

Sintering Characteristics of Red Mud Compact

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
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In

Metallurgical & Materials Engineering.

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CERTIFICATE

This is to certify that the thesis titled '**Sintering Behaviour Of Red Mud Compact**' submitted by **Rahul Agarwal**, Roll No. **10404012** and **M.Shashikanth**, Roll No **10404024** in partial fulfillment for the degree of Bachelor In Technology in Metallurgical & Materials Engineering at National Institute Of Technology is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

It is beyond doubt that activity of primary industries often yields substantial amounts of by-products. The disposal in the original industrial site is favoured by economic reasons though traditional storage in nearby dumps can be impractical owing to the considerable masses involved and environmental restrictions. The local exploitation of these by-products is therefore a growing technological aspect of basic industries and one tenable option is their re-use as starting materials for other productions.

This huge amount of industrial byproducts/wastes which is becoming a client for increasing environmental pollution & generation of a huge amount of unutilized resources. With a view to the above, this research is aimed at finding out utilization of such things/materials/industrial byproducts for value added applications & also helps to solve the environmental problems. The present piece of my research work aims at, to provide a valued input/utilization to industrial byproduct/waste .

An emblematic case is the 'red mud' discharged by industry producing alumina from bauxite: alkaline digestion of 2.5 t of bauxite affords alumina and ≈ 1.5 t of red mud ,so that an average Al_2O_3 productivity of 5×10^5 t year⁻¹ involves a mass of by-products of $\approx 7.5 \times 10^5$ t year⁻¹ discharged as slurry retaining variable water contents. This amount is composed of Fe and Ti oxides, behaving as chemically inert matter, with variable percentages of nominal SiO_2 , Al_2O_3 and Na_2O . The material is available as a watery mixture which settles slowly and may easily be conveyed from station to station by continuous fluid-carrying machinery.

The recycling of the mud, after curing or high temperature annealing — up to 1200°C — for large-rate daily mass consumption industries such as bricks and tile kilns has been put forward in a number of papers.[2,3,4,5,6,7,8,9]

Most of the above reports appear fragmentary and, to some extent surprising, characterization work is limited to the elemental analysis of the raw material and the identification of the crystalline phases in dried samples. However, the definition of thermal behaviour in a wide working range of temperatures appears mandatory for a feasible exploitation of the mud in high temperature applications. Indeed, the reactivity of red mud components on heating may promote ceramization and shrinkage and, apart from other qualities, may affect the mechanical features of clay-based items fabricated with bauxite-waste addition.

Accordingly, we focus here on the thermal behaviour of the mud, the solid-state transformations and solid–liquid phase transitions. The use of thermal analysis coupled with of X-ray diffraction methods seemed well suitable for the problem at hand. The present study is a part of a long-term project on the exploitation of red mud as a clay additive for the ceramic industry or as a compound for self-binding mortars in the fabrication of stoneware .

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INTRODUCTION

1.1) BRIEF INSIGHT

Aluminium metal is commercially produced from bauxite ore through two main process steps. In the first step alumina is obtained by the Bayer's process and in the second step the alumina is electrolysed in a Hall-Heroult cell to yield aluminum metal. Production of alumina from bauxite by the Bayer's process is associated with the generation of red mud as the major waste material. Depending upon the quality of bauxite, the quantity of red mud generated varies from 55-65% of the bauxite processed. Bauxite ore mined globally amounts to 110 MTPA in 1994, 125 MTPA in 1998 and is expected to be around 145 MTPA at the moment. Based on the economic and as well as environment related issues, resues of red mud is of imperative importance.

1.2) BAUXITE CHARACTERISATION:

Bauxite is a generic term applied to a naturally occurring mixture of minerals rich in hydrated aluminum oxides. Major impurities are the oxides of iron, silicon, and titanium while such elements as zinc, phosphorous, nickel and vanadium are found in trace amounts. The mineralogical characteristics of the bauxite ore determine the type of process needed for alumina production. As far as aluminium containing minerals are concerned, it is important to note whether (i) Gibbsite, (ii) Boehmite, or (iii) Diasporic mineralogy is dominant. This determines the type of leaching operation to be adopted. The world's metallurgical bauxite production, as per this mineralogy is listed in. Presence of silica, usually called active or otherwise is significant, since the active silica (in form of Kaolinite) determines the process required to handle it. It can be concluded that production of bauxite is continuously on a high b'coz the production of aluminium is also continuously rising.

Table 2.1: BAUXITE WORLD PRODUCTION, BY COUNTRY

(IN THOUSAND METRIC TONNES)

Country	(MTPA)	2001	2002	2004	2008 ^e	
Australia		53,799	54,135	55,602	56,593	59,959 ³
Bosnia and Herzegovina ^e		75	113	573 ^r	480 ^r	480
Brazil		13,032 ^r	13,260 ^r	17,363 ^r	19,700 ^r	19,800 ^p
China ^e		9,800	12,000	13,000	15,000	18,000
Ghana		678	684	495	498	734 ^p
Greece		2,052	2,492	2,418	2,444	2,450
Guinea ^{e, 4}		15,100	15,300 ^r	15,000 ^r	15,000 ^r	15,000
Guyana ⁴		1,950	1,690	1,701 ^r	1,466 ^r	1,500
Hungary		1,000	720	666	647	511
India		7,864	9,647	10,414	11,285	11,957 ³
Indonesia		1,237	1,283	1,263	1,331	1,400
Iran		274 ^r	57 ^r	366 ^r	420 ^r	500 ³
Jamaica ^{4, 5}		12,370	13,120	13,444	13,296	14,118 ³
Kazakhstan		3,685	4,377	4,737	4,706	4,800
Malaysia		64	40	6	2 ^r	2
Mozambique		9	9	12	7	10 ³
Pakistan ^e		9	8	8	8 ^r	9
Russia ^e		4,000	4,500	5,500	6,000	6,400
Serbia and Montenegro		610	612	540 ^r	486 ^r	610
Suriname		4,394	4,002	4,215	4,052	4,584 ³
Turkey ⁶		242	287	364	366	365
United States		NA	NA	NA	NA	NA
Venezuela		4,585	5,191	5,446	5,842 ^r	5,900
Total		137,000	144,000	153,000^r	160,000^r	169,000

^eEstimated. ^pPreliminary. ^rRevised. NA Not available.

¹World totals and estimated data are rounded to no more than three significant digits; may not add to totals shown.

²Table includes data available through June 2007.

³Reported figure.

⁴Dry bauxite equivalent of crude ore.

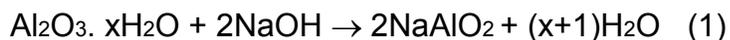
⁵Bauxite processed for conversion to alumina in Jamaica plus kiln-dried ore prepared for export.

Table 2.2: Mineral forms of some major and minor elements present in bauxite.

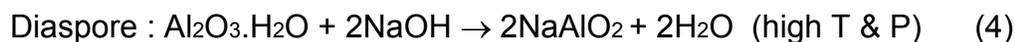
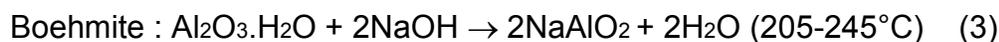
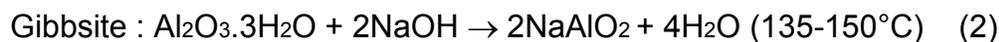
Element	Mineral	Formula
Al	Gibbsite	α - Al ₂ O ₃ , 3H ₂ O
Al	Boehmite	α - Al ₂ O ₃ , H ₂ O
Al	Diaspore	β - Al ₂ O ₃ , H ₂ O
Fe	Goethite	α - FeOOH
Fe	Hematite	α - Fe ₂ O ₃
Fe	Magnetite	Fe ₃ O ₄
Si	Kaolinite	Al ₂ O ₃ . 2SiO ₂ . 3H ₂ O

1.3) LEACHING CHEMISTRY

In the Bayers process the bauxite ore is digested in a solution of caustic soda (NaOH). During caustic digestion aluminum oxide, because of its amphoteric character, passes into solution as soluble sodium aluminate.



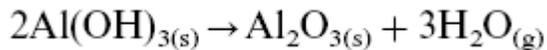
The process is far more efficient when the ore is reduced to a very fine particle size prior to the reaction. However, the digestion conditions are influenced by the nature of bauxite particularly the mineralogical form of the alumina containing phases. The ease of digestion in caustic soda decreases in the order (Gibbsite, Boehmite and Diaspore).



In general the equilibrium in above moves to the right with increase in caustic soda concentration. In fact, Gibbsite extraction is very fast and occurs within minutes. Crystalline alumina hydrate is extracted from the digestion liquor by hydrolysis.



This is basically the reverse of the digestion process. In this step, adjustment of precipitation conditions such as type of seed material, temperature of precipitation and cooling rate can control the nature of the product. Caustic soda also dissolves the silica to form sodium silicate, which can contaminate the alumina. Hence, it is necessary to control the silica. This is generally carried out during or prior to the digestion step and involves dissolution of kaolinite, which dissolves under the moderate Gibbsite dissolution conditions.



Alumina produced by the Bayer process is quite pure, containing only a few hundredths of 1 percent of iron and silicon. The major impurity, residual soda, is present at levels of 0.2 to 0.6 percent. In addition to being the primary raw material for producing metallic aluminum, alumina itself is an important chemical. It is used widely in the chemical, refractories, ceramic, and petroleum industries.

Refining four tons of bauxite yields about two tons of alumina. A typical alumina plant, using the Bayer process, can produce 4,000 tons of alumina per day. The cost of alumina can vary widely, depending on the plant size and efficiency, on labour costs and overhead, and on the cost of bauxite.

CHARACTERISTICS OF RED MUD

Red mud, as the name suggests, is brick red in colour and slimy having average particle size of <10 μm . About 35% by weight of solids have size less than 5 micrometer and 80% less than 8 micrometer for the sample of NALCO refinery, Damanjodi .It is alkaline, thixotropic and posses high surface area in the range of 13-16 with a true density of 3.30g/cc.

The leaching chemistry of bauxite suggests that the physical and chemical properties of red mud depend primarily on the bauxite used and, to a lesser extent, the manner in which the bauxite is processed by the Bayers process technology. Residues from different bauxite have a wide range of composition: Fe_2O_3 20-60%, Al_2O_3 10-30%, SiO_2 2-20%, Na_2O 2-10%, CaO 2-8%, TiO_2 traces – 28%. The important parameters which have significance in its further handling, disposal and use are: (i) moisture content, (ii)rheology, (iii) surface area, (iv) particle size, (v) contents of valuable metals, (vi) presence of rare earth metals, (vii) presence of toxic substances, etc.

Table 2.3) RED MUD CONSTITUENT OF VARIOUS PLANTS

Company	constituents, wt %				
	Fe_2O_3	Al_2O_3	TiO_2	SiO_2	Na_2O
Al. Corpn.	20.26	19.60	28.00	6.74	8.09
MALCO	45.17	27.00	5.12	5.70	3.64
HINDALCO	35.046	23.00	17.20	5.00	4.85
BALCO	33.80	15.58	22.50	6.84	5.20
NALCO*	52.39	14.73	3.30	8.44	4.00
Hungary	38.45	15.20	4.60	10.15	8.12
Jamaica	50.9	14.20	6.87	3.40	3.18
Surinam	24.81	19.00	12.15	11.90	9.29
ALCOA Mobile	30.40	16.20	10.11	11.14	2.00
Arkansas	55.6	12.15	4.5	1.5-5.0	Traces
Sherwon	50.54	11.13	Traces	2.56	9.00
FRG Baudart	38.75	20.00	5.5	13.00	8.16

2.1 Utilization Of Red Mud

The increasing concern for the environment is a promising factor for a higher activity in the field and a re-evaluation of the economical aspects.

Hind et al in their work, report a number of industrial attempts. RM has been used a pH modifier in the heap leaching of gold ores [R.E. Browner, 1992], in the removal of sulfur compounds from kerosene oil [A.P. Singh, et al, 1993], in the hydrogenation of anthracene [J.J. Llano et al, 1994, J. Alvarez, et al, 1995], coals and aromatic compounds [A. Eamsiri et al, 1992], and as a pigment in anticorrosive marine paints [T. Skoulikidis et al, 1992,].

In **India**, it is reported that 2.5 million tonnes were absorbed by the cement industry in 2006-2007

In **China**, it is reported that 10% approximately of RM produced is recycled for further metal extraction or utilized as a raw material for brick production (Fei Peng et al, Chemosphere, 2004 (expected))

In **Australia**, bricks made from bauxite residue from Alcoa's alumina processing plant at Kwinana, Western Australia, have been used to build homes in the South-West of Western Australia, according to a report in The West Australian, 1 February 2002. The use of waste bauxite residue was trialled in a test building in the early 1980s. However, the Health Department rejected the building after tests registered radioactivity readings which bordered on the maximum acceptable radiation exposure levels for 19 hours a day. The residue contained radioactive thorium and uranium A document obtained by The West Australian shows senior Alcoa employees admitting to a 1998 community meeting that the red mud stockpiles near the Kwinana plant exceeded occupational radioactivity limits. Alcoa environmental manager Graham Slessar said that this was wrong. (Source: Australian Fluoridation News Jan-Feb 2002 Edition,)

In **Japan**, plant scale tests were initiated in 2003 to confirm the possibility of using Residual Bauxite (i.e. dry "red mud") in cement production. Residual Bauxite was introduced as a raw material along with other raw materials as lime, clay, silica, iron source etc. The tests confirmed that residue added cement, as well as mortar and concrete made from this cement meet the Japanese Industrial Standards (Japan Aluminum Organisation, 2004)

2.2) RED MUD DISPOSAL

The disposal of RM remains a major problem. Reports on this issue in the open literature seem scarce. Below you can find some general information about the disposal of Red Mud as well as the common practice in the **USA, India, China, Japan, Spain, and Greece**.

In a research by Hind *et al.* in 1999, it is reported that conventional disposal methods have revolved around the construction of clay-lined dams or dykes, into which the RM slurry is simply pumped and allowed to dry naturally. The design and construction of such residue impoundments has varied considerably over the years [B. Salopek, J. Strazisar, 1993], with disposal practices generally dependent upon the nature of the immediate environment. The authors, note that the operation of these conventional disposal areas was simple and inexpensive, however the potential impact on the surrounding groundwater and environment, and difficulties associated with surface rehabilitation, forced significant changes in disposal practices [D.J. Cooling, D.J. Glenister, 1992]. This led to the construction of doubly sealed impoundments, incorporating a polymeric membrane as well as clay lining, and drained lakes, having a drainage network incorporated in the lining material, have subsequently seen widespread use. Drained disposal systems have been found to reduce the threat of the residue to the environment, while also increasing storage capacity as a result of better residue consolidation [L.K. Hudson, 1982]. As an alternative, dry disposal of bauxite residue, involving enhanced dewatering and evaporative drying, has also been found to further decrease environmental risks and lower overall disposal costs [D.J. Cooling, D.J. Glenister, 1992].

In another report by Agrawal *et al.*, it is reported that out of 84 alumina plants all over the world, only seven are still practising the sea disposal in a planned manner because of scarcity of land.

One patent on the disposal of RM has been also granted to W. M. Gerald. The title of the patent is “Treatment and disposal of red mud generated in the Bayer Process”, AU701874. The inventors propose a process that produces a RM cake low in caustic and alumina concentration permitting environmentally friendly disposal.

Quite recently, the Virotec International Ltd. (Australia), announced a treatment process for RM that renders the material safe for a variety of applications. The method is based on the use of seawater, which allows the conversion of “soluble alkalinity” (above all from sodium hydroxide) into low soluble minerals (essentially Ca and Mg hydroxides, carbonates and hydrocarbonates). The pH of RM is also reduced and can be decreased down to $\text{pH} < 9$. This technology is patented and several products with the name Bauxsol™ are available. A study on the environmental behaviour of RM processed with the above technology is also available [C. Brunori *et al.*, 2004].

Table 2.4) RESEARCH AND DEVELOPMENT WORK THAT IS PRESENTLY GOING ON IN INDIA

Organization	Investigation
1. Madras Aluminium Company	Red mud as a component in cement
2. Central building research	Production bricks with red mud and clay with equal proportions
3. Central glass and ceramic research Institute	Conversion of red mud to ceramics.
4. RRL, Bhubaneswar	Recovery of vanadium, chromium & alumina
5. RRL, Bhopal	Utilization of red mud pvc product as red mud plastic
6. NML, Jamshedpur	Recovery of V₂O₅ and Al₂O₃.
7. Metallurgical Dept. ,B.H.U.	Development of bricks, recovery of titanium and Ferro titanium
8. NALCO, Angul	Filler to PVC sheets, pipes
9 RRL, BBSR	Recovery valuable elements like V₂O₅

EXPERIMENTAL TECHNIQUES

3.1) SINTERING:

Sintering is a thermal treatment, below the melting temperature of the main constituent material, which transforms a metallic or ceramic powder (or a powder compact) into a bulk material containing, in most cases, residual porosity.

The process of sintering brings about certain physical as well as chemical changes in the material. The chemical changes can be illustrated as:

- ✓ Change in composition or decomposition
- ✓ New phase formation or decomposition followed by phase change
- ✓ . New phase formation due to chemical changes

The physical changes that take place are:

- ✓ . Change of grain size
- ✓ . Change of pore shape and pore size

All these changes bring about the complete change in microstructure, which bring about the complete change in the properties of the material. Change in grain size is brought about by recrystallization where as densification or solid state sintering is responsible for change of pore shape and size.

The various stages in the process of sintering are:

1. Primary recrystallization
2. Grain growth
3. Secondary recrystallization

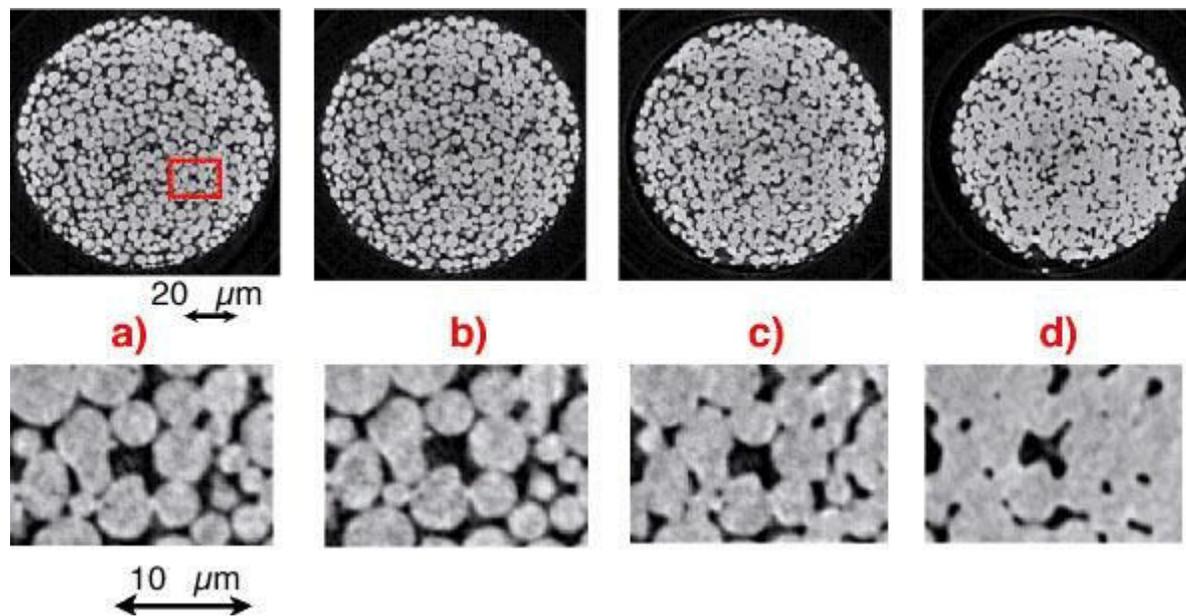


Figure 3.1) Schematic Representation of Sintering.

Primary Recrystallization

It is the process by which a new set of grains are formed from a previously deformed matrix. The grains get deformed in a particular direction. Hence all these grains are strained grains or it is a strained matrix. If there is a strain in the material then that portion is slightly warm as it possesses strain energy of the order of 0.5 to 1 cal/gram, which may lead to recrystallization and grain growth. When a body is mechanically warmed the grains are elongated and when cooled a new set of grains are formed. Primary recrystallization is dependant on primary deformation. Ceramic materials are formed from powders, which are sintered, and hence they undergo negligible mechanical deformation. Driving force for recrystallization is stored energy.

Grain Growth

This process is defined as nucleation and grain growth of the grains without changing the overall distribution of grains. Particles on heating come to form common boundary or grains start growing. Driving force for grain growth is difference between grain areas and hence difference between surface energy. As grain growth occurs surface area decreases. Smaller is the grain size

more is the surface area. The difference in surface energy or grain boundary energy is responsible for grain growth.

Factors affecting grain size during this period:

1. Temperature
2. Time
3. Presence of inclusions

Due to change of surface curvature due to the presence of inclusions the grain boundary energy decreases. So extra energy is required to overcome this barrier and move due to which movement decreases and the grain growth is not that fast. Sometimes pore spaces act as inclusions. When a ceramic product is sintered from the powders, initially the porosity is high and hence the rate of grain growth is low but when porosity is brought down to less than 15% then grain growth starts increasing.

Secondary Recrystallization

This is a process where a few grains grow abnormally or discontinually at the expense of other grains. If grains are too small at places due to inclusions, at some other places there will be abnormal growth there will be abnormal growth and once this starts they will consume the normal sized or uniform grains and grow. If the inclusions are high or there is segregated grain growth or the grains are very fine in size then there are chances of secondary recrystallization. Initial requirement for secondary recrystallization is presence of some embryos. It is unwanted as it deteriorates the mechanical properties of the material.

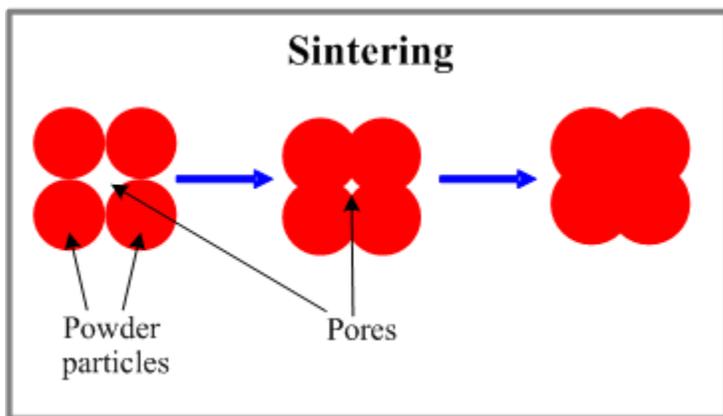
Sintering (Firing) of ceramic materials is the method involving consolidation of ceramic powder particles by heating the “green” compact part to a high temperature below the melting point, when the material of the separate particles diffuse to the neighbouring powder particles. The driving force of sintering process is reduction of surface energy of the particles caused by decreasing their vapour-solid interfaces.

During the diffusion process the pores, taking place in the “green compact”, diminish or even close up, resulting in densification of the part, improvement of its mechanical properties.

Decrease of the porosity, caused by the sintering process, is determined by the level of the initial porosity of the “green” compact, sintering temperature and time. Sintering is enhanced if a liquid phase takes part in the process (liquid phase sintering). Sintering (firing) of pure oxide ceramics require relatively long time and high temperature because the diffusion proceeds in solid state.

Applying pressure decreases sintering time and the resulted porosity

Fig 3.2) Sintering ,an Agglomeration technique



3.2) UNIAXIAL DIE PRESSING

Although many products such as pills and tablets for medical use are cold-pressed directly from powdered materials, normally the resulting compact is only strong enough to allow subsequent heating and sintering. Release of the compact from its mold is usually accompanied by small volume increase called "spring-back." In the typical powder pressing process a powder compaction press is employed with tools and dies. Normally, a die cavity that is closed on one end (vertical die, bottom end closed by a punch tool) is filled with powder. The powder is then

compacted into a shape and then ejected from the die cavity. Various components can be formed with the powder compaction process. Some examples of these parts are bearings, bushings, gears, pistons, levers, and brackets. When pressing these shapes, very good dimensional and weight control are maintained. In a number of these applications the parts may require very little additional work for their intended use; making for very cost efficient manufacturing.

Die pressing is the powder compaction method involving uniaxial pressure applied to the powder placed in a die between two rigid punches.

Uniaxial (die) pressing is effectively used for mass production of simple parts (alternative method is isostatical pressing).

The pressing process consists of the following stages:

- **Die filling**

At this stage a controlled amount of the powder is fed into the die cavity.

- **Compaction**

Upper punch moves down and presses the powder with a predetermined pressure.

- **“Green” compact part ejection and removal** (“green” compact – unsintered powder compact) .

The pressing cycle repeats , depending on the press type, powder filling properties and the part size and geometry.

Hydraulic and mechanical presses with load up to 750 tons are used for the powder die pressing.

Die pressing, which is conducted at the room temperature is called **cold pressing**.

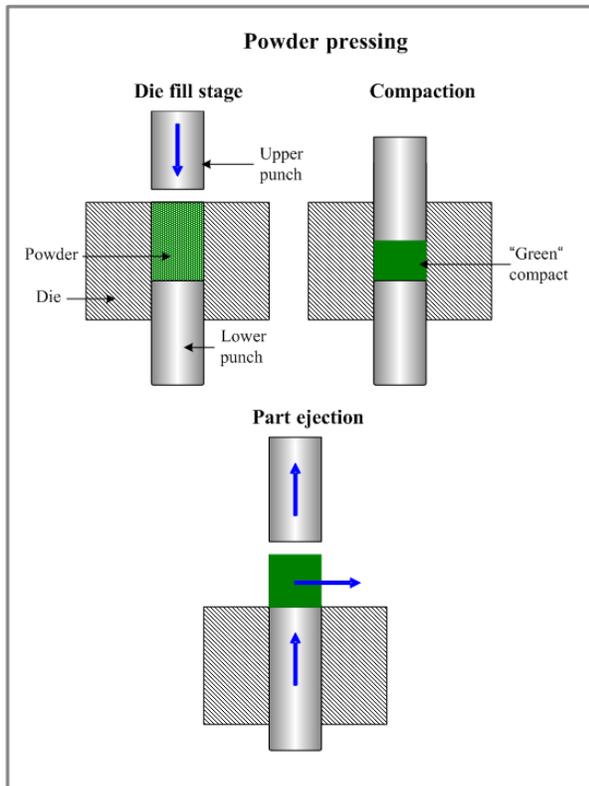
If the pressing process is conducted at increased temperature it is called **hot pressing**.

For example hot pressing of silicon carbide is carried out at temperature about 3630 °F (2000°C).

Hot pressing permits obtaining better compaction, higher green compact density and higher (than in cold pressing) strength of the part.

Die pressing is used for manufacturing insulating parts, magnetic ceramics, capacitors, substrates

Figure 3.3) The scheme of the die pressing method is presented



3.3) X-RAY DIFFRACTION

X-ray diffraction finds the geometry or shape of a molecule using x-rays. X-ray diffraction techniques are based on the elastic scattering of x-rays from structures that have long range order. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction. [1]

Single-crystal X-ray diffraction is a technique used to solve the complete structure of crystalline materials, ranging from simple inorganic solids to complex macromolecules, such as proteins.

Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, such as Rietveld refinement, can provide structural information on unknown materials. Powder diffraction is also a common method for determining strains in crystalline materials.

Thin film diffraction and grazing incidence x-ray diffraction may be used to characterize the crystallographic structure and preferred orientation of substrate-anchored thin films.

High-resolution x-ray diffraction is used to characterize thickness, crystallographic structure, and strain in thin epitaxial films. It employs parallel-beam optics. X-ray pole figure analysis enables one to analyze and determine the distribution of crystalline orientations within a crystalline thin-film sample. X-ray rocking curve analysis is used to quantify grain size and mosaic spread in crystalline materials

3.4) DTA ANALYSIS

Differential thermal analysis (or DTA) is a thermoanalytic technique, similar to differential scanning calorimetry. In DTA, the material under study and an inert reference are heated (or cooled) under identical conditions, while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature (DTA curve or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area

under a DTA peak can be to the enthalpy change and it is not affected by the heat capacity of the sample. A DTA curve can be used only as a finger print for identification purposes but usually the applications of this method are the determination of phase diagrams, heat change measurements and decomposition in various atmospheres.

DTA is widely used in the pharmaceutical and food industries. DTA may be used in cement chemistry, mineralogical research and in environmental studies. DTA curves may also be used to date bone remains[11] or to study archaeological materials.

3.5) DSC

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing.

An alternative technique, which shares much in common with DSC, is differential thermal analysis (DTA). In this technique it is the heat flow to the sample and reference that remains the same rather than the temperature. When the sample and reference are heated identically phase changes and other thermal processes cause a difference in temperature between the sample and reference. Both DSC and DTA provide similar information; DSC is the more widely used of the two techniques.

3.6) TG

Thermogravimetry (also known by acronym "TG" and obsolete names thermo-gravimetry, thermogravimetry) is a branch of physical chemistry, materials research, and thermal analysis. It is based on continuous recording of mass changes of a sample of material, as a function of a combination of temperature with time, and additionally of pressure and gas composition.

EXPERIMENTAL WORK

PLAN OF WORK

This project aims at studying the sintering behavior of red mud compacts for different variables such as composition, temperature, time of soaking during sintering and studies their effect on compaction, strength, phase transformation

- The red mud sample is to be collected from NALCO, Damanjori.
- The sample is compacted with the help of press at a load of 4 tonnes..
- The variables which are changed during sintering are as follows

- 1) Temperature – 430,650,970,1100 degrees
- 2) Soaking time – 30 mins,1hr and 2hr for each temperature

- Then testing of the sintered product is done by various tests which are:

.Micro-hardness Test – It is done in micro-hardness tester. This determines the hardness of each of the phase present.

- Compression Test – It is to be done in Instron 1195. This determines the load bearing capacity of the sintered product which can be used for building bricks.

- X-Ray Diffraction Test – It is to be done in X-Ray diffractometer. This is used to determine and study the phases present.

COLLECTION OF THE SAMPLE

Initially the red mud sample is collected from NALCO,DAMANJORI which is in coarse form having brick red colour.

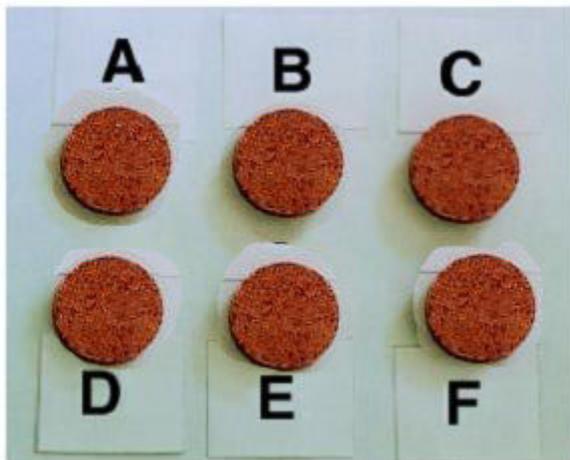
Then the sample is subjected to 110C for complete removal of moisture which's done by placing the sample in the furnace for 1hr.

COMPACTION OF THE SAMPLE

After removal of moisture the sample is crushed in a ball mill to obtain fine size. Then appropriate amount of sample is taken in a die such that the ratio of dia and thickness remains between 2-2.5.

Then compact is done in compact machine and the process is repeated for making a number of samples

Figure 3.4) SCHEMATAIC REPRESENTATION OF RED MUD COMPACTS



RESULTS

DIAMETER TAKEN:25mm

Table 3.1) **SAMPLE SINTERED AT 430°C**

	INITIAL		FINAL		
TIME (min)	THICKNESS (mm)	WEIGHT (gm)	THICKNESS (mm)	WEIGHT (gm)	Compressive strength (MPA)
30	8.56	9.30	8.55	8.9	10.71
60	8.97	9.28	8.95	8.99	12.24
120	8.82	9.12	8.8	9.05	13.59

Table 3.2) **SAMPLE SINTERED AT 650°C**

	INITIAL		FINAL		
TIME (min)	THICKNESS (mm)	WEIGHT (gm)	THICKNESS (mm)	WEIGHT (gm)	Compressive strength (MPA)
30	8.57	9.10	8.55	9.11	31.23
60	8.72	9.27	8.60	9.25	34.62
120	8.65	9.23	8.51	9.22	35.89

Table 3.3) **SAMPLE SINTERED AT 970°C**

	INITIAL		FINAL		
TIME (min)	THICKNESS (mm)	WEIGHT (gm)	THICKNESS (mm)	WEIGHT (gm)	Compressive strength (MPA)
30	8.55	9.52	8.45	9.50	33.59
60	8.66	9.63	8.65	9.60	42.94
120	8.31	9.30	8.01	9.29	44.29

Table 3.4) **SAMPLE SINTERED AT 1100°C**

	INITIAL		FINAL		
TIME (min)	THICKNESS (mm)	WEIGHT (gm)	THICKNESS (mm)	WEIGHT (gm)	Compressive strength (MPA)
30	8.11	9.04	8.11	9.02	36.89
60	8.50	9.33	8.45	9.20	45.94
120	8.46	9.21	8.45	9.16	49.81

Tabulation for Hardness

Sample Sintered at 430°C

TIME	VHN
30 mins	9.8
60 mins	11.32
120 mins	14.10

Sample Sintered at 650°C

TIME	VHN
30 mins	19.5
60 mins	21.39
120 mins	32.00

Sample Sintered at 970°C

TIME	VHN
30 mins	35.5
60 mins	41.47
120 mins	46.05

Fig 4.1) Compressive strength v/s time for 430°C

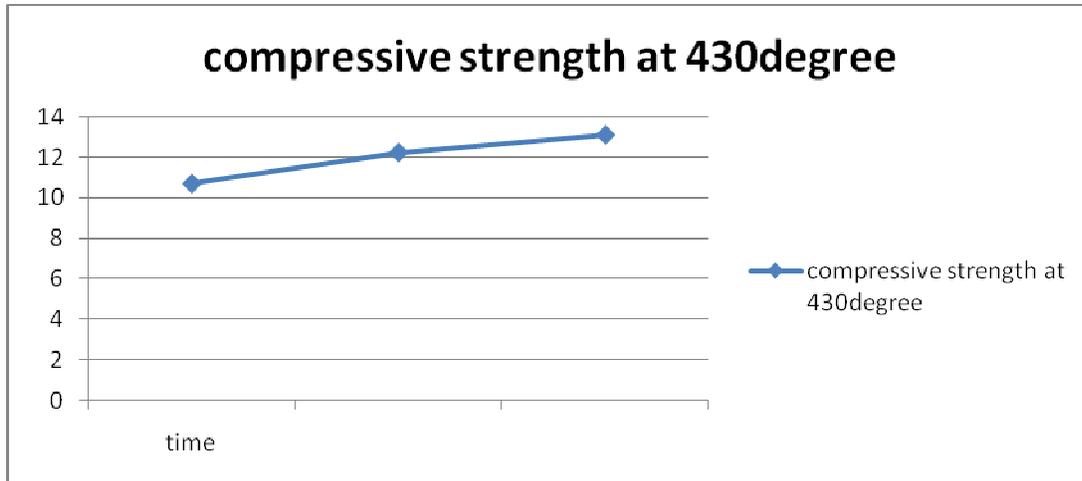


Fig 4.2) Compressive strength v/s time for 650°C

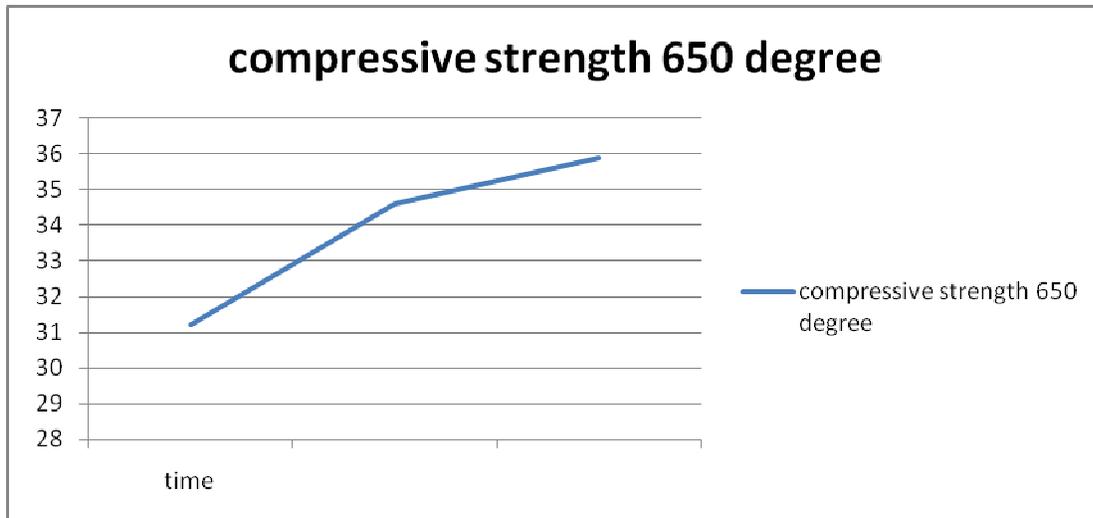


Fig 4.3) Compressive strength v/s time for 970°C

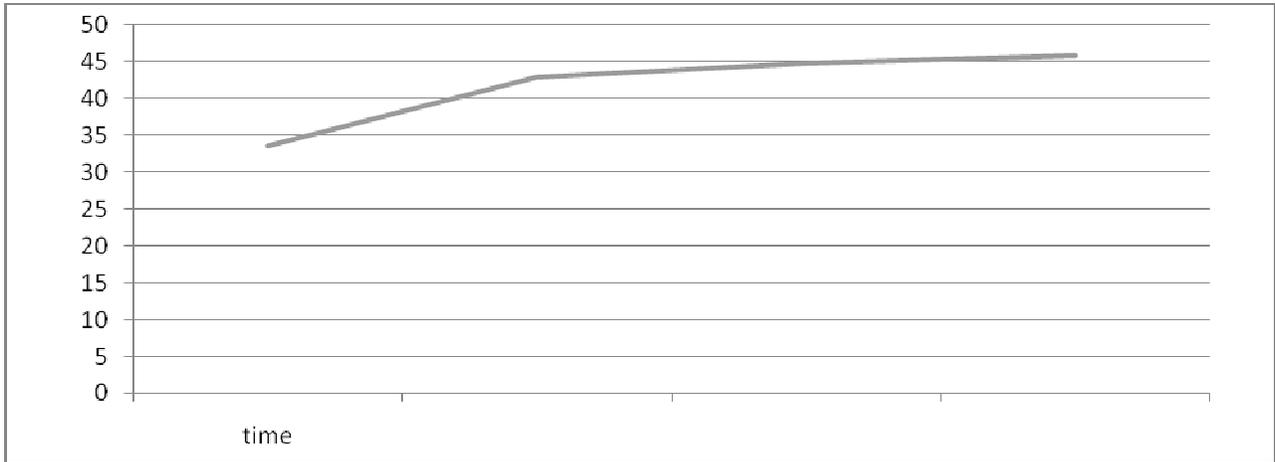


Fig 4.4) Compressive strength v/s time for 1100°C

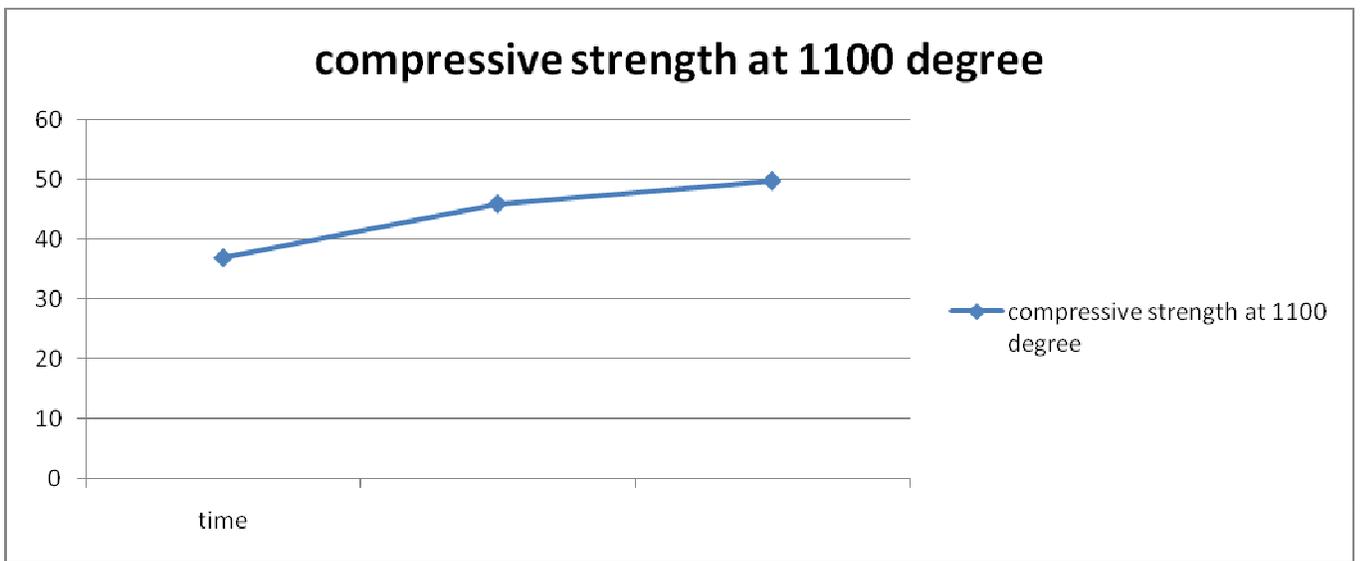
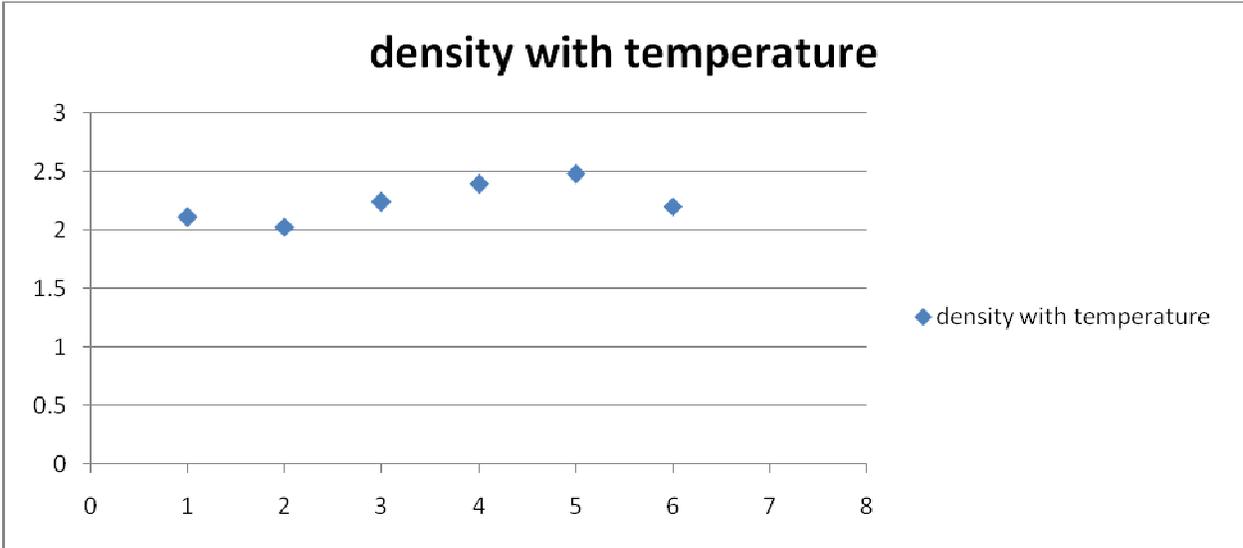


Fig 4.5) Density v/s temperature curve



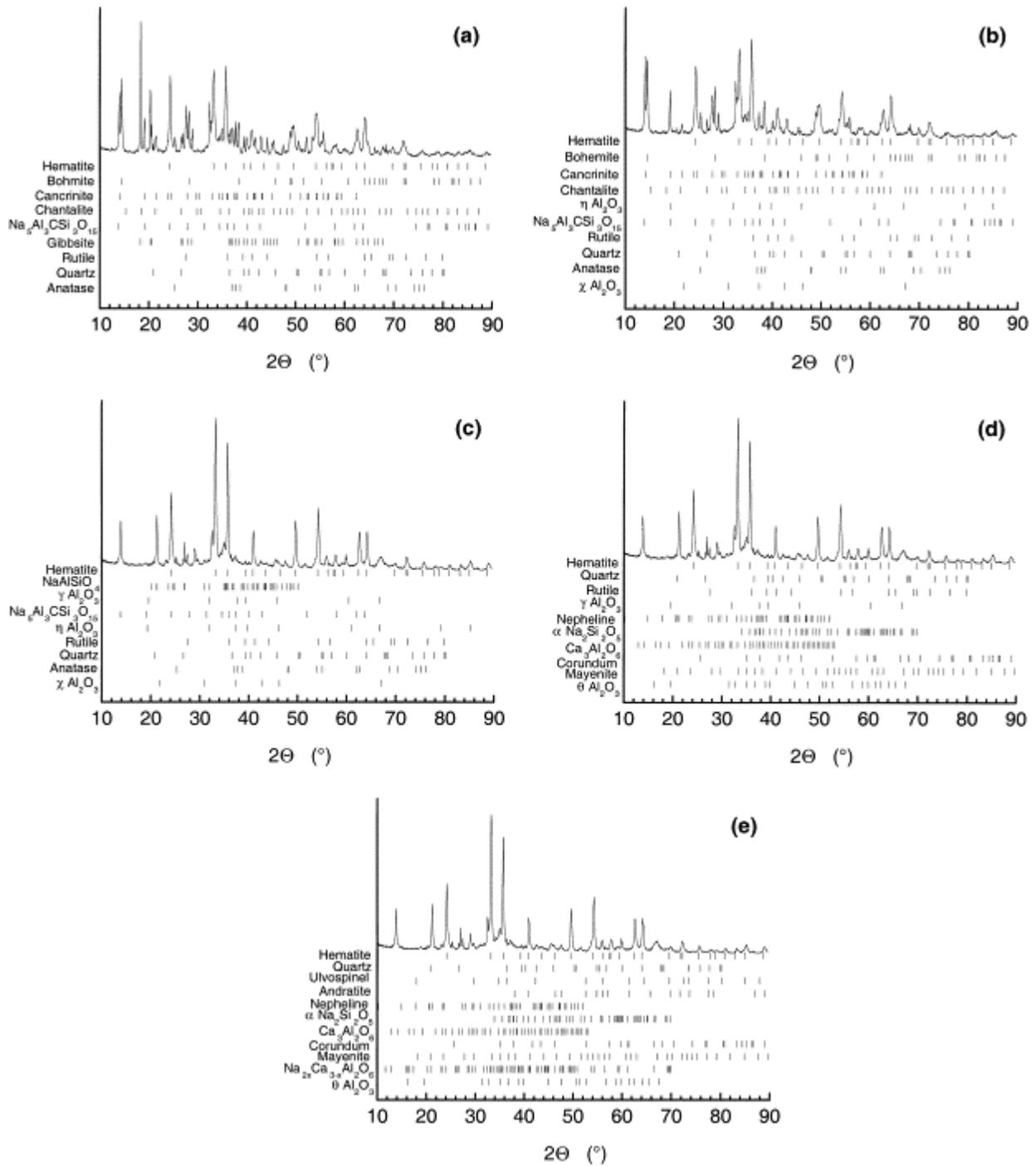


Figure 4.6) Xrd curves for (a)dried red mud (b) 430°, (c)650°, (d) 970°, (e) 1100°(sintered at these temp).

Discussions of the experimental data

DENSITY CHANGE

Initially it is observed that density decreases when the sample is sintered at 400°, but afterwards there is a constant rise in density up to 1100° after which density again decreases.

Inference: Initial decrease may be due to loss of volatiles present in the red mud sample. The trend of density as a function of temperature in the 120–600°C range may also be explained by Al³⁺ hydroxide dehydration, as aluminium oxide phases display densities $\approx 0.3 \text{ g cm}^{-3}$ higher than bayerite, gibbsite and bohemite.[17 and 21]. It is noteworthy that Ca₃Al₂O₆ displays a moderate setting character, with density of 3.04 g/cm³. The density increase from 600 to 1100°C may be due to the progressive formation of crystalline phases with higher densities (TiO₂-rutile 4.45 g cm⁻³, γ -Al₂O₃ 3.2 g /cm³, θ -Al₂O₃ 3.56 g cm³, nepheline 2.62 g cm⁻³).[16]. The density decrease observed above 1100°C (Fig. 4) reflects the occurrence of ulvospinel (density =4.79 g cm³) and andratite (density =3.86 g cm⁻³) from hematite (density =5.27 g cm⁻³).[16] This decrease is partly compensated by the increase in corundum (density =3.99 g cm⁻³) from low-density alumina phases.[17].

MECHANICAL PROPERTIES.

In all the tests for mechanical properties, the general trend is an increase in the value with increase in firing temperature. The increase is not, however, uniform. In particular a slower rate of increase is noted above 1000°C. The temperature range chosen here is the most interesting range, since the mechanical properties in this range compare well with those of commercial ceramics. Just beyond 1050°C a solid solution [15] is formed between hematite and rutile (TiO₂).

Also soda feldspar ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) and silica form a binary eutectic [16] at 1062°C . These transformations are probably responsible for the "discontinuity" in most of the curves.

To summarize, the following important conclusions may be drawn from the data and observations presented in this work:

- (i) The particle size and the mineralogy of bauxite waste allow one to develop ceramics of high strength and toughness.
- (ii) The toughness of this red mud ceramic is comparable or superior, depending on sintering temperature, to values obtained for other porous ceramics.
- (iii) The microscopic cause of the high toughness is not clear. However, it appears that the dispersion of a glassy phase in the microstructure is mainly responsible for bonding and toughening.
- (iv) It is now possible to make ceramic material with sufficiently high toughness for practical engineering applications from 100% red mud, unlike previous attempts [1, 2] where a number of additives, organic or otherwise, were added.

CONCLUSIONS

"Red mud" is a very complex material. It is a mixture of several oxides and minerals which respond in a complex way to heat treatment. As such one can only be guided by the behaviour of the prominent constituents of the mud in any analysis. In this respect, iron oxide, titania, alumina and limestone form the major components of red mud. None of these softens at the temperatures considered here. It is, however, possible that some of the known constituents of some low softening temperature glasses such as SiO_2 , CaO , Na_2O and P_2O_5 may be responsible for the glassy phase, leading to the network-like structure seen at 1075 and 1100 °C This is consistent with the idea that as the temperature is increased the viscosity of the glassy phase would be sufficiently reduced, above a certain temperature, for it to flow and disperse in the microstructure. On cooling it would act to bind the agglomerates of the major constituents, thus increasing the fracture toughness and other mechanical properties. This softened, high viscosity glassy phase could also be responsible for coating the surface of agglomerate particles, thus rendering them smooth in appearance .At present attempts are under way to identify the bonding phases.

In general heat treatment of Red Mud can be classified into 3 major temperatures.

Upto 700°C

Quartz and hematite are not affected by the heating process. The most important phenomenon is that of aluminium hydroxide transformations yielding η -, χ - and γ - Al_2O_3 , accompanied by an endothermic peak in the DT curve . $\text{Al}(\text{OH})_3$ phases (Bayerite, Gibbsite and Bohmite), originated during bauxite chemical digestion.

Upto 1000°C

This temperature interval is dominated by the occurrence of Nepheline and $\text{Ca}_3\text{Al}_2\text{O}_6$. The Nepheline presence fits quite well with the decomposition of $\text{Na}_5\text{Al}_3\text{CSi}_3\text{O}_{15}$, Chantalite and Cancrinite. NaAlSiO_4 forms initially, while definite amounts of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$) are produced later at higher temperatures ($\approx 1000^\circ\text{C}$).

Above 1000°C

Reduction of Fe³⁺ to Fe²⁺ characterizes thermal behaviour above 1100°C and promotes important chemical transformations. It may be pointed out that the evolution of gaseous HCl and SO₂ at 1100°C is related to the decomposition of alkaline salts, namely NaCl and Na₂SO₄, which make Na₂O available for reaction. The density decrease observed above 1100°C reflects the occurrence of ulvospinel (density =4.79 g cm³) and andratite (density =3.86 g cm⁻³) from hematite (density =5.27 g cm⁻³). This decrease is partly compensated by the increase in corundum (density =3.99 g cm⁻³) from low-density alumina phases.

Thermal effects above 1100°C are visually indicated by a definite change in colour which turns from red to brown. This phenomenon is associated with the Fe³⁺ reduction to Fe²⁺ in Ulvospinel dark grey.

The obtained results represent a fundamental starting point for any re-use of red mud as raw material for the ceramic industry. The moderate reactivity up to 900°C makes the red mud useful as an inert component in the fabrication of traditional clay-based ceramics, such as tiles or bricks, which are usually fired at temperatures lower than 1000°C. In this case, the red colour and the extremely fine particle size of the mud represent an interesting factor. At higher temperatures, red mud can constitute the source of low melting point sodium silicates thus promoting liquid phase sintering in ceramic bodies which can result in higher strength and lower porosity. Also in this case, depending on the firing temperature, different colour gradations can be produced.

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Bauxite 'red mud' in the ceramic industry. Part 1: thermal behaviour

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