation (or alternatively, dehydration) begins at 550–600 °C to produce disordered metakaolin, \( \text{Al}_2\text{Si}_2\text{O}_7 \), but continuous hydroxyl loss (-OH) is observed up to 900 °C and has been attributed to gradual oxalation of the metakaolin [5].

\[
2 \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow 2 \text{Al}_2\text{Si}_2\text{O}_7 + 4 \text{H}_2\text{O}.
\]

Further heating to 925–950°C converts metakaolin to a defect aluminium-silicon spinel, \( \text{Si}_3\text{Al}_4\text{O}_{12} \), which is sometimes also referred to as a gamma-alumina type structure:

\[
2 \text{Al}_2\text{Si}_2\text{O}_7 \rightarrow \text{Si}_3\text{Al}_4\text{O}_{12} + \text{SiO}_2
\]

Upon calcination to ~1050 °C, the spinel phase (\( \text{Si}_3\text{Al}_4\text{O}_{12} \)) nucleates and transforms to mullite, \( 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \), and highly crystalline cristobalite, \( \text{SiO}_2 \):

\[
3 \text{Si}_3\text{Al}_4\text{O}_{12} \rightarrow 2 \text{Si}_2\text{Al}_6\text{O}_{13} + 5 \text{SiO}_2
\]

2) Montmorillonite

Montmorillonite is a very soft phyllosilicate group of minerals that typically form in microscopic crystals, forming a clay. It is named after Montmorillon in France. Montmorillonite, a member of the smectite family, is a 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometer. Members of this group include saponite.

Montmorillonite is the main constituent of the volcanic ash weathering product, bentonite.

The water content of montmorillonite is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide \( (\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O} \). Potassium, iron, and other cations are common substitutes, the exact ratio of cations varies with source. It often occurs intermixed with chlorite, muscovite, illite, cookeite, and kaolinite.
3) **Illite**

Illite is a non-expanding, clay-sized, micaceous mineral. Illite is a phyllosilicate or layered alumino-silicate. Its structure is constituted by the repetition of tetrahedron – octahedron – tetrahedron (TOT) layers [6]. The interlayer space is mainly occupied by poorly hydrated potassium cations responsible for the absence of swelling. Structurally illite is quite similar to muscovite with slightly more silicon, magnesium, iron, and water and slightly less tetrahedral aluminium and interlayer potassium. The chemical formula of illite is given as \((K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_{2},(H_2O)]\), [6] but there is considerable ion substitution. It occurs as aggregates of small monoclinic grey to white crystals. Illite occurs as an alteration product of muscovite and feldspar in weathering and hydrothermal environments. It is common in sediments, soils, and argillaceous sedimentary rocks.

4) **Chlorite**

The chlorites are a group of phyllosilicate minerals. Chlorites can be described by the following four end-members based on their chemistry via substitution of the following four elements in the silicate lattice: Mg, Fe, Ni, and Mn.

- **Clinochlore**: \((Mg_5Al)(AlSi_3)O_{10}(OH)_8\)
- **Chamosite**: \((Fe_5Al)(AlSi_3)O_{10}(OH)_8\)
- **Nimite**: \((Ni_5Al)(AlSi_3)O_{10}(OH)_8\)
- **Pennantite**: \((Mn,Al)_6(Si,Al)_4O_{10}(OH)_8\)

The typical general formula is:

\((Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2\cdot(Mg,Fe)_3(OH)_6.\)

This formula emphasises the structure of the group. Chlorites have a 2:1 sandwich structure (2:1 sandwich layer = tetrahedral-octahedral-tetrahedral = t-o-t...), this is often referred to as a talc layer [7].
2.3 Classification of clay

Clay is commonly divided into two types:

- **Primary clay**

  Primary clay is also called residual clay, formed at the site of the parent rock. It is less common than secondary (transported or sedimentary) clay, but generally whiter and free from impurities. Because this clay is broken down by ground water, etc. and not transported, particle size is mixed (no opportunity for sorting or grinding) and the clay is usually not very plastic, and is refractory. Most kaolins are primary clays.

- **Secondary clay**

  Secondary clay is that clay which has been transported from multiple sources by water, or wind and has sort particle sizes. Many secondary clays contain organic (carbonaceous) and other impurities (iron, quartz, mica, etc.).

On the other hand, on the basis of general composition and properties, clay is classified as:

- **Kaolin** is a fine white clay consisting chiefly of the mineral kaolinite.
- **Ball clay** contains kaolinite and certain micas, and has strong bonding properties.
- **Fire clay** is basically kaolinite with some iron oxides, magnesia, and alkalis. It can resist high temperatures.
- **Common clay** contains more impurities than fire clay, and does not have as great resistance to heat.
- **Bentonite** consists largely of montmorillonite. Some types that contain sodium swell when mixed with water.
- **Fuller's earth** is composed of montmorillonite and attapulgite (magnesium aluminium phyllosilicate with formula \((\text{Mg,Al})_2\text{Si}_4\text{O}_{10}((\text{OH})\cdot4(\text{H}_2\text{O}))\) and is high in magnesia.
2.4 Uses of clay

2.4.1 Historical and modern uses

From prehistoric times, clay has been indispensable in architecture, in industry, and in agriculture. Clays exhibit plasticity when mixed with water in certain proportions. When dry, clay becomes firm and when fired in a kiln, permanent physical and chemical changes occur. Because of these properties, clay is used for making pottery items, both utilitarian and decorative. Different types of clay, when used with different minerals and firing conditions, are used to produce earthenware, stoneware, and porcelain.

Prehistoric humans discovered the useful properties of clay, and one of the earliest artifacts ever uncovered is a drinking vessel made of sun-dried clay. Depending on the content, clay can appear in various colors, from a dull gray to a deep orange-red.

Clays sintered in fire were the first form of ceramic. Bricks, cooking pots, art objects, dishware, and even musical instruments such as the ocarina can all be shaped from clay before being fired. Clay is also used in many industrial processes, such as paper making, cement production, and chemical filtering. Clay is also often used in the manufacture of pipes for smoking tobacco. Until the late 20th century bentonite clay was widely used as a mold binder in the manufacture of sand castings.

Clay, being relatively impermeable to water, is also used where natural seals are needed, such as in the cores of dams, or as a barrier in landfills against toxic seepage [8].

2.4.2 Medical and agricultural uses

A traditional use of clay as medicine goes back to prehistoric times. An example is Armenian bole, which is used to soothe an upset stomach [9]. Kaolin clay and attapulgite (magnesium aluminium phyllosilicate with formula (Mg,Al)$_2$Si$_4$O$_{10}$(OH)$_2$(H$_2$O)) have been used as anti-diarrheal medicines.

2.4.3 Clay as a building material

Clay is one of the oldest building materials on Earth, among other ancient, naturally-occurring geologic materials such as stone and organic materials like wood. Between one-half and two-thirds of the world's population, in traditional societies as well as in developed countries, still live
or work in a building made with clay as an essential part of its load-bearing structure. Also a primary ingredient in many natural building techniques, clay is used to create adobe, cob, cordwood, and rammed earth structures.

2.5 Characterization of clay

Moisture content, bulk density, volatile matter content, pH, alkalinity, Atterberg limit etc are generally used to characterize any particular clay. X-ray fluorescence analysis, X-ray diffraction analysis, Thermogravimetric and Differential thermal analysis are the additional routes for characterization of clay. Besides the firing shrinkage, water absorption etc can be found out by making of bricks from the clay and firing them.

2.5.1 Moisture content

Moisture content of a clay is the ratio of the weight of water present to the weight of dry clay in a given clay mass. Moisture content plays an important role in understanding the behavior of clay. It is the moisture content which changes the clay from liquid state to plastic and solid states. The property is used in a wide range of scientific and technical areas, and is expressed as a ratio, which can range from 0 (completely dry) to the value of the materials’ porosity at saturation. Compaction of clay in the field is also controlled by the quantity of water present [10].

Moisture may be present as adsorbed moisture at internal surfaces and as capillary condensed water in small pores. At low relative humidity’s, moisture consists mainly of adsorbed water. At higher relative humidity’s, liquid water becomes more and more important, depending on the pore size.

2.5.2 Bulk density

Bulk density is the ratio of the mass of unit volume of clay at a stated temperature to the mass of the same volume of gas-free distilled water at the stated temperature. The bulk density of clay is often used in relating a weight of clay to its volume. Although the density is employed in the identification of minerals, it is of limit value for identification or classification of clay because the density values of most clay fall within a narrow range. It is an important factor required for computing the most of the clay properties e.g. void ratio, particle size and degree of saturation of a clay etc.
2.5.3 Organic matter

Clays always contain organic material of various types and origins. In clays dating from more recent eras we can find lignin and humic acids, in colloidal form and with notable ionic exchange properties due to the functional groups -CH e –COOH present in their molecules. In clays of older eras, carbonaceous and bituminous substances are more frequent, with few functional groups capable of influencing colloidal and ionic exchange properties. Generally the calcareous material is found in the form of lignite, in grains of variable dimensions that form agglomerates or layers, or in the form of colloidal particles clinging to the crystals of argillaceous material. In so-called “ball clays” the material in colloidal form can also be composed of humic acids which facilitate the deflocculation process.

Combustion of organic substances occurs between 300 and 600°C and they decompose entirely if the quantity of oxygen is sufficient for complete reaction development.

During the firing process of ceramic parts, the organic substances present in the clays can cause the development of a central area (in the ceramic object) of a different color, varying from black to yellow. This is known as the “black core”. This phenomenon is due to the thermal decomposition of the organic material and to oxidation-reduction reactions of the inorganic components [11, 12].

Basically, whenever the quantity of organic substances is higher than a certain value or whenever low permeability of the ceramic object does not permit complete combustion due to lack of oxygen, carbon remains in the center of the matrix up to higher temperatures (where these can cause reduction of the iron). The size of the black core depends on various factors, such as temperature and firing cycle, forming method, porosity of the ceramic object and oven atmosphere [13, 14].

2.5.4 pH

The hydrogen ion concentration of clay is designated as its pH value. The pH value of a solution indicates its acidic or alkaline nature. A pH value of the order of 7 suggests a neutral solution, less than 7 as acidic and more than 7 as alkaline. The pH value of a solution is expressed as the logarithm of the reciprocal of hydrogen ion concentration as shown below:

\[
pH = \log_{10} \left( \frac{1}{[H^+] \right]
\]
The pH value is determined by electrometric, calorimetric and indicator methods. For accurate work the electrometric method is a standard.

The electrometric method is based on the principle that the solution to be tested can be considered as an electrolyte of a voltaic cell. The reference electrode remains at a constant voltage with respect to the solution and is not affected by the changes in pH values. The other electrode is of such type that its potential is affected by the pH of the solution under test. The measured voltage of the cell immersed in the unknown pH solutions is converted to pH units.

The process of forming a ceramic object usually involves filling a form (mold) with a ceramic suspension (such as clay). The suspension will gradually settle out due to gravity. It is important in ceramic processing to have the particles settle out individually to achieve the closest packing of the particles because the strength of a ceramic is partially determined by its density.

The rate of settling depends on the size of the particle (big particles or particle clusters settle faster) and the charge that may be on the particles in solution. The charge on each particle may repel the other particles and keep the material in suspension, or it may cause the particles to be attracted to each other and form clusters (or Flocs) which settle faster. By adjusting the pH of the solution, ceramic processors can control the degree of flocculation (settling out) of the ceramic particles and thus control the properties of the product. The chemicals that control flocculation is called deflocculating agents.

2.5.5 Alkalinity

Alkalinity measures the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. The alkalinity is equal to the stoichiometric sum of the bases in solution. In the natural environment carbonate alkalinity tends to make up most of the total alkalinity due to the common occurrence and dissolution of carbonate rocks and presence of carbon dioxide in the atmosphere. Other common natural components that can contribute to alkalinity include borate, hydroxide, phosphate, silicate, nitrate, dissolved ammonia, the conjugate bases of some organic acids and sulfide. Alkalinity is sometimes incorrectly used interchangeably with basicity. For example, the pH of a solution can be lowered by the addition of CO₂. This will reduce the basicity; however, the alkalinity will remain unchanged.

Clay alkalinity is mainly associated with the presence of sodium carbonates (Na₂CO₃) in it, either as a result of natural mineralization of the clay particles or brought in by irrigation and/or
floodwater. The sodium carbonate, when dissolved in water, dissociates into 2Na+ (two sodium cat-ions, i.e. ions with a positive electric charge) and CO$_3^{2-}$ (a carbonate an-ion, i.e. an ion with a - double - negative electric charge).

The sodium carbonate can react with the water to produce carbon-dioxide (CO$_2$), escaping as a gas, and sodium-hydroxide (Na\(^+\)OH\(^-\)), which is alkaline and gives high pH values (pH>10).

The causes of clay alkalinity are natural or they can be man-made. The natural development is due to the presence minerals producing sodium carbonate upon weathering. The man-made development is due to the application of irrigation water (surface or ground water) containing a relatively high proportion of sodium bicarbonates.

2.5.6 Atterberg limit

The Swedish scientist Albert Atterberg originally defined seven “limits of consistency” to classify fine-grained soils, but in current engineering practice only two of the limits, the liquid and plastic limits, are commonly used (a third limit, called the shrinkage limit, is used occasionally). The Atterberg limits are based on the moisture content of the clay. The plastic limit is the moisture content that defines where the clay changes from a semi-solid to a plastic (flexible) state. The liquid limit is the moisture content that defines where the clay changes from a plastic to a viscous fluid state. The shrinkage limit is the moisture content that defines where the clay volume will not reduce further if the moisture content is reduced. ASTM D-4318 [15] is the standard test method for measuring liquid and plastic limit.

The proper and efficient clays as raw materials for ceramic materials require considerable knowledge of their engineering properties. The engineering properties are those which describe the behavior of clay under various usages. The important properties are liquid limit, plastic limit, plasticity index, shrinkage limit etc. These properties are of great interest to ceramics makers who are called upon to select clays for ceramics making.

In a laboratory test, liquid limit is the water content at which the clay has such small shear strength that it flows to close a groove of standard width when jarred in a specified manner and plastic limit is the water content at which the clay begins to crumble when rolled into threads of specified size. Liquid limit is the boundary between liquid and plastic states. The amount of water which must be added to change the clay from its plastic limit to its liquid limit is an indication of the plasticity of the clay. The plasticity is measured by the ‘Plasticity Index’ which is equal to the liquid limit minus the plastic limit.
In general chlorite, illite and kaolinite clay minerals have relatively low shrinkage, good plastic properties and a long vitrification range. A small amount of smectite can be tolerated, but a large amount would give undesirable shrinkage and drying properties [16].

Prakash and Jain [10] quoted some standard liquid limit values to explain the compressibility behavior of soils. These are given in the following table:

Table 2.1: Standard liquid limit values for clay.

<table>
<thead>
<tr>
<th>Liquid limit values</th>
<th>Behavior of clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 35</td>
<td>Low Compressibility</td>
</tr>
<tr>
<td>35 – 50</td>
<td>Medium Compressibility</td>
</tr>
<tr>
<td>&gt; 50</td>
<td>High Compressibility</td>
</tr>
</tbody>
</table>

2.5.7 X-ray diffraction (XRD)

X-ray diffraction is a rapid analytical technique primarily used for phase identification of a crystalline material. X-ray diffraction analysis is widely used in the study of clays primarily to identify the phases present in a particular clay sample [17].

2.5.8 X-ray fluorescence (XRF)

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) x-rays from a material that has been excited by bombarding with high-energy x-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis of clays.

2.5.9 Thermogravimetric analysis and differential thermal analysis (TGA-DTA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature. This can be used to determine how much of a substance was lost at a particular temperature or over a temperature range where a reaction takes place, such as dehydroxylation [18, 19]. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. Again, interpretation is limited without further modifications of the overlapping peaks may be required.
Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. The complementary information obtained allows to investigate the exothermic and endothermic effects of reactions, such as carbon oxidation and dehydroxylation respectively [20-22].

Differential thermal analysis (DTA), thermal gravimetric analysis (TG or TGA), and derivative thermal gravimetric (DTG) analysis are reported for each of the eight Source Clay minerals using commonly available commercial instruments. The DTA curves show the effect of energy changes (endothermic or exothermic reactions) in a sample. For clays, endothermic reactions involve desorption of surface H$_2$O (e.g. H$_2$O on exterior surfaces) and dehydration (e.g. interlayer H$_2$O) at low temperatures (100°C), dehydration and dehydroxylation at more elevated temperatures, and, eventually, melting. Exothermic reactions are related to recrystallization at high temperatures that may be nearly concurrent with or after dehydroxylation and melting. Discriminating between desorption and dehydration or dehydration and dehydroxylation may be problematic. The TG curves ideally show only weight changes during heating. The derivative of the TG curve, the DTG curve, shows changes in the TG slope that may not be obvious from the TG curve. Thus, the DTG curve and the DTA curve may show strong similarities for those reactions that involve weight and enthalpy changes, such as desorption, dehydration and dehydroxylation reactions.

In thermal analytical studies of clay minerals, results from different laboratories often show significant variations in the desorption and dehydration properties of these minerals. Koster van Groos, Guggenheim [23] found that the temperature of an event involving H$_2$O is greatly affected by the fugacity of water $f$H$_2$O, at the hydrated site. Hence, the response of materials during thermal analysis will be strongly influenced by a variety of factors, including the humidity surrounding the sample at the time of the experiment. Evidence for this is shown by the effect of purging the atmosphere surrounding the sample with nitrogen. In addition, the grain size of clay aggregates, as well as the size of the individual crystals, will affect the diffusivity of H$_2$O and, consequently, $f$H$_2$O at the hydrated site. More uniform experimental conditions may be obtained using high-pressure thermal analysis (HP-DTA), because the sample capsule may be sealed after water is added, thus controlling $f$H$_2$O.
2.5.10 Firing

During firing brick, several processes take place, such as: loss of water (surface and chemically combined), mineral decomposition, carbon burn out, the quartz inversion and vitrification. Most hygroscopic water evaporates close to 100°C [24]. Clays also loose water through dehydroxylation, which is the removal of chemically combined water. This reaction occurs at different temperatures for different minerals. For example dehydroxylation occurs from about 400°C to 700°C in kaolin by the reaction

\[
\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3.2\text{SiO}_2 + 2\text{H}_2\text{O} \quad [25]
\]

Dehydroxylation in montmorillonite occurs by the reaction

\[
\text{Al}_2\text{O}_3.4\text{SiO}_2.2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3.4\text{SiO}_2+2\text{H}_2\text{O}
\]

The reaction occurs in two steps, and the first larger reaction in montmorillonite occurs from about 600°C to 800°C. The second smaller reaction occurs from about 850°C to 925°C [25]. Muscovite mica is another mineral that can be present and it dehydroxylates close to 700°C [17].

Occasionally the material making up the brick contains accessory minerals such as pyrite (FeS₂) and limestone (CaCO₃). Pyrite decomposes by a two step exothermic oxidation reaction. The first step reaction occurs at 380°C where the pyrite breaks down into iron sulfide and sulfur dioxide by the following reaction:

\[
\text{FeS}_2 + \text{O}_2 \rightarrow \text{FeS} + \text{SO}_2
\]

In the second step the iron sulfide is oxidized into red iron and sulfur dioxide at around 412°C.

\[
\text{FeS} + 7\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2
\]

Limestone decomposes into calcium oxide and carbon dioxide at close to 800°C by an endothermic reaction [24].

Most of the carbon in clay is from decayed plant or animal matter that has not oxidized from natural processes. This carbon will being to oxidize at 290°C to 340°C by the combustion reaction:

\[
\text{C} + \text{O}_2 \rightarrow \text{CO}_2
\]
And the reaction mainly occurs at the surface. The quartz inversion occurs at 573°C at one atmosphere pressure and due to quartz changing from its low temperature to high temperature form, α to β (Fig. 2.1).

Fig. 2.1. Pressure temperature phase diagram for SiO₂ [26].

### 2.6 Beneficiation

Beneficiation is mainly the treatment of raw material (such as pulverized ore) to improve physical or chemical properties in preparation for further processing. Beneficiation techniques include washing, sizing of particulates, and concentration (which involves the separation of valuable minerals from the other raw materials received from a grinding mill). Vast quantities of metals and minerals are essential to the survival of industrial societies. Most of these commodities do not occur naturally in forms suitable for direct use but must be concentrated and purified and this process of concentration is minerals beneficiation. Beneficiation also is used in the ceramics and clay industries.

The presence of iron bearing materials impairs the usefulness of industrial raw materials such as quartz, clay and affects their utility for various applications [27]. Traditionally iron is removed by physical separation techniques, but hydrometallurgical treatment such as acid washing is the more effective and widely employed process [28-31]. Recent studies have shown that even traces of iron can be removed by acid washing [32]. In the present study the raw material, clay was beneficiated with an aim to remove iron in it.
2.6.1 Hydrometallurgical treatment

Hydrometallurgy is a process of beneficiation as well as extraction. Hydrometallurgical processing is generally carried out on low grade ores. Hydrometallurgical beneficiation of clay usually refers to the removal of unwanted materials by leaching.

2.6.2 Leaching

Leaching was performed to remove iron oxides contained in the clay, in other words the clay was washed by an acid solution. Both inorganic and organic acids have been used for washing of clays. Results of investigations on leaching of iron oxides in clays in oxalic acid solutions dominate the published literature. Chiaraizia and Horwitz [33] studied dissolution of goethite in several organic acids in the presence of reducing agents. They found the ascorbic acid, sodium dithionite and sodium formaldehyde-sulfoxylate (SFS) as the effective reducing agents. They also found that SFS was the best agent because the ascorbic acid is effective only at high temperature, and Na2S2O4 rapidly decomposes in the acidic medium generating colloidal sulfur which can slow down the dissolution process at low temperatures. Panias et al. [34] examined the mechanisms of dissolution of iron oxides in aqueous oxalic acid solution. They found that the dissolution of iron oxide with organic acids comprises three distinct steps-first one is chemisorption, adsorption of organic ligands on the iron oxide surface. The second one is non-reductive dissolution which is simply desorption process of surface iron ligand complexes and the third one is reductive dissolution which is the main mechanism of iron oxide dissolution with organic acids. Sung Oh Lee et al. [35] worked on the optimization of pH level and pH control of the leaching solution of oxalic acid. They showed that when a control on pH is required NH₄OH offers the best solution to be used for the neutralization as more soluble oxalate species was found in the leachant and NaOH and KOH form more stable and less soluble species which decrease the level of soluble oxalate species in the solution. Ambikadevi and Lalithambika [36] tested several organic acids such as formic, acetic, succinic, tartaric, citric, L-ascorbic and oxalic acid and concluded that oxalic acid is the most efficient that can be used to dissolve iron oxide from ceramic minerals.

Results of investigations on leaching of iron oxides in clays in inorganic acids solutions, on the other hand, are rather limited. Sidhu et al investigated the dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids [37]. Some researchers also intended to determine the rate of reactions, rate controlling steps and reaction mechanisms for the leaching of iron with both organic (i.e. Oxalic acid) and Inorganic acid (i.e. HCl) [31, 38, 39].
2.6.3. Leaching kinetics

Leaching is a heterogeneous reaction that takes place at the interface between a solid and liquid phase and sometimes also a gaseous phase. At the boundary between the two phases a diffusion layer is formed. In the case of a solid in an aqueous phase this layer consists of a stationary aqueous layer. The diffusion layer can be thinned by vigorous stirring but never be completely removed. Typical thickness of the diffusion layer in a well stirred system is in the range of 1-10 μm. The schematic representation of a mineral surface during leaching is shown in Fig. 2.2.

![Schematic representation of mineral surface during leaching](image)

Fig. 2.2: Schematic representation of mineral surface during leaching

The kinetic step that determines the rate of leaching can be one or a combination of the followings:

1. Diffusion of reagent through the diffusion layer
2. Adsorption of reagent on surface
3. Reaction on the surface
4. Desorption of product from surface
5. Diffusion of product through the diffusion layer
The slowest step in the leaching reaction is the rate-controlling step. Depending on which process is rate-controlling, three different type reactions may be obtained, i.e., reaction controlled leaching, diffusion controlled leaching and intermediate controlled leaching whose are shown in Fig. 2.3.

![Different rate controlling steps in leaching kinetics](image)

**Fig. 2.3: Different rate controlling steps in leaching kinetics**

In fluid particle reaction kinetics, in which a gas or liquid contact with a solid, the reactions may be represented as follows:

\[
A \text{ (fluid)} + bB \text{ (solid)} = \text{ fluid products} \quad (2.1)
\]

\[
= \text{ solid products} \quad (2.2)
\]

\[
= \text{ fluid and solid products} \quad (2.3)
\]

As shown in Fig. 2.4, solid particles may remain unchanged in size during reaction when they contain large amounts of impurities which remain as a non-flaking ash or if they form a firm product material by the reactions of Eq. 2.2 or Eq. 2.3. Particles shrink in size during reaction when a flaking ash or product material is formed or when pure B is used in the reaction of Eq. 2.1.
2.6.3.1. Kinetic model selection

For the non-catalytic reaction of particles with surrounding fluid, two simple idealized models, the progressive-conversion model and the shrinking unreacted-core model can be considered [40]. In Progressive conversion model (PCM) reactant liquid enters and reacts throughout the particle at all times, most likely at different rates at different locations within the particle. In Shrinking core model (SCM), reaction occurs first at the outer skin of the particle. The zone of reaction then moves into the solid, leaving behind completely converted material and inert solid. Thus, at any time there exists an unreacted core of material which shrinks in size during reaction. In real situation, it is usually found that unreacted solid material is surrounded by a layer of ash. Evidence from a wide variety of situations indicates that in most cases the shrinking-core model (SCM) approximates real particles more closely than does the progressive conversion model (PCM). The following models are generally considered for the Shrinking core model.

1. Liquid film diffusion controlled
2. Chemical reaction controlled
3. Product layer diffusion controlled
4. Mixed kinetic mechanism

2.6.3.1.1. Liquid film diffusion controlled

The fraction of particle reacted at any time, t, in a liquid film diffusion control situation can be calculated from the following equation which apply to small particle moving in Stokes regime [41]

\[ t/\tau = 1-(1-X)^{2/3} \]

Where \( X = \frac{\text{Amount of reacted particle}}{\text{Total amount of particle}} \)

The time for complete disappearance of particle, \( \tau = \frac{\rho R_0^3}{2bCD} \)

Where, \( \rho \) is the molar density of the solid particle,
Ro = Original particle size
b = Stoichiometric coefficient of the reaction
D = Diffusion coefficient of the leaching reagent
C = Concentration of the leaching reagent

2.6.3.1.2 Chemical reaction controlled

The fraction of solid particle reacted at any time, t, in a chemical reaction controlled process can be calculated from the following equation which applies to both small and large particle moving in Stokes regime, considering those particles as shrinking spheres and also to the constant size sphere particles.

\[ t/\tau = 1-(1-X)^{1/3} \]

Again, the time for complete disappearance of particle, \( \tau = \frac{\rho R_0}{bkC} \)

Here, k = Rate constant of the reaction
2.6.3.1.3 Product layer diffusion controlled

Diffusion of the reagent or dissolved species through a solid reaction product at any time, t, can be calculated from the following equation

\[ \frac{t}{\tau} = (1-2X/3)-(1-X)^{2/3} \]

In this case, \( \tau = \frac{\rho R_0^2}{6 D C_0} \)

2.6.3.1.4 Mixed kinetic mechanism

Mixed controlled process is the combination of surface reaction and diffusion. The fraction of particle reacted at any time t under mixed controlled process can be expressed as follows.

\[ \frac{t}{\tau} = [(1-2X/3)-(1-X)^{2/3}] + b[1-(1-X)^{1/3}] \]

Where, \( b = \) Multiplying factor for chemical reaction.

2.6.4 Determination of activation energy

The energy that must be overcome for a chemical reaction to occur is called the activation energy. Activation energy can be thought of as the height of the potential barrier (sometimes called the energy barrier) separating two minima of potential energy (of the reactants and products of a reaction). For a chemical reaction to have a noticeable rate there should be a noticeable number of molecules with energy equal to or greater than the activation energy.
It is always possible to find out more than one set of configurational changes capable of providing a given transformation, called ‘reaction paths.’ However, because different transition configurations are involved, the activation energy is different. Only those with excess free energy equal to or greater than the activation energy will transform (Fig. 2.8). Those with insufficient free energy can transform by thermal activation [42].

The following effects of activation energy on reaction rate are generally considered:

1. Reactions with high activation energies are very temperature sensitive. Conversely, low activation energies imply lower temperature sensitivity of rate.
2. Temperature sensitivity of rate is more pronounced at lower temperature.
3. The pre-exponential factor in Arrhenius law has little effect on temperature sensitivity of reaction rate.
Chapter 3

Experimental

3.1 Introduction

The sample of clay for this study was collected from Narsingdi (near Dhaka), Bangladesh. The sample of clay was characterized. Subsequently it was leached in acids to examine if leaching could remove the iron contained in the clay sample.

3.2 Characterization of the sample

The clay was characterized by its moisture content, bulk density, organic matter content, pH, alkalinity, liquid limit, plastic limit, firing properties etc. X-ray fluorescence analysis, X-ray diffraction analysis, Thermogravimetric analysis and Differential thermal analysis were also done for the characterization of the sample.

3.2.1 Moisture content

Moisture content of clay is the ratio of the weight of water present to the weight of dry clay in a given mass. For the determination of moisture content in the clay sample, 5 gm of sample was weighed \( W_w \) and taken on a watch glass. The sample was then dried in an oven at 110°C to a constant weight. After drying, the sample was weighed \( W_d \) again and the difference between the two weights was used for the determination of moisture content of the clay.

\[ m = \frac{W_w - W_d}{W_d} \times 100 \]
3.2.2 Bulk density

Bulk density is the ratio of the mass to the bulk volume of clay particles plus pore spaces in the sample. The pycnometer method was used to determine the bulk density of the clay. In this method an empty pycnometer of 50 ml capacity ($V_p$) was weighed ($W_p$). It was half filled with clay sample and then filled with distilled water and weighed ($W_p+W_s+W_{rl1}$). The sample of clay and water were removed and the pycnometer was again filled with water and weighed ($W_p+W_{rl2}$). The bulk density of the clay sample was determined as follows:

- **Calculation**
  1. Weight of the sample; $W_s = (W_p+W_s) - W_p$.
  2. Weight of the liquid; $W_l = (W_p + W_{rl2}) - W_p$.
  3. Density of the liquid; $\rho_l = W_l/V_p$.
  4. Weight of the liquid used to immersed the sample; $W_{il} = (W_p+W_s+W_{rl1}) - (W_p+W_s)$.
  5. Volume of liquid used to immerse the sample; $V_{il} = W_{il}/\rho_l$.
  6. Volume of the sample; $V_s = V_p - V_{il}$.
  7. Density of the sample; $\rho_s = W_s/V_s$.

3.2.3 Organic matter content

Organic matter influences many of the physical, chemical and biological properties of clay. It affects the water holding capacity and the ceramic properties of the clay too. The presence of organic matter in clay may cause the development of a ‘black core’ (a central area of different color, varying from black to yellow in the ceramic parts). These black cores are not expected in the finished products. The organic matter in the clay sample was determined according to the ASTM D 2974 [43]. Firstly an empty, clean and dry porcelain dish was weighed ($M_P$). Then a part of entire oven dried test specimen was placed in the dish and the weight of the dish and clay specimen was determined ($M_{PDS}$). The dish was then placed in a muffle furnace and the temperature of the furnace was gradually increased to 440°C and the specimen was left there.
overnight. Then the dish was removed carefully using tongs and it was allowed to cool to room
temperature and the mass of the dish containing burned clay was determined ($M_{PA}$).

- **Calculation**
  
i) Mass of the dry clay; $M_D = M_{PDS} - M_P$.
  
ii) Mass of the burned clay; $M_A = M_{PA} - M_P$.
  
iii) Mass of the organic matter; $M_O = M_D - M_A$.
  
iv) Organic matter content; $OM = (M_O/M_D) \times 100$.

### 3.2.4 pH

The pH is a measure of its acidity or basicity. The pH measurement was made on a 1:2 clay :
water mixture. 10 gm of the clay sample was shaken for 30 minutes with 20 ml of distilled water.
The pH of the supernatant was determined.

### 3.2.5 Alkalinity

Alkalinity was determined by acid neutralization method. 5 gm of clay was treated with 50 ml of
0.5N HCl in a 250 ml beaker. The mixture was boiled gently for 5 minutes and then cooled and
filtered. The residue was washed thoroughly with distilled water to remove excess acid. The
filtrate along with the washings was titrated against 0.25 N NaOH solution.

- **Calculation**
  
  \[
  \text{Alkalinity} = \left( \frac{cm^3 \text{ of HCl} \times N - cm^3 \text{ of NaOH} \times N}{gm \text{ oven dry clay}} \right) \times 0.05 \times 100
  \]

### 3.2.6 Atterberg limit

The Swedish scientist Albert Atterberg originally defined ‘seven limits of consistency’ to classify
fine-grained clays. In current practice only two of these limits, the liquid limit and the plastic
limit are commonly used. These Atterberg limits are based on the moisture content of the clay.
The liquid limit is defined as the moisture content at which clay changes from a plastic to a
viscous fluid state. The plastic limit is the moisture content where the clay changes from a semi-
solid to a plastic (flexible) state. The procedures for determining these limits are described below:
**Liquid limit determination**

Fig 3.1 shows the apparatus used for the determination of liquid limit.

1) A certain quantity of clay sample was taken and placed on the porcelain dish. Clay was air-dried, and pulverized.

2) The clay was thoroughly mixed with a small amount of distilled water until a smooth uniform paste was obtained. The dish was covered to prevent moisture from escaping.

3) Adjustment of the liquid limit apparatus was done by checking the height of drop of the cup.

![Liquid limit device with grooving tool](image)

Fig. 3.1: Liquid limit device with grooving tool.
4) A portion of the previously mixed clay was placed into the cup of the liquid limit apparatus at the point where the cup rests on the base. The clay was squeezed down to eliminate air pockets and was spread into the cup to a depth of about 10 mm at its deepest point. The clay pat formed an approximately horizontal surface (Fig. 3.2).

5) The grooving tool was used carefully to cut a clean straight groove down the center of the cup (Fig. 3.3). Care was taken to prevent sliding of the sample relative to the surface of the cup.
6) The crank of the apparatus was turned at a rate of approximately two drops per second and the number of drops, N which takes to make the two halves of the clay pat come into contact at the bottom of the groove was counted (Fig. 3.4).

7) Sample for moisture determination was taken from the edges of the clay pat by using a spatula. The sample included clay from both the sides of where the groove came into contact. Then it was placed into the moisture can, covered and weighed immediately. The sample was then placed into the oven. Moisture can was left in the oven for 16 hours.
8) The entire clay specimen was remixed in the porcelain dish. A small amount of distilled water was added to increase the water content so that the number of drops required to close the groove decrease.

9) Steps 4 to 8 were repeated for producing successively lower numbers of drops to close the groove.

10) Water content of each of the moisture cans was calculated after it has been in the oven for 16 hours.

11) Number of drops (N) were plotted against the water content (w) and a best fit straight line was drawn though the plotted points and the water content at 25 drops was reported as the liquid limit (LL).
Plastic limit determination

1) Original clay sample was taken and distilled water was added until the clay is at a consistency where it can be rolled without sticking to the hands.

2) The clay was formed into an ellipsoidal mass which was rolled between the fingers and the glass plate.

3) Sufficient pressure was used to roll the mass into a thread of uniform diameter as shown in Fig. 3.5(a) by using about 90 strokes per minute. (A stroke is one complete motion of the hand forward and back to the starting position.) The thread was deformed so that its diameter reaches 3.2 mm (1/8 in.).

![Fig.3.5: Threading (a) and crumbling (b) of clay mass.](image)

4) When the diameter of the thread reached the correct value, the thread was broken into several pieces. The pieces were kneaded and reformed into ellipsoidal masses and re-rolled. These alternate rolling, gathering together, kneading and re-rolling were continued until the thread crumbles under the pressure required for rolling and can no longer be rolled into a 3.2 mm diameter thread (Fig.3.5 (b)).
5) The portions of the crumbled thread were gathered together and placed into a moisture can and covered. The moisture can containing the clay was weighed and placed into the oven and left for 16 hours.

6) Steps 2 to 5 were repeated for the successive determination of plastic limit of the clay.

7) Water content of each of the moisture cans was calculated after they have been in the oven for 16 hours and the average water content was computed to determine the plastic limit (PL).

8) Plasticity index was calculated as, $\text{PI} = \text{LL} - \text{PL}$.

3.2.7 X-ray diffraction analysis

X-ray diffraction analysis was conducted to identify the phases present in the clay sample. The diffraction patterns were recorded on powdered sample using an X-Ray diffractometer (Model: Philips X-Pert).

Fig. 3.6: Analytical X-ray diffraction machine.
Before recording the pattern the sample of clay was prepared by using the following procedure:

1) Two gm of samples was finely ground in an agate mortar.

2) The diffraction patterns were recorded in the 2θ range of 0° to 45° with a Cu Kα radiation (λ=1.54056 Å) with an accelerating voltage of 40 KV and a scanning speed of 2°/min.

3) The diffraction lines in the recorded patterns were matched with data in the Powder Diffraction Files of ICDD (International Center for Diffraction Data). Major peaks in the diffraction pattern were marked.

The operating conditions that were maintained during the recording of the patterns were:

- Voltage and current: 40 KV and 30 mA
- Water flow rate: 4.7 L/min
- X-ray generator source: Cu anode [Wavelength of CuKα: 1.54016 Å]
- Window for X-ray filter: Be window

3.2.8 X-ray fluorescence (XRF) analysis

The chemical composition of the clay sample was determined by using an X-ray fluorescence equipment (Model: Rigaku ZSX Primus XRF, SN:FR0800g-2). The sample for X-ray fluorescence analysis was prepared in the following way.

1) About 2 gm of samples was finely ground in an agate mortar. The prepared powder was made moisture free.

2) The powder was placed in a die and then pressed in a hand press machine to prepare disk shaped sample for analysis.

3) The disk shaped samples were placed in the machine for analysis.

4) During analysis the following operating conditions were maintained:

   - Operating current: 40 mA; Operating voltage: 50 KV.
   - P10 gas (90% argon and 10% methane gas mixture) flow rate: 5.0 ml/min.
3.2.9 Thermogravimetric analysis and differential thermal analysis (TGA-DTA)

Thermogravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature and temperature change. During the analysis the temperature is increased at a predetermined and preferably linear rate. Thermogravimetric analysis is commonly employed in research to determine such characteristics as degradation temperatures, absorbed moisture content, the level of organic and inorganic components in materials, etc. Differential thermal analysis (DTA) on the other hand measures...
heat absorption or evolution in a sample. The results indicate crystallization, phase changes, etc as well as reactions. Together, they form a powerful tool for analysis.

Simultaneous TGA-DTA/DSC measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties simplifies the interpretation of the results. The complimentary information obtained allows differentiation between endothermic and exothermic events with no associated weight loss (e.g., melting, crystallization) and those that involve a weight loss (e.g., degradation).

For the experiment the inert (N\textsubscript{2}) and oxidative (O\textsubscript{2}) gas flow rates were set to provide the appropriate environments. The test material was placed in the specimen holder and the furnace was raised. The initial weight reading was set to 100\% and the heating program was initiated. The gas environment was preselected for either a thermal decomposition (inert - nitrogen gas), an oxidative decomposition (air or oxygen), or a thermal-oxidative combination. A plot of percent weight loss versus temperature was obtained.
3.2.10 Firing properties

3.2.10.1 Making of bricks

To test the firing properties of the clay four sets of bricks (each set containing 2 bricks) were made and fired at four different temperatures. The bricks were made in a metal mould [Fig.3.9] by manual hammering of the clay sample. The length and width of the metal mould were 77.1 mm and 38.15 mm respectively. For making of bricks at first, the clay sample was mixed with water (below plastic limit) and the mould was filled with the mixed sample. Then the sample was compacted by manual hammering and green bricks were obtained.

![Metal mould used for brick making.](image)

3.2.10.2 Firing of bricks

The bricks were fired at four different temperatures. Before firing in the high temperature furnace the bricks were dried in an oven at 110°C. Table 3.1 lists the temperatures of firing.

Table 3.1: Firing temperatures of bricks.

<table>
<thead>
<tr>
<th>No. of sets</th>
<th>Firing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900°C</td>
</tr>
<tr>
<td>2</td>
<td>950°C</td>
</tr>
<tr>
<td>3</td>
<td>1050°C</td>
</tr>
<tr>
<td>4</td>
<td>1100°C</td>
</tr>
</tbody>
</table>
The heating scheme for firing of bricks in a high temperature furnace is shown in Fig. 3.9. It can be seen that in the first step of heating to 570°C the rate was 5°C/min. At 570°C, the specimen was held for 1 hour to allow the total conversion of quartz (i.e. from α-quartz to β-quartz). Then, in the second step of heating, the sample was heated up to the desired temperature at a heating rate of 5°C/min. The specimen was held at the desired temperature for a period of 4 hour. After the holding period the sample was cooled to room temperature at a cooling rate of 1.2°C/min.

![Temperature profile of firing.](image)

**3.2.10.3 Dry weight of bricks (D)**

All the bricks were dried in an oven at 110°C. The dry weight \((D)\) in grams of all the bricks was then measured. The length, width and height of all the green and dried bricks were also determined.
3.2.10.4 Saturation

- The test specimens were placed in water and boiled for 2 hours. During boiling the specimens were entirely immersed in water and no contact with the heated bottom of the container was allowed.

- After boiling the specimens were cooled to room temperature while still immersed in water and kept immersed in water for 12 hours.

3.2.10.5 Suspended weight of bricks (S)

After boiling and cooling to room temperature, the suspended weight (S) of each brick was determined in grams by keeping the bricks suspended in water.

3.2.10.6 Saturated weight of bricks (W)

After determining the suspended weight, each brick was blot with a moistened cotton cloth to remove all drops of water from the surface. All the bricks were then weighed in air to determine the saturated weight (W) in grams. The blotting operation was performed carefully by rolling the bricks lightly on the cloth which was previously saturated with water so that the withdrawing of water from the pores of bricks can be avoided.

3.2.10.7 Calculations

- **Exterior volume:**

  The exterior volume (V) of the bricks in cubic centimeters was determined by subtracting the suspended weight (S) from the saturated weight (W).

  \[ V, \text{ cm}^3 = W - S \]

- **Volume of open pores and impervious pores:**

  Calculations for the open pores and impervious pores in the bricks were as follows:

  \[ \text{Volume of open pores, cm}^3 = W - D. \]

  \[ \text{Volume of impervious pores, cm}^3 = D - S. \]

  where, \( W = \text{Saturated weight of brick.} \)
D = Dry weight of brick.

S = Suspended weight of brick

- **Apparent porosity \((P)\):**

  The apparent porosity is expressed as the percentage of the volume of the open pores in the specimen to its exterior volume. The apparent porosity, \(P\) was calculated as follows:

  \[
P, \% = \frac{W - D}{V} \times 100
  \]

  where,
  
  \(W\) = Saturated weight of brick.

  \(D\) = Dry weight of brick.

  \(V\) = Exterior volume of brick.

- **Water absorption \((A)\):**

  The water absorption, \(A\) is expressed as the percentage of the weight of water absorbed to the weight of dry specimen. The water absorption, \(A\) was calculated as follows:

  \[
  A, \% = \frac{W - D}{D} \times 100.
  \]

  where,
  
  \(W\) = Saturated weight of brick.

  \(D\) = Dry weight of brick.

- **Apparent specific gravity \((T)\):**

  The apparent specific gravity, \(T\), was calculated as follows:

  \[
  T = \frac{D}{D - S}.
  \]

  where,
  
  \(D\) = Dry weight of brick.

  \(S\) = Suspended weight of brick.

- **Bulk density \((B)\):**

  Dry weight of the specimen divided by its exterior volume (including pores) was reported as the bulk density of the specimen.
3.2.10.8 Cold crushing strength of bricks

The dimensions of the test specimen were measured along its length, width and height to find out its average cross-sectional area. Then the specimen was placed centrally in between the two compression plates. Load was applied on the specimen by moving the movable head until the specimen fails. The maximum load was recorded.

Fig.3.11: Crushing test assembly.

Calculations

The cold crushing strength was calculated as follows:

\[ S = \frac{W}{A} \]

where,

\[ S = \text{cold crushing strength.} \]

\[ W = \text{total maximum load indicated by the testing machine.} \]
A = Average of the areas of the top and the bottom of the specimen perpendicular to the line of the application of load.

3.3 Hydrometallurgical treatment of clay

The sample of clay under investigation, as determined by X-ray fluorescence spectroscopy, contained 27.5% of alumina, 59.5% of silica and 8.15% of iron oxide. As the iron bearing materials affect the utility of clay for various applications, an attempt was made to remove iron from the clay by acid washing. This beneficiation of the clay sample was done by both an organic (oxalic) and an inorganic (hydrochloric) acid. The concentrations of acid, time, temperature and stirring speed were optimised and the kinetic parameters were determined.

3.3.1 Leaching for iron removal

Leaching was done in an organic (oxalic acid) and an inorganic acid (hydrochloric acid). Leaching was carried out in a round bottom flask with a reflux condenser attached to it. The round bottom flask was heated by a mantle heater. The experimental setup is shown in Fig. 3.11. Leaching reagents oxalic acid and hydrochloric acid of different concentrations were prepared in a 500 ml volumetric flask. For all leaching experiments, 6 gm of solids (i.e. clay) was leached in a 400 ml leaching solution in the temperature range of 40°C to 100°C. The maximum time period for each leaching experiment was 100 minutes. During leaching the solution was continuously stirred by a mechanical stirrer. Leach liquor samples were taken for analysis at definite intervals during leaching. 10 ml leach liquor was taken with 10 ml pipette for analysis by UV spectrophotometry. Leaching parameters used to investigate in this work is summarized in Table3.2.
3.3.2 Leaching variables

In the leaching experiment the acid concentration was varied for both the oxalic and hydrochloric acid as well as the time, temperature and stirring speed to get the optimized leaching condition at which the best iron removal is possible. All the parameters that studied during leaching experiment are summarized in Table 3.2.

3.3.2.1 Effect of acid concentrations

To find out the optimum acid concentrations (i.e. oxalic acid and hydrochloric acid) at which the best iron removal is possible, the sample was leached at different acid concentrations at 100°C for 100 minutes. The stirring speed was 400 rpm. The concentrations used for both acids were 0.2 M, 0.4 M, 0.6 M, 0.8 M, 1.0 M, 1.2 M, 1.4 M, 1.6 M, 1.8 M, 2.0 M and 2.2 M. Then the
concentration of iron was plotted against the different concentrations of acids and the desired concentration was found out.

**3.3.2.2 Effect of time**

Effect of time on the leaching was studied for both the acids. During this study the acids concentrations were 1.8 M for oxalic acid and 1.6 M for hydrochloric acid, the temperature was 100°C and the stirring speed was 400 rpm. The time intervals were 1, 2, 4, 5, 10, 20, 30, 45, 60, 90 and 100 minutes. The concentrations of iron in the leach liquor were plotted against the time and the desired time at which the maximum iron removal is possible was determined.

**3.3.2.3 Effect of temperature**

To find out the temperature at which the maximum iron removal is possible, the effect of temperature on leaching was studied. The temperatures used for this study were 40°C, 50°C, 60°C, 70°C, 80°C, 90°C and 100°C. During this study the acids concentrations were 1.8 M for oxalic acid and 1.6 M for hydrochloric acid and the stirring speed was 400 rpm and the leaching period was 90 minutes. The concentrations of iron in the leach liquor were plotted against different temperatures and the temperature at which the maximum iron removal is possible was determined.

**3.3.2.4 Effect of stirring speed**

The effect of stirring speed was also investigated in this study. The different stirring speeds for this work were 200, 400, 600, 800 and 1000 rpm while the acids concentrations were 1.8 M for oxalic acid and 1.6 M for hydrochloric acid, the leaching period was 90 minutes and the temperature was 80°C. The concentrations of iron in the leach liquor were plotted against different stirring speeds and the desired speed at which the maximum iron removal is possible was determined.
Table 3.2: List of leaching parameters that has been used in this study.

<table>
<thead>
<tr>
<th>Name of the parameters</th>
<th>Values of the parameters</th>
<th>Constant parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of leaching reagents (i.e. Oxalic acid and HCl)</td>
<td>0.2 M</td>
<td>Time 100 minutes, temperature 100°C, stirring speed 400 rpm.</td>
</tr>
<tr>
<td></td>
<td>0.4 M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6 M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8 M</td>
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<td></td>
<td>1.0 M</td>
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<td>1.2 M</td>
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<td></td>
<td>1.4 M</td>
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<td></td>
<td>1.6 M</td>
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</tr>
<tr>
<td></td>
<td>2.0 M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.2 M</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>1 minute</td>
<td>Acid concentrations 1.8 M (Oxalic acid) and 1.6 M (HCl), temperature 100°C, stirring speed 400 rpm.</td>
</tr>
<tr>
<td></td>
<td>2 minutes</td>
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<td></td>
<td>4 minutes</td>
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<td>90 minutes</td>
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<tr>
<td></td>
<td>100 minutes</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>40°C</td>
<td>Acid concentrations 1.8 M (Oxalic acid) and 1.6 M (HCl), time 90 minutes, stirring speed 400 rpm.</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
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<td></td>
<td>60°C</td>
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<td>70°C</td>
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<td></td>
<td>80°C</td>
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<td></td>
<td>90°C</td>
<td></td>
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<tr>
<td></td>
<td>100°C</td>
<td></td>
</tr>
<tr>
<td>Stirring speed</td>
<td>200 rpm</td>
<td>Acid concentrations 1.8 M (Oxalic acid) and 1.6 M (HCl), time 90 minutes, temperature 80°C.</td>
</tr>
<tr>
<td></td>
<td>400 rpm</td>
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<td></td>
<td>600 rpm</td>
<td></td>
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<tr>
<td></td>
<td>800 rpm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000 rpm</td>
<td></td>
</tr>
</tbody>
</table>
3.3.3 UV spectrophotometric determination of iron dissolution

For the analysis of iron dissolution in Shimadzu UV-vis spectrophotometer, tartaric acid, thyoglycholic acid, nitric acid and ammonia solution were used as complexing agents. The details of the procedure [44] are shown in the following flow sheet:

![Flow sheet for iron estimation](image_url)

Fig.3.13: Flow sheet for iron estimation.
3.3.4. Kinetic study of iron dissolution

While leaching, the rate of reaction and the reaction mechanism for both the oxalic acid and hydrochloric acid were also determined. For this kinetic study the particles of the clay sample were assumed to be perfectly spherical and the shrinking core model was used for investigation as it is preferred for solid spherical particle reaction kinetics. For the kinetics of dissolution of iron, experimental data was matched with the data of the following models:

1. Chemical reaction controlled process:

\[
t/\tau = 1 - (1-X)^{1/3} \]

(1)

2. Liquid film diffusion controlled process:

\[
t/\tau = 1 - (1-X)^{2/3} \]

(2)

3. Diffusion controlled process:

\[
t/\tau = 1 - 2/3X - (1-X)^{2/3} \]

(3)

4. Mixed controlled process:

\[
t/\tau = [1 - 2/3X - (1-X)^{2/3}] + b[1 - (1-X)^{1/3}] \]

(4)

Where,

\[
X = \text{Fraction of reacted particles.} \\
\tau = \text{Time for the complete conversion of a particle.} \\
b = \text{Multiplying factor for chemical reaction.}
\]
3.3.5 Determination of activation energy

The Arrhenius equation was used for the determination of activation energy.

Arrhenius equation: \( K = A \exp\left(-\frac{E}{RT}\right) \)
Therefore, \( \ln K = \ln A - \frac{E}{RT} \)

Where,
E= Activation energy
R= Universal gas constant
T = Reaction temperature
A = Pre-exponential factor.

3.3.5.1 Integral approach

In the integral form, \( t/\tau \) versus time (t) were plotted. The reaction rate constants, k, at various temperatures for both oxalic acid and hydrochloric acid leaching were obtained from linearised plots of \( t/\tau \) versus time (t). The rate constant, k was then plotted against temperature according to the Arrhenius type equation.

The plot of \( \ln K \) vs. \( 1/T \) was a straight line and the slope of this straight line is equal to \(-E/R\).

3.3.5.2 Differential approach

In the differential approach, the time \( (t_x) \) required for a given value of X (i.e., fraction of reacted particle) was calculated first and then plots of \( \ln(t_x) \) versus temperature were obtained.

As before the slop of this curves are equal to \(-E/R\) and the activation energies were estimated.
Chapter 4

Results and Discussion

4.1 Characterization of the sample

All the experimental results of moisture content, bulk density, organic matter, pH, alkalinity, liquid limit, plastic limit, firing properties etc of clay are discussed in the proceeding sector. Also the X-ray fluorescence analysis, X-ray diffraction analysis, Thermogravimetric analysis and differential thermal analysis have been shown for the characterization of the clay.

4.1.1 Moisture content

For the moisture content determination in the clay, 5 gm of sample was weighed and dried in an oven at 110\(^0\) C to a constant weight. After drying, the sample was again weighed and the difference between the two weights was used for the determination of moisture content of the clay and it was found that the average moisture content (\%m) in the clay is 3.27 \% which is very low.

4.1.2 Bulk density

Bulk density of the clay was measured by pycnometer method where the pycnometer was of 50 ml capacity. The bulk density (\(\rho_s\)) of the sample was found to be 2.28 g/cc.

4.1.3 Organic matter

The organic matter content in the clay is the ratio, expressed as a percentage of a mass of the organic matter in a given mass of clay to the mass of the dry clay solids. For the present study the ASTMD 2974 method was followed for the determination of the organic matter in clay sample. It was found that the organic matter in the clay was about 6.31\%.

4.1.4 pH of the clay

The pH of clay sample was measured on 1:2 clay: water mixture basis. 10 gm of the clay sample was shaken for 30 minutes with 20 ml of distilled water. The pH of the supernatant was
determined with combined glass electrode and pH meter and it was found that the pH of the clay is 5.16 which means that the clay is acidic in nature.

4.1.5 Alkalinity

For the determination of alkalinity of the clay, 5 gm of sample was treated with 50 ml of 0.5N HCl and the filtrate along with the washings was titrated against 0.25 N NaOH solutions. The alkalinity of the clay was found 4.41 (wt.%).

4.1.6 Atterberg limit

The Atterberg limits that illustrate the three different states were determined. These three states define the water content borders between viscous fluid, plastic and non-plastic states. The final values for Atterberg limit of the clay was as follows:

The average liquid limit is 45.27, the plastic limit is 33.81 and the plasticity index is 11.46. The liquid limit of the clay was also calculated from the graph shown in Fig.4.1. In the graphical method the water content (wt%) in the clay at the blow number of 25 is considered as the liquid limit [11]. From the graph in Fig.4.1 it was found that the liquid limit of the clay is 44.9 as the water content is 44.9% at blow number of 25.

Fig.4.1: Plot of moisture content (w%) versus number of blows for determining liquid limit of the clay.
4.1.7 X-ray diffraction (XRD)

The mineralogical composition of the clay was investigated with X-ray diffraction. The sample contains mostly quartz and small amount of kaolinite.

Fig.4.2: XRD pattern of the clay (as received).
4.1.8 X-ray fluorescence (XRF)

The clay sample was analyzed by X-ray fluorescence to determine the composition and the result is given in table 4.1.

Table 4.1: Compositional analysis of the clay

<table>
<thead>
<tr>
<th>No.</th>
<th>Components</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al₂O₃</td>
<td>27.49</td>
</tr>
<tr>
<td>2</td>
<td>Fe₂O₃</td>
<td>8.14</td>
</tr>
<tr>
<td>3</td>
<td>SiO₂</td>
<td>59.45</td>
</tr>
<tr>
<td>4</td>
<td>CaO</td>
<td>0.21</td>
</tr>
<tr>
<td>5</td>
<td>K₂O</td>
<td>2.59</td>
</tr>
<tr>
<td>6</td>
<td>MgO</td>
<td>0.52</td>
</tr>
<tr>
<td>7</td>
<td>Na₂O</td>
<td>0.22</td>
</tr>
<tr>
<td>8</td>
<td>TiO₂</td>
<td>0.85</td>
</tr>
<tr>
<td>9</td>
<td>MnO</td>
<td>0.08</td>
</tr>
<tr>
<td>10</td>
<td>Cr₂O₃</td>
<td>0.03</td>
</tr>
<tr>
<td>11</td>
<td>SO₃</td>
<td>0.11</td>
</tr>
<tr>
<td>12</td>
<td>Cl</td>
<td>0.02</td>
</tr>
<tr>
<td>13</td>
<td>P₂O₅</td>
<td>0.08</td>
</tr>
<tr>
<td>14</td>
<td>Co₂O₃</td>
<td>0.005</td>
</tr>
<tr>
<td>15</td>
<td>CuO</td>
<td>0.007</td>
</tr>
<tr>
<td>16</td>
<td>ZnO</td>
<td>0.005</td>
</tr>
<tr>
<td>17</td>
<td>Ga₂O₃</td>
<td>0.004</td>
</tr>
<tr>
<td>18</td>
<td>SrO</td>
<td>0.003</td>
</tr>
<tr>
<td>19</td>
<td>Y₂O₃</td>
<td>0.01</td>
</tr>
<tr>
<td>20</td>
<td>ZrO₂</td>
<td>0.032</td>
</tr>
<tr>
<td>21</td>
<td>BaO</td>
<td>0.07</td>
</tr>
<tr>
<td>22</td>
<td>PbO</td>
<td>0.008</td>
</tr>
<tr>
<td>23</td>
<td>Rb₂O</td>
<td>0.013</td>
</tr>
<tr>
<td>24</td>
<td>NiO</td>
<td>0.01</td>
</tr>
</tbody>
</table>
From the above table it can be seen that the major constituent of the clay is silica. The clay also contains a significant amount of alumina. The sample contains 8.23% iron. This makes the clay red in colour. Other elements are insignificant and can be considered as the trace elements.

**4.1.9 Thermogravimetric analysis and differential thermal analysis (TGA-DTA)**

During the thermogravimetric analysis the change in mass of the sample was determined at a heating rate of 20°C/minute. Both inert gas atmosphere (nitrogen) and oxidative atmosphere (air) were used for the thermogravimetric analysis. The TGA and DTA curve of the as-received sample in the nitrogen atmosphere is shown in Fig. 4.3. It can be seen that the sample lost mass up to a temperature of about 500°C and after that the curve indicates gain in mass in the sample. The mass loss up to about 500°C may be related to the loss of moisture and the organic matters contained in the raw sample. The sample showed continuous gain in mass as the heating continued above 500°C. This gain in weight at temperatures above 500°C was rather interesting.

A similar trend could be noticed during heating in air (Fig. 4.4). In other words the gain in weight could be observed during heating in both the inert environment (i.e. N₂ gas) and in the oxidative environment (i.e. air).

To investigate further the as-received sample was heated to 500°C, soaked at that temperature for 30 minutes and then subjected to thermogravimetric analysis. Fig. 4.5 and Fig. 4.6 show the TG-DTA curves of the heat treated sample for the inert nitrogen environment and the air environment respectively. These curves do not show any loss of mass during heating to 500°C. In the as-received sample the weight loss at temperatures up to 500°C has been attributed to the loss of moisture and organic matters contained in the as-received sample. In the heat treated samples moisture and organic matter was lost during the heat treatment. Thus no mass loss occurred during thermogravimetric analysis.

Fig 4.3 and Fig.4.4 show that the loss in mass of the as-received sample in nitrogen environment (9.5%) was more than that in the air environment (2.9%) This difference in loss in mass during heating to 500°C in the two environments also calls for an explanation. Nitrogen gas used in these experiments was not free from oxygen, i.e., the gas contained oxygen as impurities. One possible explanation could be as follows: In the nitrogen environment only little oxygen was available (as impurities) and this was probably just sufficient to cause burning of the organic matters contained in the sample. In the air environment, on the other hand, enough oxygen was available to cause burning of the organic matter as well as for some other reactions which could
Fig. 4.3: TGA-DTA curve of the as-received sample (N₂ environment).

Fig. 4.4: TGA-DTA curve of the as-received sample (air environment).
Fig. 4.5: TGA-DTA curve of the heat treated sample (N\textsubscript{2} environment).

Fig. 4.6: TGA-DTA curve of the heat treated sample (air environment)
be the reason for some gain in mass in the first region of TG-DTA curves (i.e. before 500°C). Thus a part of loss of mass in the air environment due to loss of moisture and organic matter was compensated by the gain in mass due to the reaction products. This led to a lower loss of mass in air environment.

The heat treated sample (i.e. sample heated to 500°C and soaked at this temperature) was also subjected to x-ray diffraction analysis. The x-ray diffraction patterns of as-received sample and the heat treated sample is superimposed in Fig.4.7. It can be seen that the diffraction lines in both the patterns appear at the same angles. In other words the diffraction patterns recorded on as-received and on heat treated samples are identical. Thus the difference in weight loss cannot be related to any phase change during heating.

A continuous gain in mass was observed during heating of as-received sample at temperatures above 500°C and in the heat treated samples at all temperatures. The reason for this gain in mass could not be ascertained and needs further investigation.

![Fig.4.7: XRD pattern of as-received sample and the heat treated sample (i.e. treated at 500°C).](image-url)
4.1.10 Properties of fired bricks

The properties of interest of the fired bricks are density, porosity, water absorption and specific gravity because these properties are related to the durability of bricks. Fig.4.8 shows a brick after firing.

From the Fig.4.9 and Fig.4.10 it is evident that the porosity decreases and density increases with higher firing temperatures which are expected. Higher firing temperature increases the density because more energy is delivered to the brick which drives the sintering reaction further.

![Fig.4.8: Brick after firing.](image)

![Fig.4.9. Plot of apparent porosity versus temperature for fired bricks](image)
From the Fig.4.11 it is also evident that the apparent porosity decreases as the bulk density increases.
Fig. 4.12 shows that as the bulk densities of the bricks increase with the firing temperature, the water absorption capacity decreases. This is to be expected.

Fig. 4.12: Plot of water absorption versus bulk density of the fired bricks.

Fig. 4.13: Plot of water absorption and shrinkage versus temperature.
Fig.4.13 shows the reciprocal relationship between the total shrinkage of the bricks and the water absorption. As the temperature for firing increases the shrinkage increases and the water absorption decreases. The fired properties of the bricks are summarized in Table 4.2.

Table 4.2: Fired properties of bricks.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Firing temperature(°C)</td>
<td>1100°C</td>
<td>1050°C</td>
<td>950°C</td>
<td>900°C</td>
</tr>
<tr>
<td>Exterior volume (V,cm³)</td>
<td>50.108</td>
<td>64.749</td>
<td>69.092</td>
<td>83.091</td>
</tr>
<tr>
<td>Apparent porosity (%P)</td>
<td>10.43</td>
<td>14.44</td>
<td>18.27</td>
<td>21.41</td>
</tr>
<tr>
<td>Apparent specific gravity (T)</td>
<td>2.51</td>
<td>2.51</td>
<td>2.44</td>
<td>2.53</td>
</tr>
<tr>
<td>Bulk density (gm/cm³)</td>
<td>2.25</td>
<td>2.15</td>
<td>2.01</td>
<td>2.0</td>
</tr>
<tr>
<td>Total shrinkage (%)</td>
<td>23.3</td>
<td>20.8</td>
<td>10.1</td>
<td>4.8</td>
</tr>
<tr>
<td>Water absorption (%A)</td>
<td>4.64</td>
<td>6.71</td>
<td>8.83</td>
<td>10.75</td>
</tr>
</tbody>
</table>

4.1.11 Cold crushing strength

The cold crushing strength was measured in the Universal Testing Machine by crushing the fired bricks. Fig.4.14 shows the results on the measurement of crushing strengths of the bricks. From the figure it can be seen that the crushing strength increases with an increase in firing temperature. Maximum strength of 40.724N/mm² was obtained for the brick fired at 1100°C.

Fig.4.14: plot of compressive strength versus firing temperature.
4.2 Leaching results

4.2.1 Acid concentration optimization

The concentrations used for leaching for both oxalic acid and hydrochloric acid were 0.2 M, 0.4 M, 0.6 M, 0.8 M, 1.0 M, 1.2 M, 1.4 M, 1.6 M, 1.8 M, 2.0 M and 2.2 M. Fig. 4.15 shows the plot of concentration of iron in the leaching solution versus acid concentrations. From the figure it can be seen that the rate of iron dissolution is directly affected by hydrogen ion [H+] concentration in the leach liquor. The higher the concentration of acids, the higher is the extent of dissolution of iron oxide. The increase in the extent of removal of iron is negligible at concentrations higher than 1.8 M for oxalic acid and 1.6 M for hydrochloric acid.

![Effect of acid concentration on the dissolution of iron for both oxalic acid and hydrochloric acid.](image)

4.2.2 Time optimization

The optimum time for leaching was determined by leaching for times of 1, 2, 4, 5, 10, 20, 30, 45, 60, 90 and 100 minutes. Fig. 4.16 shows the results obtained. It can be seen that the curves become almost flat within a very short period of time and later on the removal of iron is almost negligible. For both the acids (i.e. oxalic acid and hydrochloric acid) the maximum removal of iron could be obtained in about 50 minutes.
4.2.3 Temperature optimization

Effects of temperature on leaching were studied by leaching at 40°C, 50°C, 60°C, 70°C, 80°C, 90°C and 100°C (Fig.4.17). It can be seen that the removal of iron is negligible at temperatures above 80°C. Thus 80°C was taken to be the optimum temperature for leaching operation.

Fig.4.16: Effect of time on the dissolution of iron for both oxalic acid and hydrochloric acid.

Fig.4.17: Effect of temperature on the dissolution of iron for both oxalic acid and hydrochloric acid.
4.2.4 of Stirring speed optimization

Effects of stirring speed were studied by leaching at stirring speeds of 0, 200, 400, 600, 800 and 1000 rpm and the results are shown in Fig.4.18. It is evident that for oxalic acid, 800 rpm is the optimum speed. The removal of iron does not increase significantly when stirring speeds greater than 800 rpm is used. For leaching in hydrochloric acid the optimum speed was 600 rpm.

![Graph showing effect of stirring speed on Fe (ppm)]

Fig.4.18: Effect of stirring speed on the dissolution of iron for both oxalic acid and hydrochloric acid.

The optimum conditions for leaching both in oxalic acids and hydrochloric acid are summarized in the Table 4.3.

Table 4.3: Optimized values for leaching in both acids (i.e. oxalic acid and hydrochloric acid).

<table>
<thead>
<tr>
<th>Property</th>
<th>Optimized value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxalic acid</td>
</tr>
<tr>
<td>Acid concentration</td>
<td>1.8 M</td>
</tr>
<tr>
<td>Time</td>
<td>50 min</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Stirring speed</td>
<td>800 rpm</td>
</tr>
</tbody>
</table>
4.2.5 Characterization of the leached clay

4.2.5.1 X-ray diffraction (XRD)

X-ray diffraction analyses of clay in the as-received condition as well as after leaching (in both oxalic acid and hydrochloric acid) were done. Fig.4.19 shows the superimposed x-ray diffraction patterns under the three different conditions (i) Narshingdi clay in the as received condition, (ii) clay leached in oxalic acid and (iii) clay leached in hydrochloric acid. It can be seen that there is no significant change in the three x-ray diffraction patterns, the diffraction lines appear at the same angles in the three diffraction patterns. The intensity of the peaks, on the other hand, has changed to some extent for the leached clays. Appearance of diffraction lines at the same angles before and after leaching indicates that no phase change has occurred due to leaching. The intensity of the diffraction lines, on the other hand, is related to the quantity of the phases present. During leaching some components of clay was leached out leading to a change in the quantity of the phases present. This change in quantity caused the change in the intensity of the diffraction lines in the x-ray diffraction patterns.
Fig. 4.19: Three XRD patterns of (1) Narsingdi clay (as received), (2) leached in oxalic acid and (3) clay leached in hydrochloric acid.

1. As-received
2. Oxalic Acid
3. Hydrochloric acid
4.2.5.2 Thermogravimetric analysis and differential thermal analysis (TGA-DTA)

The phenomenon of gain in mass in the sample was also observed during the thermogravimetric analysis of clay leached in oxalic acid and in hydrochloric acid. In the as-received sample there was a loss in mass up to a temperature of about 500°C (Fig.4.3 and Fig.4.4). This was attributed to the loss of moisture and organic matter contained in the sample.

The thermogravimetric curves of the leached samples (leached both in oxalic acid and in hydrochloric acid) in air environment showed a little loss in mass and then the mass gain phenomenon was observed (Fig.4.20). For the nitrogen environment, on the other hand, no loss in mass could be detected and the curves showed only gain in mass (Fig.4.21).
Fig. 4.20: TGA-DTA analysis of leached clay (air environment).

Fig. 4.21: TGA-DTA analysis of leached clay (N₂ environment).
4.2.5.3 Atterberg limit

The average liquid limit for the clay leached in oxalic acid was 41.72 and the plastic limit was 28.37. The plasticity index was 13.35. On the other hand the liquid limit for the clay leached in hydrochloric acid was 40.46 and the plastic limit was 29.1. The plasticity index was 11.36. Table 4.4 shows a comparison of the values in the as received clay and in the leached samples of clay. It can be seen that there is no significant change in the Atterberg limit values of leached clays compared to that of as received clay.

Table 4.4: Atterberg limit in as-received clay and in samples leached in acids.

<table>
<thead>
<tr>
<th>Atterberg limit</th>
<th>As received sample</th>
<th>Leached sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oxalic acid</td>
</tr>
<tr>
<td>Liquid limit</td>
<td>45.27</td>
<td>41.72</td>
</tr>
<tr>
<td>Plastic limit</td>
<td>33.81</td>
<td>28.37</td>
</tr>
<tr>
<td>Plasticity index</td>
<td>11.46</td>
<td>13.35</td>
</tr>
</tbody>
</table>

Leaching did not modify the Atterberg limits significantly. However, the plasticity index could be improved by leaching in oxalic acid.

4.2.5.4 Organic matter content

Table 4.5 shows the organic matter content in the as received clay as well as in leached clays (both in oxalic acid and hydrochloric acid).

Table 4.5: Organic matter content in as received and leached clays.

<table>
<thead>
<tr>
<th></th>
<th>As received clay (%)</th>
<th>Leached clay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oxalic acid</td>
</tr>
<tr>
<td>Organic matter content</td>
<td>6.31</td>
<td>4.58</td>
</tr>
</tbody>
</table>

Leaching in both the acids (oxalic acid and hydrochloric acid) reduced the organic matter content. Hydrochloric acid was more effective than oxalic acid in removing organic matter. The organic matter content of the sample leached in oxalic acid was 4.58 % of and in the sample leached in hydrochloric acid was about 3.1%. It may be recalled that the organic matter content of the as-received sample was 6.31%.
4.2.5.5 Cold crushing strength

After leaching in optimized condition the clay sample was collected and two bricks were made-one from the clay leached in oxalic acid and one from the clay leached in hydrochloric acid. These bricks were fired at 1100°C and then were crushed. The cold crushing strength of these bricks were found 37.26 N/mm² (clay leached in hydrochloric acid) and 40.9 N/mm² (clay leached in oxalic acid). Table 4.6 shows a comparison of the cold crushing strength values in the received clay brick and in the leached clay brick.

Table 4.6: Cold crushing strengths in the as-received clay brick and leached clay brick.

<table>
<thead>
<tr>
<th></th>
<th>As received clay (N/mm²)</th>
<th>Leached clay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oxalic acid (N/mm²)</td>
</tr>
<tr>
<td>Cold crushing strength</td>
<td>40.724</td>
<td>40.9</td>
</tr>
</tbody>
</table>

4.3 Kinetic modeling

For the kinetic study of leaching reaction the particles were assumed to be perfectly homogenous spherical solid phases and the shrinking core model was selected to analyze the rate of dissolution of iron. Shrinking core model are quite extensively used in kinetic studies [13]. The kinetic relationships are expressed in terms of the fraction of reacted particle X, with time.

Three established models i.e. Chemical reaction controlled process, Liquid film diffusion controlled process, Diffusion controlled process and also a Mixed controlled process were considered for initial selection of the reaction mechanism.

The equations for these models are as follows:

1. Chemical reaction controlled process:

\[ \frac{t}{\tau} = 1 - (1-X)^{1/3} \]  

(1)

2. Liquid film diffusion controlled process:

\[ \frac{t}{\tau} = 1 - (1-X)^{2/3} \]  

(2)
3. Diffusion controlled process:

\[ \frac{t}{\tau} = (1-2X/3)-(1-X)^{2/3} \] .............................................(3)

4. Mixed controlled process:

\[ \frac{t}{\tau} = [(1-2X/3)-(1-X)^{2/3}] + b[1-(1-X)^{1/3}] \] .........................(4)

Where,
\( X \) = Fraction of reacted particles.
\( \tau \) = Time for the complete conversion of a particle.
\( b \) = Multiplying factor for chemical reaction.

**4.3.1 Effect of time and temperature on the rate of leaching**

Fig. 4.22 and Fig.4.23 show the effects of time and temperature on the rate of leaching of iron oxide in the clay sample in 1.8M oxalic acid and 1.6M hydrochloric acid. It can be seen that during the initial period of leaching at all temperatures under investigation, the rate of leaching was rather fast. However, the curves became almost flat within a very short period of time, after which the increase in the extent of removal of iron was negligible. It can also be seen that the rate of leaching was faster at higher temperatures.

Fig. 4.22: Effect of time and temperature on the extent of dissolution of iron during leaching.
4.3.2 Identification of reaction mechanism

From Fig. 4.22 and Fig. 4.23, time for different fractions of reacted particle of iron were calculated at 40°C, 60°C and 80°C. Data was then plotted according to equation 1 in Fig 4.24 and Fig.4.25. The correlations of coefficient values are also shown in the figure. It can be seen that the correlation is not high enough at all temperatures to suggest that the dissolution of iron oxide in the clay sample is a chemical reaction controlled process.
Fig. 4.25: plot of $1-(1-X)^{1/3}$ versus time at various temperatures for Iron dissolution in hydrochloric acid.

The plot of $1-(1-X)^{2/3}$ versus time at different temperatures is shown in Fig. 4.26 and Fig. 4.27. This equation was considered to test if the process is a liquid film diffusion controlled process. It can be seen from both figures that the correlation factor is low and the lines do not pass through the zero point. The model cannot, therefore, be selected for dissolution of iron in the present system.

Fig. 4.26: Plot of $1-(1-X)^{2/3}$ vs time at different temperatures for iron dissolution in oxalic acid.
To test if the process is diffusion controlled process, the right hand side of Equation 3 was plotted against time for different temperatures (Fig.4.28 and Fig.4.29).

Fig.4.27: Plot of $1-(1-X)^{2/3}$ versus time at different temperatures for iron dissolution for hydrochloric acid.

Fig.4.28: Plot of $(1-2X/3)-(1-X)^{2/3}$ vs time at different temperatures for iron dissolution in oxalic acid.
From the Fig.4.28 it can be seen that the correlation factor is not that much satisfactory to be selected as the model for oxalic acid, but from Fig.4.29 it can be seen that the plots yielded a very high correlation at all temperatures under investigation. Moreover, the plotted lines passed through the zero point. Therefore, the data could be correlated to a diffusion controlled process.

Finally, for oxalic acid the reaction was assumed to follow a mixed kinetic mechanism, where the overall rate-controlling factor is a combination of diffusion controlled process and chemical reaction.

The change in proportion of dominating reaction was done by setting “b” in equation (4) between 0 and 1. The values of “b” for each reaction were determined graphically by plotting the experimental data according to equation (4) for different values of “b”. The value that produced the best liners fit with the smallest 0-intercept was the one used to calculate the rate constant.

“b” is a direct function of chemical reaction and according to this mixed kinetic mechanism when “b” is very small or equal to zero, the reaction at the particle surface does not control the kinetics of dissolution and diffusion process becomes the rate controlling factor. When “b” equals 0 equation (4) becomes:
\[ t/\tau = (1-2X/3)-(1-X)^{2/3} \]

The small value of “b” obtained (i.e. 0.08) suggests that the diffusion controlled process was the most dominating reaction. The graphs produced straight lines and passing through the zero and the correlation factor is very high compared to other mechanisms, hence the data fits the model (mixed kinetics reaction model) [Fig.4.30].

Fig.4.30: Plot of \[ [(1-2X/3)-(1-X)^{2/3}] + b[1-(1-X)^{1/3}] \] vs. time at different temperatures for iron dissolution in oxalic acid (b=0.08).

For finding out the best fitting of kinetic data and exact value of “b”, different values of “b” were tested in equation 4. For example Fig.4.31 and Fig.4.33 are showing the plots of mixed kinetic data for the “b” values of 0.07 and 0.09. Comparing the three figures, Fig.4.30 (b=0.08), Fig.4.31 (b=0.07) and Fig.4.32 (b=0.09), it can be seen that the “b” value of 0.08 provides the best fitting and best correlation factor.
Fig.4.31: Plot of \[\frac{1}{3} (1 - \frac{2X}{3} - (1 - X)^{2/3}) + b(1 - (1 - X)^{1/3})\] vs. time at different temperatures for iron dissolution in oxalic acid (b=0.07).

Fig.4.32: Plot of \[\frac{1}{3} (1 - \frac{2X}{3} - (1 - X)^{2/3}) + b(1 - (1 - X)^{1/3})\] vs. time at different temperatures for iron dissolution in oxalic acid (b=0.09).
### 4.4 Evaluation of activation energy

Both the conventional integral approach and differential approach were used to evaluate the activation energy of the leaching reaction.

#### 4.4.1 Integral approach

In the integral form, \( t/\tau \) versus time (t) was plotted. The reaction rate constants, \( k \), at various temperatures for hydrochloric acid and oxalic acid leaching were obtained from linearised plots (Fig.4.29 and Fig.4.30). The rate constant was then plotted against temperature according to the Arrhenius type equation in Fig.4.33 (i.e. oxalic acid) and Fig.4.34 (i.e. hydrochloric acid).

The plot of \( \ln K \) vs. \( 1/T \) was a straight line and the slope of this straight line is equal to \(-E/R\).

The apparent value of activation energy for the dissolution of iron with oxalic acid was estimated 41.03458 kJ/mole (Fig.4.33) and for hydrochloric acid was estimated 50.82 kJ/mole (Fig.4.34).

![Fig.4.33: Arrhenius type plot of Fig.4.30.](image)

\[ E = \text{41.03458 kJ/mol} \]

\[ y = -4.9356x + 11.992 \]

\[ 10^{-3} / T (K^{-1}) \]
4.4.2 Differential approach:

For oxalic acid leaching, in the differential approach, the time required for a given value of X was calculated first and then plots of \( \ln(t_x) \) versus temperature were obtained from Fig.4.35.

As before the slope of this curve are equal to \(-E/R\) and the activation energies were estimated in the range of 35.58 kJ/mole to 44.98 kJ/mol for X values of 0.3 to 0.5. On the other hand the activation energy obtained from the integral approach is 41.03458 kJ/mole. So the activation energy values obtained by the two processes are nearly identical. This may be taken as the evidence to support the kinetic model identified for the leaching process in oxalic acid.
Also for HCl leaching, the same procedure was followed for calculating the activation energy. At first, the time required for a given value of X was calculated and then plots of ln(t) versus temperature were obtained from Fig. 4.36 and the slope of this curve is equal to –E/R and the activation energies were estimated in the range of 48.70 kJ/mole to 57.94 kJ/mol for X values of 0.3 to 0.5 which is nearly identical to the activation energy obtained from the integral approach (i.e.50.82 kJ/mole).

Fig. 4.35: Plots for calculation of apparent activation energy using differential approach.

Fig. 4.36: Plots for calculation of apparent activation energy using differential approach.
Chapter 5

Conclusion

This thesis work can be divided into three steps:

- Characterization of the clay.
- Beneficiation of the clay by hydrometallurgical route.
- Study of kinetic behaviors of leaching.

5.1 Characterization of the clay

1. The moisture content of the clay is about 3.27%, the bulk density is 2.28 g/cc, the pH is 5.16, the alkalinity is 4.5 (wt.%).
2. The average liquid limit is 45.27, the plastic limit is 33.81 and the plasticity index is 11.46. From the graphical method the liquid limit is 44.9% (at blow number of 25).
3. Silica and the kaolinite are the prominent phases in the clay found from XRD pattern.
4. Alumina content is about 27%, silica content is about 59% and the iron oxide is about 8% of the clay.
5. From TGA-DTA analysis weight loss is observed till 500°C and then a weight gain phenomena is visible in all cases.
6. The XRD patterns of heat treated clay (i.e. at 500°C and soaking time ½ hour) proves that no phase change is occurred due to heating and can’t explain the weight gain phenomena in TGA-DTA pattern after 500°C.
7. From the firing properties of bricks, the apparent porosity and the water absorption decrease with higher firing temperatures as well as the bulk density and the shrinkage increase.
8. Cold crushing strength increases with higher firing temperature.
5.2 Beneficiation of the clay

By removing iron, the clay was beneficiated and for this purpose a comparative study was carried out in between an organic (i.e. oxalic acid) and an inorganic acid (i.e. hydrochloric acid).

The optimum condition for leaching in oxalic acid:
Acid concentration = 1.8 molar; Time = 50 minutes;
Temperature = 80°C; Stirring speed = 800 rpm.

The optimum condition for leaching in hydrochloric acid:
Acid concentration = 1.6 molar; Time = 50 minutes;
Temperature = 80°C; Stirring speed = 600 rpm.

The liquid limit, organic matter content and cold crushing strength for the beneficiated clays, both in oxalic acid and hydrochloric acid, were determiner.

The average liquid limit for the clay leached in oxalic acid was 41.72 and the plastic limit was 28.37. The plasticity index was 13.35. On the other hand the liquid limit for the clay leached in hydrochloric acid was 40.46 and the plastic limit was 29.1. the plasticity index was 11.36.

The sample leached in oxalic acid contained about 4.58 % of organic matter and the sample leached in hydrochloric acid contained about 3.1 % of organic matter.

The cold crushing strength of bricks made from beneficiated clays were found 37.26 N/mm² (clay leached in hydrochloric acid) and 40.9 N/mm² (clay leached in oxalic acid).

5.3 Kinetic study

1. The kinetic data for iron dissolution in 1.8 M oxalic acid fits the mixed controlled process and the small value for “b” is 0.08, so the diffusion controlled process is the dominating reaction.

\[ t/\tau = [(1-2X/3)-(1-X)^{2/3}) + b[1-(1-X)^{1/3}] \]

2. The kinetic data of iron dissolution by 1.6 M hydrochloric acid fits the Diffusion controlled process.

\[ t/\tau = (1-2X/3)-(1-X)^{2/3} \]
3. The apparent activation energy evaluated from the experimental data is 41.03458 kJ/mole for Oxalic acid and for hydrochloric acid, 50.82 kJ/mole.

5.4 Summary

In this thesis work the main aim was the characterization and beneficiation of the clay and during beneficiation the intention for using an organic acid (i.e. oxalic acid) instead of an inorganic acid (i.e. hydrochloric acid) was to remove iron or iron bearing impurities selectively without affecting the alumina content specially. But by investigating the leach liquors, both from oxalic acid and hydrochloric acid it was found that oxalic acid also affects the alumina content as well as the hydrochloric acid. About 36% Al was present in the oxalic acid liquor where the hydrochloric acid liquor contained about 56% of Al. On the other hand oxalic acid removes about 98% of iron and the hydrochloric acid removes about 86% of iron. Though oxalic acid removes greater iron than that of hydrochloric acid, it also affects the alumina content which is not satisfactory.

5.5 Recommendation for further work

The aim of this study was to beneficiate the clay by removing iron without affecting the alumina content in it for improving its industrial importance. Two different acids were used-oxalic acid and hydrochloric acid. The intention for using the organic acid was not to affect the alumina content of the clay. Contrary to findings by other workers, leaching in oxalic acid also was found to affect the alumina content of the clay. Further investigations are required to see whether there is any organic acid or mixture of acids suitable for the selective removal of iron.

The mass gain phenomena observed specially after 500°C in all cases needs further investigations. It was unusual and the reason could not be established.
References

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