Sintering Characteristics of Red Mud Compact

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
In
Metallurgical & Materials Engineering

By
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&
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Under the Guidance of
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CERTIFICATE

This is to certify that the thesis entitled, "**SINTERING CHARACTERISTICS OF RED MUD COMPACT**" submitted by Sri Sushil Panigrahi & Satyabrata Sutar in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Metallurgical & Materials Engineering at National Institute of Technology, Rourkela (Deemed University) 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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Sushil Panigrahi
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(*B.Tech Final Year MME*)

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ABSTRACT

Scientific inventions & technological developments has raised the human life to a great height. In last few decades worldwide scientific & technical innovations for processing /development /utilization of new materials (as per the need of the society), is tremendously increasing. But, looking at the other side of the coin also implies the generation of a 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 (viz.. red mud), being produced in huge quantity from Alumina plants, not bearing any commercial values .From the available research literatures/resources,it's clearly understood that very little attempts have been made for finding high valued utilization of this material. Considering all these above our investigation are to process red mud for high valued applications.

By now search/studies are going on for finding new ways & means available in literature regarding utilization of this material.

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CHAPTER-1

Introduction

INTRODUCTION

The enormous quantity of `red mud' discharged by industries producing alumina from bauxite represents an environmental and economical problem. Numerous reports proposing re-uses of `red mud' have been advanced, especially for the production of ceramic bodies or cements. Along this line of research, a deep characterization of the red mud has been presented in a companion paper; hereafter special attention has been paid to the structural transformations and cross-reactions induced by heating representative batches of red mud. A full knowledge of the thermal behavior seemed to us of prior concern for possible applications requiring mixing with other raw materials and firing at different temperatures. Dried red mud was substantially inert up to 900^0C, the loss of H_2O from aluminum hydroxides and of CO_2 from silico-alumino-carbonates being the only detect- able effects. Between 900 and 1100^0C complementary reactions occurred, yielding $Ca_3Al_2O_6$, $NaAlSiO_4$ and Na_2SiO_5. Concurrent with the melting of nepheline-like compounds, the colour turned from orange-red to dark red. At higher temperatures major components such as Fe_2O_3 and TiO_2 reacted to give Fe_2TiO_4 with O_2 evolution. This reaction was responsible for the intensification of the brown colour above 1200^0C. The general trend of today for the industrial wastes or by-products, which are produced in industrial countries, is to examine alternative ways for their exploitation in order to eliminate cost of disposal and avoid soil and water contamination. Many of these undesirable industrial materials contain significant amounts of inorganic ingredients, such as oxides of silicon, aluminum, calcium and iron, which, at suitable combinations,

Aluminium metal is commercially produced from bauxite ore through two main process steps. In the first step alumina is obtained by the Bayers 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 MTPY in 1994, 125 MTPY in 1998 and is expected to be around 145 MTPY at the moment. Based on economic as well as environment related issues, enormous efforts have been directed worldwide towards red mud management issues of utilization, storage and disposal.

CHAPTER-2

Literature Review

2.1 BAUXITE CHARACTERIZATION

Bauxite is a generic term applied to a naturally occurring mixture of minerals rich in hydrated aluminum oxides. The deposits are formed due to *in situ* weathering of different rock types for which a number of other minerals also co-exist in the deposit. The principal constituent of bauxite is aluminum oxide. 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.

Table-1: World Metallurgical Bauxite Production in year 2000(Thousand Metric Tons).

Country	Ore type	1994
Australia	G & B (20%)	41700
Brazil	G	8120
P.R. China	D	3700
Ghana	G	426
Greece	D	2200
Guinea	B & D (10%)	14400
Guyana	G	2100
Hungary	B	900
India	G	5400
Indonesia	G	1300

Jamaica	G	11700
Malaysia	G	162
Romania	D	184
Sierra-Leone	G	735
Suriname	G	3440
Turkey	D	500
USSR(ex)	B	5430
Venezuela	G	4790
Yogoslavia (ex)	B	85
Others	D	192
Total World		106864
Total G (Gibbsitic)	69.6%	74413
Total B (Boehmitic)	24.6%	26275
Total D (Diasporic)	5.8%	6176

Table -2: Major, minor and trace element constituents of a typical India bauxite ore.

Constituent	Wt%	Constituent	ppm	Constituent	ppm
Al_2O_3	41.60	Sc	8.57	Sr	5.27
Fe_2O_3	26.90	V	91.44	Y	2.77
SiO_2	2.54	Cr	84.75	Nb	12.52
TiO_2	3.00	Co	2.32	Cs	0.23
P_2O_5	0.17	Ni	5.41	Ba	23.52
MnO_2	0.15	Cu	12.34	Hf	3.32
Na_2O	0.37	Zn	19.62	Ta	10.64
K_2O	0.06	Ga	40.83	Pb	8.51
CaO	0.03	Rb	35.70	Th	35.14
MgO	0.13	Zr	46.36	U	2.55

Table -3: Mineral forms of some major and minor elements present in bauxite.

Element	Mineral	Appx. Formula
Al	Gibbsite	α- Al_2O_3, $3H_2O$
	Boehmite	α- Al_2O_3, H_2O
	Diaspore	β- Al_2O_3, H_2O
Fe	Goethite	α- FeOOH
	Hematite	α- Fe_2O_3
	Magnetite	Fe_3O_4
	Ilmenite	$FeO.TiO_2$
Si	Kaolinite	Al_2O_3. $2SiO_2$. $3H_2O$

	Quartz	SiO_2
	Sillimanite	$Al_2O_3.\ 3SiO_2.\ 2H_2O$
	Halloysite	
Ti	Anatase	TiO_2
		TiO_2

2.2 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.

$$Al_2O_3.\ xH_2O + 2NaOH \rightarrow 2NaAlO_2 + (x+1)H_2O \tag{1}$$

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).

Gibbsite $Al_2O_3.3H_2O + 2NaOH \rightarrow 2NaAlO_2 + 4H_2O$ ($135\text{-}150^{o}C$) (2)

Boehmite $Al_2O_3.H_2O + 2NaOH \rightarrow 2NaAlO_2 + 2H_2O$ ($205\text{-}245^{o}C$) (3)

Diaspore $Al_2O_3.H_2O + 2NaOH \rightarrow 2NaAlO_2 + 2H_2O$ (high T & P) (4)

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.

$$2NaAlO_2 + 4H_2O \rightarrow Al_2O_3.3H_2O + 2NaOH \tag{5}$$

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.

$$Al_2O_3.SiO_2 + NaOH \rightarrow Na_2SiO_3 \tag{6}$$

The reaction of kaonilite silica gives rise to appreciable loss of caustic soda. But the quartz is very less reactive under these conditions and passes into the red mud.

Disilication is then done via precipitation of sodalite

$$Na_2SiO_3 + NaAlO_2 \rightarrow Na_2O.Al_2O_3.\ 2SiO_2 \quad (7)$$

Dissolution is necessary to supersaturate the liquid to a point where the sodalite formed acts as a seed to precipitate more sodalite. The rate of precipitation is found to increase with temperature. But at the Gibbsite digestion temperature i.e. 130-150^oC the rate is very slow. Hence it is necessary to hold the material at the digestion temperature long enough to allow the silica to precipitate. The product of reaction (7) is known as the combined soda.

The basic iron oxides formed in the digestion process remain essentially insoluble, but fine-grained iron reacts at high temperature, particularly in the presence of lime. Aluminum locked in the goethite does not dissolve. The titanium containing phases are insoluble in caustic but are partially soluble at high temperature especially anatase and amorphous titania. Most alumina producers add lime at some point in the process and the lime forms a number of compounds that end up with the bauxite residue. The dissolved titania reacts with Na and Ca to form insoluble titanates

When aluminum is present as monohydrate i.e. as Boehmite or Diaspore, it has to be digested at high temperature (240-300^oC) and pressure. When there is a mixture of Gibbsite and Boehmite, then double digestion is required.

Diasporic bauxite needs high temperature and high pressure digestion. A recent study by Zhao indicated economic dissolution of diasphoric bauxite at 280^oC in Bayers process using lime addition of over 16% of Bauxite. Na_2O in red mud still remains less than 2.5

2.3 CHARACTERISTICS OF RED MUD

Red mud, as the name suggests, is brick red in colour and slimy having average particle size of <10 μm. A few particles of greater than 20 μm are also available. About 35% by weight of solids contain less than 5 μm and about 80% less than 8 μm in the red mud of NALCO refinery, Damanjodi. It is alkaline, thixotropic and possesses high surface area in the range of 13-16m^2/g 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. Composition of red mud samples from some randomly selected locations is given in Table 4 .

Table 4: Composition of red mud generated in plants of different parts of world.

Country		Major constituents, wt %				
		Fe_2O_3	Al_2O_3	TiO_2	SiO_2	Na_2O
India	Al. Corpn.	20.26	19.60	28.00	6.74	8.09
	MALCO	45.17	27.00	5.12	5.70	3.64
	HINDALCO	35046	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(EM)
USA	ALCOA Mobile	30.40	16.20	10.11	11.14	2
	Arkansas	55.6	12.15	4.5	4.50	1.5-5.0
	Sherwon	50.54	11.13	Traces	2.56	9.00
FRG Baudart		38.75	20.00	5.5	13.00	8.16

2.4 UTILIZATION OF RED MUD

Till today, almost all over the world, red mud is disposed off the plant site in two main ways depending on the facilities available and the surroundings. In countries such as France, England, Germany or Japan where availability of land for dumping is less and sea are nearby, the practice is to discharge the mud into the sea. Where free land is available nearby, the mud is pumped into pools and ponds constructed for this purpose. The water overflowing from the ponds after settling of the mud is recycled to the plant for partial recovery of the alkali carried away with the mud and the solid is left for sun drying. Before proceeding to possible solutions for recovery and use of red mud it is pertinent to have a brief discussion on the issues of environmental concerns, red mud dewatering and disposal status, since they are interlinked.

Red mud is not a particularly toxic material. Brown and Kirkpatrick applying Toxic Characteristic Leaching Procedure (TCLP- an EPA test procedure designed to determine the morbidity of wastes) and Multiple Extraction Procedures (MEP), conducted at Tulane on the red mud of Kaiser Aluminium & Chemical Corporation, Gramercy, conformed this aspect. Concentrations of all metal species were well below the EPA Regulatory Threshold and Drinking Water Standards. In reality then the environmental concerns relate to two aspects: (i) the very large quantity of the red mud generated, and (ii) its causticity. A typical alumina plant produces large amount of red mud. In addition up to 2 tons of liquor at 5-20 gpl caustic (as Na_2CO_3) accompany with every ton of dry mud solids. Discussing the red mud production and disposal problems in Australia, whose aluminum production constitutes 39% of world production and the red mud generation is 50% of that in the world, indicated that the treatment and disposal of red mud is a major operation and may account for 30-50% of operations in an alumina refinery. Dewatering and disposal technologies assume great significance.

2.4.1 Status of Mud Disposal

Mud disposal means transporting and depositing it in a tailing pond or lake or in a landfill covering the aspects of landscaping, rehabilitation and the environmental impact. Of course the important objectives remain the same i.e. (i) reduced mud volume, (ii) reduced caustic content, (iii) reduced environment impact, (iv) improved reclamation potential, and (v) improved rehabilitation possibilities. The usual earlier trend was to pump slurry with 20-30% solids to the artificial ponds or lakes requiring bottom sealing to avoid caustic leakage, high pumping energy etc. Improved dewatering techniques have facilitated semi dry disposal methods by separating fine mud from the sand fractions and dewatering to a solid concentration of 50-60% before transporting by pipelines. At the disposal dam, the discharged mud is spread and allowed to consolidate and dry in layers following the method of thickened discharge and dry stacking. This type of disposal strategy has many advantages such as (i) reduced pumping costs, (ii) effective use of land, and (iii) minimum environment impact.

Hyperbolic filters result in a mud of typically 70-80% solids and hence either a conveyer belt or trucks can be used for transportation. The latter appears preferable because of (i) more flexibility with respect to number of trucks or location of dumping, (ii) less capital investment, (iii) less operating cost etc. This type of mud is also advantageous from the point of view of (i) mud deposition, (ii) mud drying (solar or otherwise), (iii) landscaping, (iv) closure and rehabilitation, and (v) environmental impact.

2.4..2 Mud Reclamation / Preparation for Reuse

Aluminum producers have dumped large amounts of mud in artificial ponds/lakes. Any opening for a beneficial use of red mud will call for re-claiming these dumped materials for reuse seeking easy and economic techniques to do so would be preferred. Recently, Kaiser Aluminium & Chemical Corporation has ventured such activities. Kaiser Gramercy discharges the red mud into the lake as slurry with 20% solids content, which consolidates to about 45% solids over several weeks. Lake drying was achieved by aggressively pumping off the surface water and trenching the mud lake surface, followed by perimeter trenching with cross drains. By this way the lake surface solids content increased to almost 60% allowing utility vehicles with oversized tires to run over it in order to disc the lake surface. The discing allows the surface to quickly dry to above 75% solids, allowing subsequent use of large unmodified bulldozers. This way the mud could be reclaimed for reuse. Many similar methods will come up slowly.

2.4.3 Approach to utilization

A lot of efforts are being made globally to find out suitable uses of red mud so that alumina industry may end up with no residue at all. For complete utilization of red mud Nikolaev Alumina Plant proposed the following avenues:

- Building material production as an additive to cement;
- Production of colouring agent for paint works for ground floors of industrial and other buildings;
- Production of toned paper in the wood-pulp and paper industry;
- Production of iron ore sinter and pellets in the ferrous metallurgy;
- In agriculture for the purpose of improvement of the soil structure and as a micro fertilizer and a neutralizer of pesticides;
- As a technogenic raw material to be used for extraction of rare-earth metals and alumo-ferric coagulants.

Kaiser Aluminium & Chemical Corporation have also started making beneficial uses of their Gramercy Lousiana Plant residue. Their uses include (i) land-fill cover, (ii) liquid waste absorbent, (iii) road bed and levee construction material, (iv) alternative to natural marsh sediment, and (v) metal recovery. The plant at EURALLUMINA in SW of Sardinia proposes the following uses of its red mud:(a) industrial application as ceramic, building bricks, pigments, (b) use for reclamation of mining and quarrying areas as filling material after decreasing its water content and making it inert material. Thus a general approach to the solution can be broadly classified into three categories:

i) Bulk utilization in terms of landfill, land reclamation, etc.
ii) Specific use as building materials, inorganic chemicals, adsorbents etc.
iii) Recovery of major metallic constituents

In addition to these, there are attempts to face this problem through reducing the generation at the source through suitable beneficiation of the starting bauxite material. This aspect will be dealt with prior to the discussion on the above three approaches.

2.4.4 **Reducing Red Mud Generation through Beneficiation of Bauxite and Process Improvement**

Looks to the red mud analysis reveals that iron, aluminium, titanium, combined soda, silica are the bulk constituents. When iron content in the feed is high (near or above 20% as oxide) its content in the mud is high (above 50% as oxide) as seen from Jamaican, NALCO and some other bauxite in Tables-2, 3 and 5. Similarly, a low value of ~ 10% as iron oxide, as in Surinam Bauxite, results in a mud with around 30% iron oxide. A good number of studies are available in literature, which report a substantial reduction of the iron content of bauxite by various beneficiation methods have reported beneficiation of an Indian bauxite ore by removing iron through magnetic separation. A starting material without any pretreatment containing 42.2% Al_2O_3 and 14.2% Fe_2O_3 could be converted into a product containing 92.6% Al_2O_3 and 2% Fe_2O_3 with 72% recovery. Use of such a material in Bayers process would be highly beneficial side by side reducing red mud generation substantially.

It is also possible to decrease combined soda content of the red mud through control of leaching conditions. As already indicated gibbsite, which usually constitutes nearly two thirds of the bauxite raw materials, responds to low temperature pressure digestion. Banvolgi and Siklosi proposed an Improved Low Temperature Digestion (ILTD) process where not only the combined soda reporting in the red mud is low but also a new by-product in the form of Bayer-Sodalite (desilication product) is generated, thereby increasing the profitability. In this process the bauxite charge is so adjusted that the dissolved alumina is fairly close to the equilibrium solubility for gibbsite so that dissolution of gibbsite consumes the reactive OH^- ions in a short reaction time and a significant part of kaolinite remains un-attacked. The bauxite residue (red mud) is separated immediately after the digestion. The pregnant liquor is subjected to a pressure post-desilication operation in order to maintain low dissolved silica content and to make Bayer sodalite for further use. In this way a soda (Na_2O) content of 1.5-2.5% results in the red mud and, Bayer sodalite bi-product, mostly containing Na_2O, Al_2O_2, SiO_2 (sodium aluminium hydrosilicate-SAHS) and suitable for preparing zeolite, is obtained.

2.4.5 Bulk utilization in terms of Land fills and Land reclamation.

It is already indicated that red mud is dumped in ponds or lakes identified for this purpose, if not dumped into the sea. Probably the easiest use for the mud will be some sort of useful land fill instead of just dumping. Some such attempts in this direction are: filling material for mined or quarrying areas, land fill cover, road bed and levee material, alternative to Natural Marsh Sediment, agricultural land soil neutralization, composting domestic waste etc. For use in many of these areas some sort of neutralization or red mud amendment becomes necessary. The following is a brief description of these uses.

2.4.6 Filling material for mines and quarries

Bauxite mines or other quarries can be filled up by red mud. For this purpose the slurry must be neutralized and high solids pipeline transportation is necessary. Considerable progress has been made on the latter aspect as discussed briefly beforehands. For neutralization lime, gypsum, sea water or other materials having similar neutralization properties is mixed with the red mud. In Australia and Hungary neutralization is done by adding gypsum after which the red mud is called red mud amended with gypsum (RMG). Recently CVG – Bauxilum with Atomaer – KD Engineering Co. have successfully pilot tested neutralization of red mud pulp from 12.20 to 7.60 pH by using carbon dioxide and the atomaer gas. Mine filling is a good use though the values (metal) in red mud are left to be recovered in future.

2.4.7 Land fills cover

Good progress has been reported by Kaiser Aluminium & Chemical Corporation [Brown and Kirkpatrick 1999, Kirkpatrick 1996] in this regard. After caustic neutralization red mud and local clay mixtures have been successfully used as land covers.

2.4.8 Road bed and levee materials

Again Kaiser has reported use of red mud as road bed and levee material. Using the compatibility of the red mud to good effect disced red mud was stacked and then compressed by heavy equipment to form hard road surfaces on the mud lake, which are used extensively to support the large trucks carrying the land fill cover and to move equipments around the lake. The roads remained in good condition even after long use and heavy rains. Kaiser has also used disced, compressed mud as a base material to raise one of the Gramercy Mud Lake Levee by five feet. A clay cap was placed over the material to facilitate vegetative growth. They are contemplating to increase the life of the existing lakes by at least 20 years by this way. Nunn has indicated that the common practice is to treat only the upper 0.5 to 1.0 meters of the surface to neutralize the caustic soda. Organics and fertilizers are also added to facilitate vegetation growth which prevents wind and water erosion of the treated soil.

2.4.9 Alternative to natural marsh sediment

A study at Tulane University has shown that over 25 square miles of Louisiana wetlands are lost per year due to sediment starvation, coastal erosion and subsidence. Quite often the dredged sediments are found polluted and unsuitable for placement in the wetlands. Red mud has been proposed to be a suitable alternative provided the partitioning and bioavailability of key trace metals do not affect aquatic organisms.

2.4.10 Agricultural land neutralization/composting

Wherever the agricultural land soil is acidic, red mud can be mixed with the manures/composts to neutralize the soil. Besides, red mud slurry is a good disinfectant and stabilizing agent for municipal sewage. It can eliminate organic infectants from the sewerage to convert it to sludge suitable for use as a wetland soil or inclusion in a fertilizer. Kaiser has found good results of flourishing plant life in composted solids / red mud in both fresh and brackish wetland environments. RMG have been successfully used in Australia and Hungary for soil amelioration, composting domestic waste and for treatment of domestic sewage or effluents of animal farms.

2.4.11 Specific Use as Building Materials, Inorganic Chemicals, Adsorbents etc.

Numerous uses for red mud have been reported in the literature, well documented in the book by Thakur and Das. In this section only the developments beyond 1994 are discussed briefly. The uses range from making various building materials, adsorbents, colouring agents, to preparation of exotic ceramic glass materials, and even plasma spraying. Banvolgyi and Siklosi have claimed that production of a mud containing 1.5-2.5% Na_2O following their ILTD process, is welcome in the cement industry as an additive. The plant of EURALLUMINA, in SW of Sardinia also proposes building bricks as a possible use for their red mud. Smirnov propose a technology of sulfuric acid processing of the deactivated red mud with coagulation and granulation of Fe-Al coagulants followed by burdening, forming and heat treatment to produce the building materials. Borovkov proposed flotation of Cu-Mo from the red waste followed by (addition) using the tailings to prepare bricks with good physico-mechanical and service properties.

Red-mud can be used as an adsorbent and colouring agent. Taking the special properties of Bauxaline, Gardanne Pechiney plant reported its suitability for use as arsenic fixation on co-disposal projects and coloring of various materials. Liu evaluated the use of red mud to remove toxic materials from wastewater. Laboratory studies indicated that only 0.5 mg/liter red mud was sufficient for near complete removal of all the metals except selenium (IV) at an initial water pH of 8.0 and at retention time as low as one minute. Selenium removal is very pH dependent with an optimum pH around 6.0.

The predominant mechanisms with red-mud coagulants are adsorption-charge neutralization and sweep coagulation. Other authors have used red mud to adsorb nickel. Red mud can also be used as sorbent for flue gases. It has also been tested as cracking and dechlorination catalyst for thermal and catalytic degradation of poly vinyl chloride containing polymer mixtures into fuel oil.

Red mud may be used in ceramic industry. The red mud from Seydischir Aluminium Plant, Turkey was investigated for use in the making of ceramic glazes such as porcelain, vitreous (sanitary ware glazes), tile and electro porcelain glazes in the ceramic industry. It was found that the addition of up to 37 weight per cent of the red mud waste was possible in the production of the glazes. Recently Balasubramanian used specific mixtures of red mud, fly ash and spent pot liner to prepare glass-ceramic products which showed excellent properties and aesthetic appearance for possible applications as decorative tiles in the building industry. Xhang and Yan, through Mossbauer and FTIR spectroscopy and XRD study of the structure and crystallization of glass ceramics prepared using red mud as raw material, concluded that such glasses have the precursor structure capable of producing the primary crystalline phase.

A recent study by Mahata confirmed formation of Aluminium Titanate-Mullite composite from red mud rich in titanium. This was achieved by preferentially removing Fe_2O_3 from red mud through dilute hydrochloric acid leaching leaving a residue rich in Al_2O_3, TiO_2 and SiO_2. Then pure Al_2O_3 powder was added to adjust the molar ratios of $\{(Al_2O_3 + Fe_2O_3) / TiO_2\} = 1.0$ and $\{Al_2O_3 + SiO_2] = 1.5$. Thus a composite material consisting of aluminium titanate (Al_2TiO_5) – iron titanate (Fe_2TiO_5) solid solution and mullite ($3Al_2O_3.2SiO_2$) phases after final reaction synthesis, was obtained. This material has potential uses as liquid metal flow regulators, risers, thermocouple sleeves, burner nozzles, ceramic filters etc..

A recent study has reported use of red mud as plasma-spray coatings on aluminum and copper metal substrates. This way the coating can be used as a wear resistant coating with applications for machine components, slide gates, slag holes, excavators and conveyer belts.

There can be many such uses for red mud. However, they can take care of only a small fraction of the waste material. For bulk use either the metal extraction processes and/or land fill etc. may be considered.

2.4.12 Recovery of Metal Values

The analysis presented in Table-5 shows that iron is the major constituent of red mud followed by Al_2O_3, Na_2O, SiO_2 and TiO_2. Of these constituents, recovery of silica is not significant. The titania has the most potential value and, if successfully recovered, iron can be obtained as a value added product whereas alumina and alkali can be recycled in the Bayers process stream. Depending on their amount in red mud, economic extraction of other metals can also be significant.

2.4.13 A General Strategy

Rayzman and Filipovich and Misra, Staley and Kirtepatrick have indicated a general strategy to utilize red mud. The former authors have suggested an integrated method where coal combustion and red mud sintering are combined in the alumina refinery. After soda and alumina recovery the residue can be utilized by metallurgical or chemical technology. A double stage pyrometallurgical process for the decomposition of similar material has been tested on a bench-scale level. Iron can be recovered either as a reduced iron or pig iron, and the slag is enriched for titanium, and rare metals. The latter authors also suggest a similar approach with removal of aluminium and soda through sintering and alkali washing stages followed by pyrometallurgy of the residue to get pig iron and a slag rich in titanium. The slag can further be leached with sulphuric acid to recover titanium.

However, this type of strategy strongly depends on the composition of red mud. First of all the combined soda is to be considered. In case it is high then an attempt should be made to reduce it in the Bayers process itself with advanced technology. In case it is not possible then both Al and soda can be removed either by sintering or pressure leaching. The residue then can be treated for iron and titanium recovery.

2.5 RESEARCH & DEVELOPMENT WORKS 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 and lab scale product as red mud plastic**
6. NML, Jamshedpur	**Recovery of V_2O_5 and Al_2O_3.**
7. Metallurgical Dept. ,B.H.U.	**Development of bricks, recovery of titanium and Ferro titanium**
8. NALCO, Angul	**Filler to PVC sheets, pipes and pigment as per ISI**
9 RRL, BBSR	**Recovery valuable elements like V_2O_5**

2.6 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

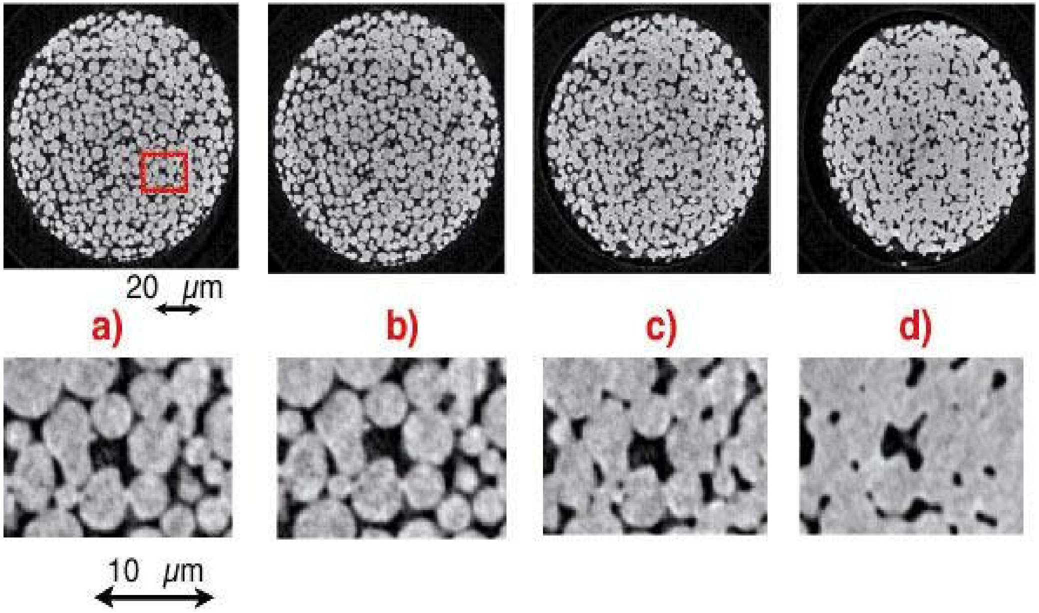
The physical changes that take place are:

- 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



6.1 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.

6.2 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.

6.3 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.

CHAPTER-3

EXPERIMENTAL

3.1 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 and magnetic properties.

- **The red mud sample is to be collected from NALCO, Damanjori.**

- **The sample is either in compacted form or compacted with the help of press.**

- **Some extra constituents such as graphite or silica(from other waste) are added to enhance sintering and mullite formation respectively.**

- **The variables which are changed during sintering are as follows**
  1) Temperature – 300^{O}C, 900^{0}C,1100^{O}C
  2) Soaking time – 30 mins,1hr and 2hr for each temperature
  3) Composition

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

. **1) Hardness Test – It is done in Vicker's or Brinell's hardness tester. This determines the resistance to indentation.**
  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.**

3.2 EXPERIMENTAL PROCEDURE

- **Sample collection from NALCO, Damanjori**
- **Subjection of the sample to 1100^{0}C for removal of moisture .**
- **Compaction of the sample**
- **Sintering of the compact**
- **Determination of compressive strength of the compact (both sintered as well as unsintered)**
- **X-ray analysis of the sintered compact.**

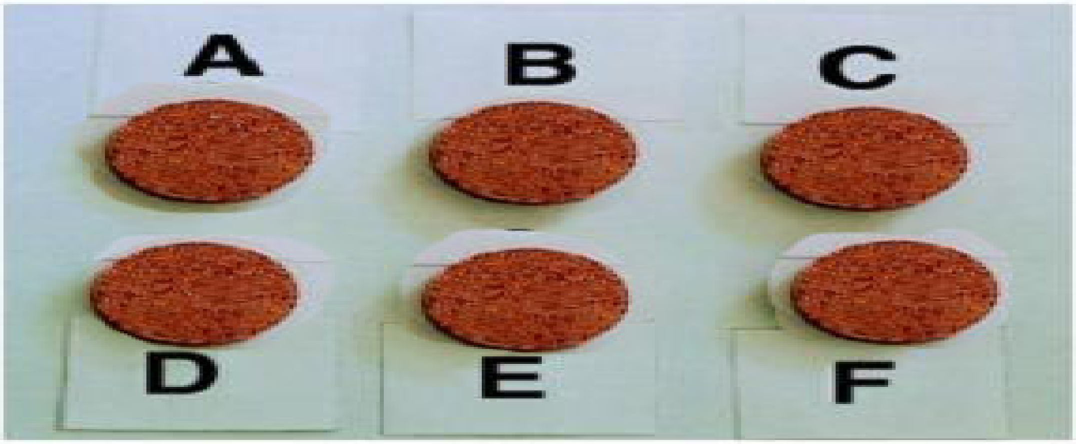
3.3 COLLECTION OF THE SAMPLE

- **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 1100C for complete removal of moisture which's done by placing the sample in the furnace for 1hr.**

3.4 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 15 samples.**

RED MUD COMPACTS



3.5 SINTERING OF THE COMPACT

- **Sintering of the red mud compact is carried out at 3 different temperatures as well as time.**

Sintering temp.	**sintering time**
300^0C	**30 mins.,1hr,2hr**
900^0C	**30 mins.,1hr,2hr**
1100^0C	**30 mins.,1hr,2hr**

CHAPTER-4

RESULTS

&

DISCUSSIONS

EXPERIMENTAL RESULTS:

RESULTS FOR SAMPLE SINTERED AT 300^{0}C

sintering time	Initial wt of sample(gm)	Dia of sample (mm)	Final wt of sample (gm)	Length of sample (mm)	Compressive strength (mpa)
30 min	**2.69**	**15**	**2.6**	**6.03**	**32.24**
1 hr	**2.71**	**15**	**2.5**	**6.04**	**41.66**
2 hr	**2.72**	**15**	**2.47**	**6.03**	**43.27**

RESULTS FOR SAMPLE SINTERED AT 900^{0}C

sintering time	Initial wt of sample(gm)	Dia of sample (mm	Final wt of sample (gm)	Length of sample (mm	Compressive strength (mpa)
30 min	**2.71**	**15**	**2.4**	**6.03**	**33.59**
1 hr	**2.70**	**15**	**2.4**	**6.032**	**42.94**
2 hr	**2.71**	**15**	**2.4**	**6.03**	**44.79**
4 hr	**2.71**	**15**	**2.4**	**6.03**	**49.18**

RESULTS FOR SAMPLE SINTERED AT 1100^{0}C

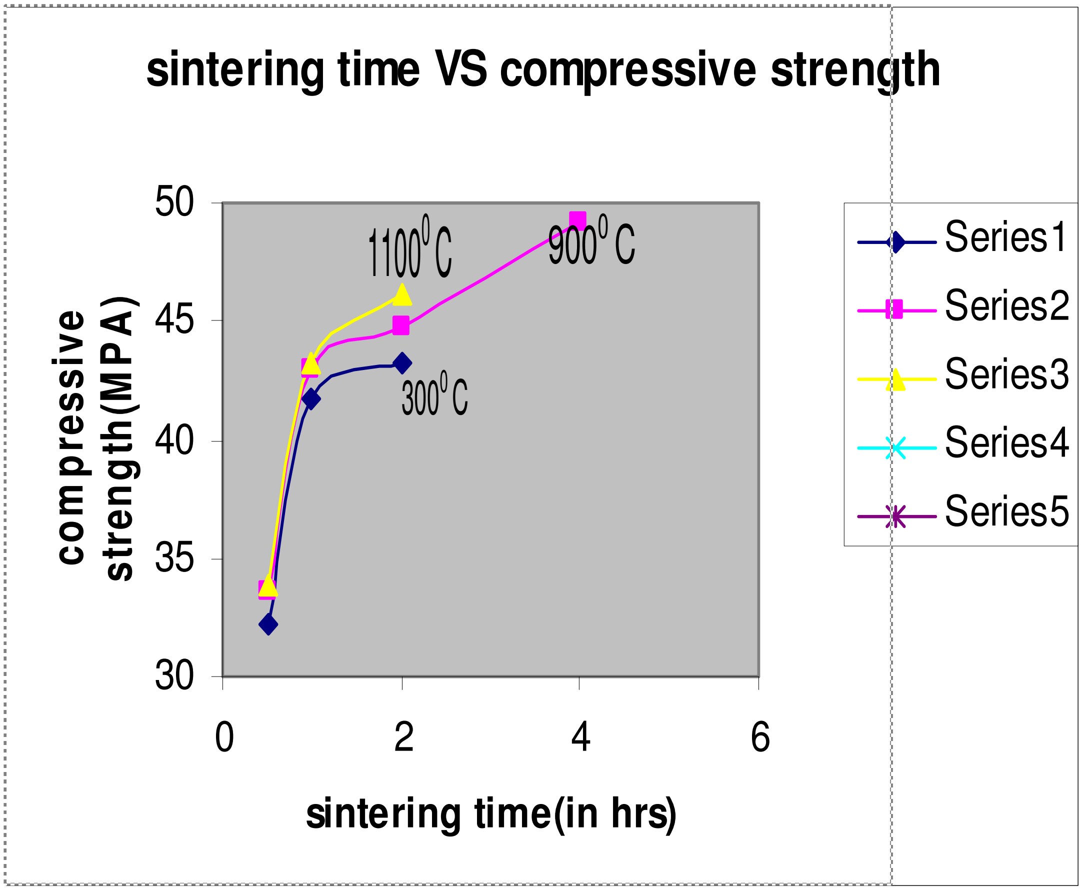
sintering time	Initial wt of sample(gm)	Dia of sample (mm	Final wt of sample (gm)	Length of sample (mm	Compressive strength (mpa)
30 min	**2.71**	**15**	**2.4**	**6.03**	**33.59**
1 hr	**2.70**	**15**	**2.4**	**6.032**	**42.94**
2 hr	**2.71**	**15**	**2.4**	**6.03**	**44.79**

DISCUSSION:

After conducting the above experiments and characterization tests for the red mud pellets samples prepared by compaction of grounded red mud powder the following results are obtained which can be discussed with the help of the graphs plotted are as follows:

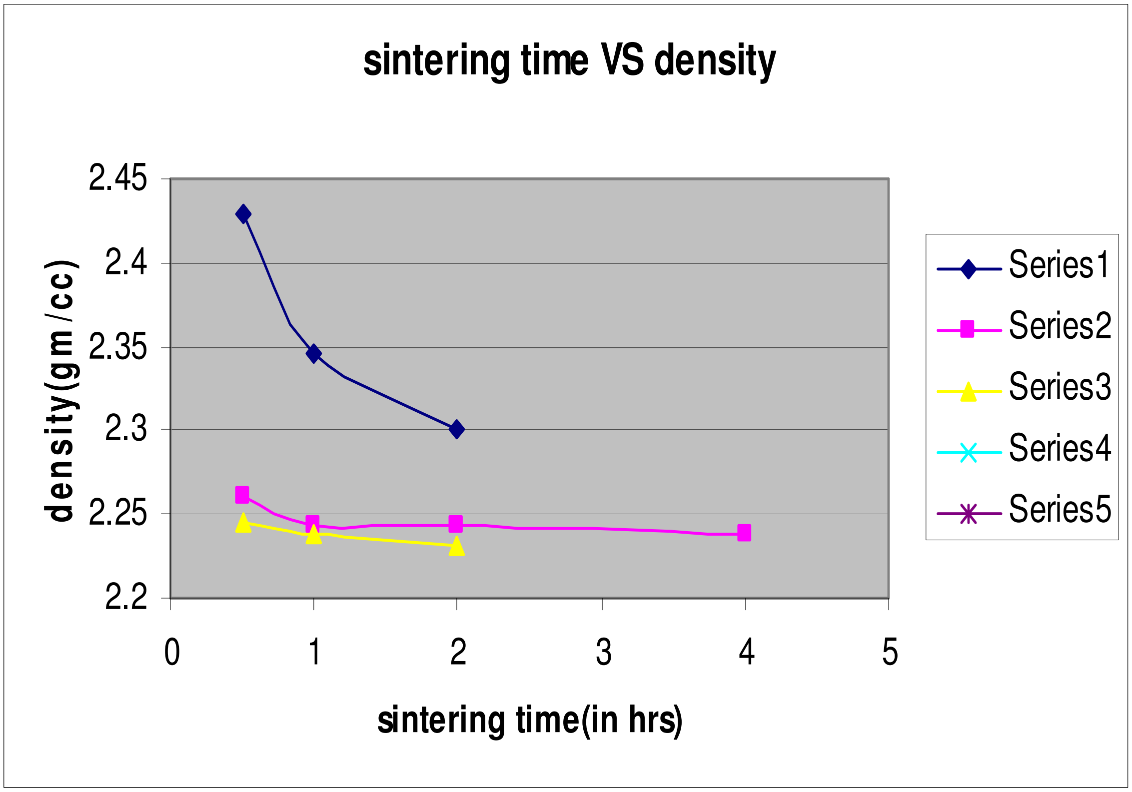
1) SINTERING TIME VS COMPRESSIVE STRENGTH

The sintered samples were tested for compressive strength and the graph is plotted which showed a increasing trend with time as well as with temperature. It is due to phase transformation.



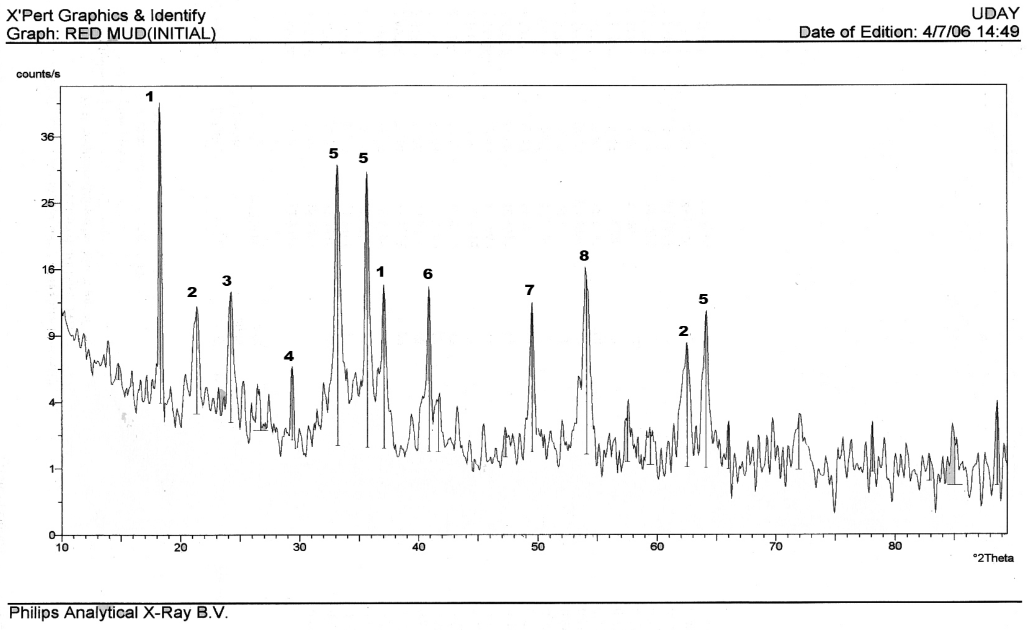
2) <u>SINTERING TIME VS DENSITY</u>

The sintered compacts are air cooled and their Sintered density was measured. Graph is plotted which showed a decreasing trend with time as well as with temperature.



<u>XRD Graph of Initial Red Mud Sample</u>

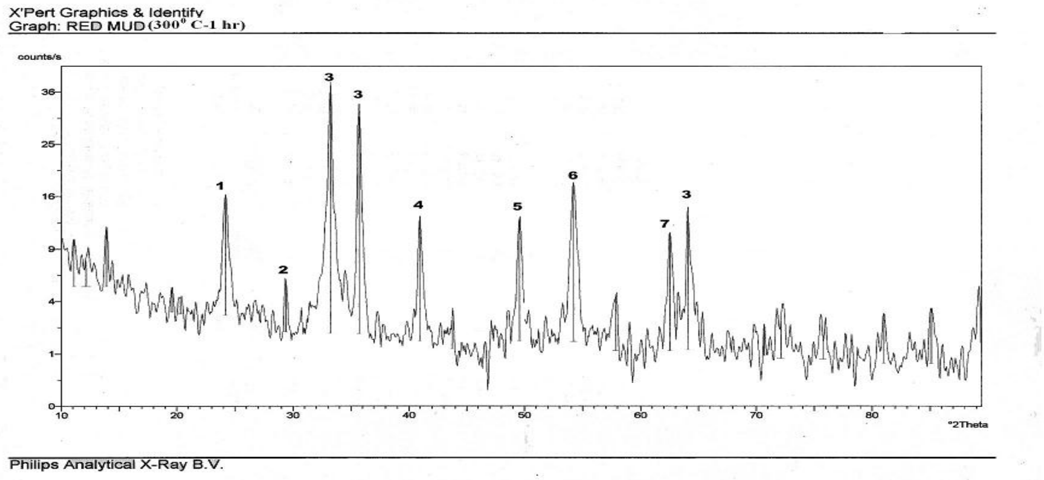
1-Al(OH)$_3$
2-SiO$_2$
3-TiO$_2$
4-Na$_2$O
5-Fe$_2$O$_3$
6-Al$_2$O$_3$
7-CaCO$_3$
8-MgO



XRD Graph of Red Mud Sample sintered at 300^{0}c for 1 hr

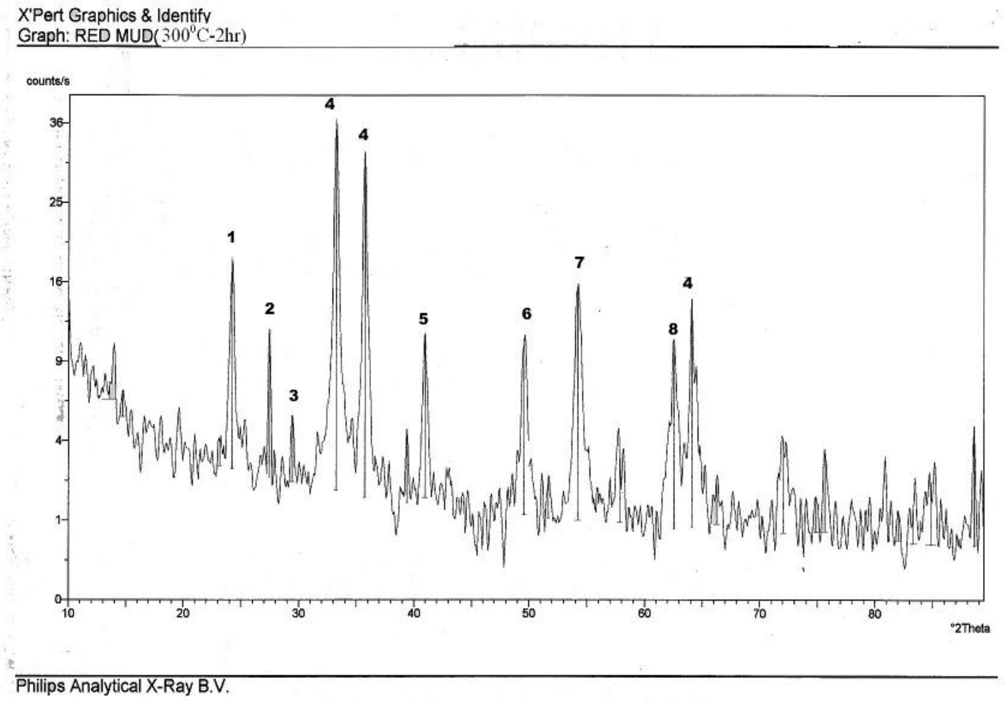
1-TiO_2
2-Na_2O
3-Fe_2O_3
4-Al_2O_3
5-$CaCO_3$
6-MgO
7-SiO_2

In this graph the $Al(OH)_3$ phase is missing from the initial sample.



XRD Graph of Red Mud Sample sintered at 300^{0}c for 2hrs

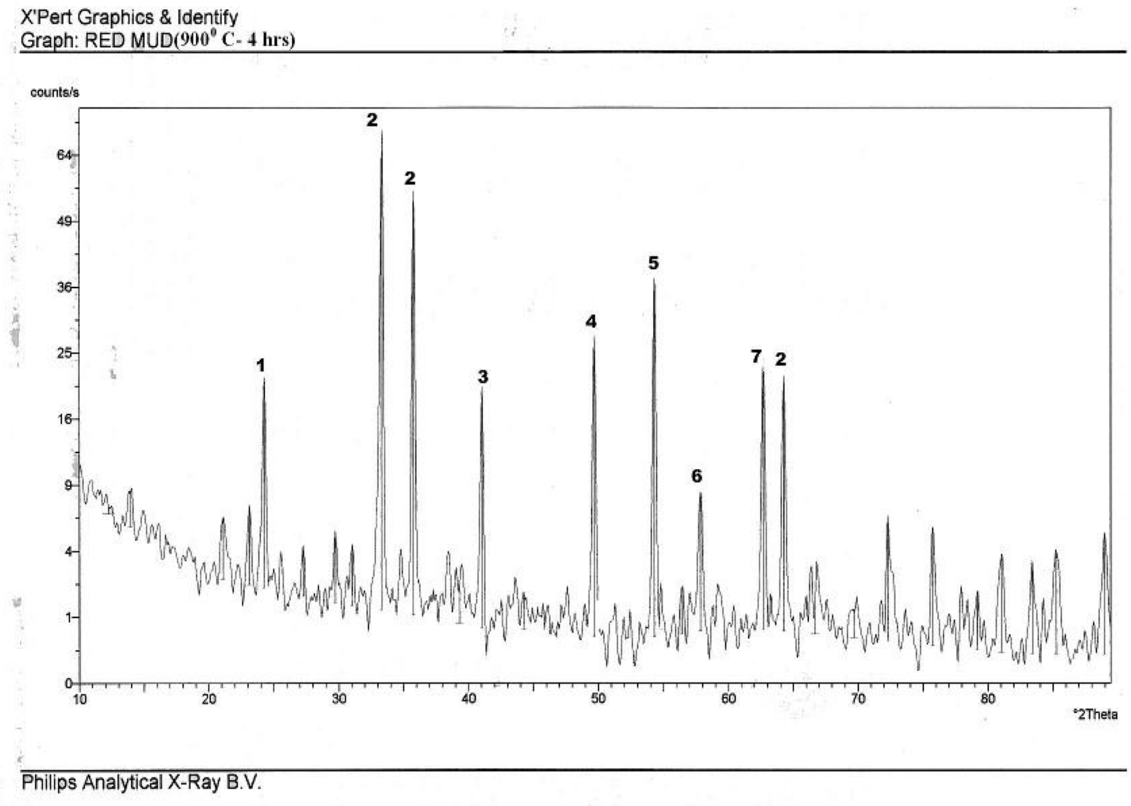
1-TiO_2
2-$FeO.Fe_2O_3$
3-Na_2O
4-Fe_2O_3
5-Al_2O_3
6-$CaCO_3$
7-MgO
8-SiO_2



In this graph the spinel ($FeO.Fe_2O_3$) phase comes which was not present in the previous sintered sample.

XRD Graph of Red Mud Sample sintered at 900^{0}c for 4hrs

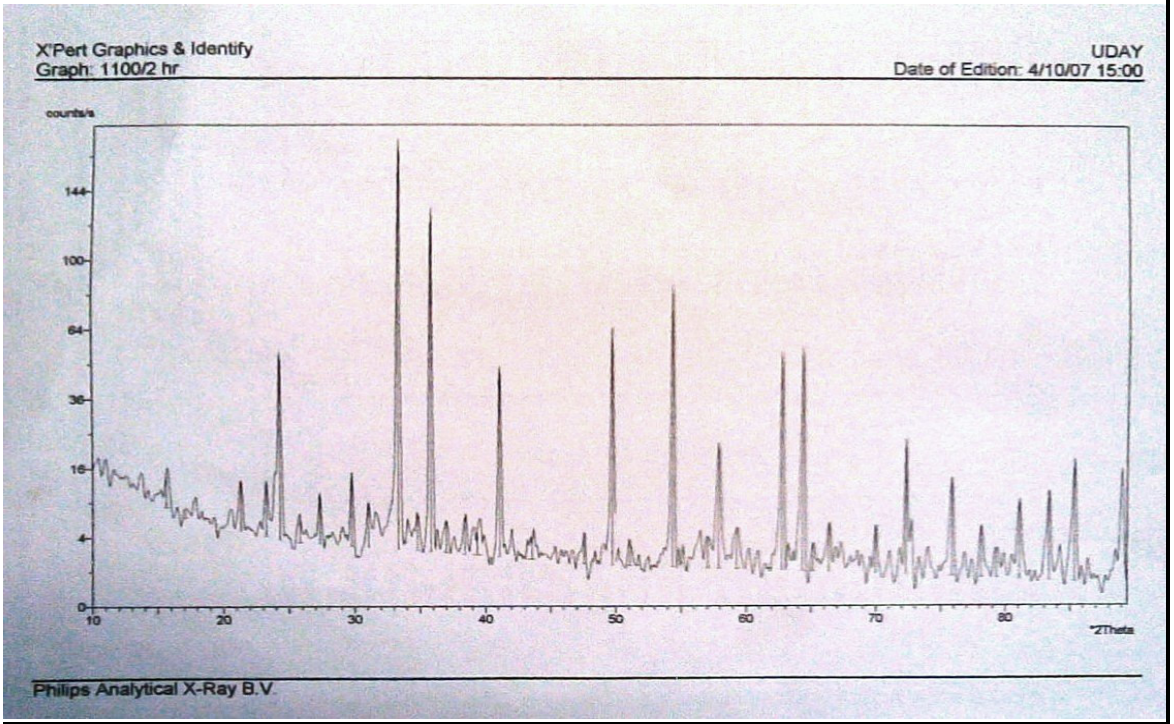
1-TiO_2
2-Fe2O_3
3-Al2O_3
4-$CaCO_3$
5-MgO
6-MgFe2O_4
7-SiO_2
8-$NaCaAlSi_2O_7$



In this graph the $MgFe_2O_4$ and Na_2O phases are absent and the new phase Magnesioferrite ($MgFe_2O_4$) and $NaCaAlSi_2O_7$ comes in.

XRD Graph of Red Mud Sample sintered at 1100^{0}c for 2hrs

1-TiO_2
2-$Fe2O_3$
3-$Al2O_3$
4-$CaCO_3$
5-MgO
6-$MgFe_2O_4$
7-SiO2
8-$NaAlSiO_4$



In this graph the NaCaAlSi$_2$O$_7$and Na$_2$O phases are absent and the new phase Nepheline (**NaAlSiO$_4$**) comes which was not present in earlier graphs.

CHAPTER-5

CONCLUSIONS

CONCLUSION

- **Sintering of red mud results in increase in its compressive strength by formation of new phases and dissolution old one. Hence it can be used for building brick, land fill cover and road bed.**
- **Substantial development has taken place in the area of disposal of red mud.**
- **Considerable work has also been done for its product development and utilization.**
- **It is still too early to tell which uses of red mud could become economically viable but complete red mud utilization may be achieved in the near future.**

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