

VALUE ADDED METAL EXTRACTION FROM RED MUD

Thesis submitted in partial fulfilment of the requirements for the award of the degree of

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In

Mechanical Engineering

[Specialization: Steel Technology]

Submitted by

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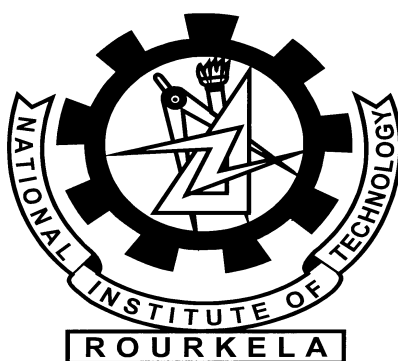


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Certificate

*This is to certify that the thesis entitled “Value added metal extraction from red mud” submitted by **Ankur pyasi** in partial fulfilment of the requirement for the degree of “Master of Technology” in Mechanical Engineering with specialization in Steel technology, is a bonafide work carried out by him under our supervision and guidance. In our opinion, the work fulfils the requirement for which it is being submitted.*

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ABSTRACT

In the presented thesis work, utilization of red mud for extraction of value added product is discussed. Huge quantity of red mud is being generated by aluminium industry which is a potentially hazardous material and creating environmental pollution. Red mud samples collected from Nalco Indicates apart from Iron oxide the other phase of interest is titanium oxide. In the present work Ferro titanium extraction is tried by carbothermic reduction in export arc plasma furnace utilizing both nitrogen and Argon as the ionizing gases. Also for efficient extraction of metallic phases lime has been added to generate slagging phases which melts at comparatively lower temperature. Also in the present work, Aluminium dross has been added to the charge material to facilitate the metal extraction at a comparatively lower temperature .After fusion the fused material is crushed to separate the metal and gaunge phase which has been characterised by XRD and microscopy. The analysis indicates good degree of metallization in form of Ferro-titanium.

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CHAPTER 1

INTRODUCTION

1.1. Background:

Red mud is the solid waste material which is produced during the production of alumina (Al_2O_3) in the bauxite industry. Red mud is generated by Bayer's process. Quality and processing of ores containing aluminium defines the amount of red mud produced. 1 to 15 tonnes of dry red mud is generated during production of 1tonnes of alumina. There is no other economic method which generates red mud during production of aluminium from bauxite. In India 1.892 million tons per year aluminium is produced by aluminium industry. Metal production of 6×10^5 tonnes/ year generates nearly 2×10^6 tonnes of red mud every year. Globally 9×10^7 tonnes of red mud is produced. The red mud has high alkalinity (pH 11-12.5). It contains Fe_2O_3 , Al_2O_3 , SiO_2 , Na_2O and CaO . Zr, Y, Th, U elements also present in trace amount. It has reddish-brown colour. [1, 2, 10, 12, 15]

1.2. Inspirations for project:

The expenses involved in the transportation and pollution abatement are serious problems faced by industry of aluminium in dumping of Red mud. A 30%-50% Fe_2O_3 and remaining Al_2O_3 and SiO_2 is the typical composition for red mud. Trace amount of metallic elements such as Vanadium, chromium, magnesium and Zirconium are also present in red. Haematite, goethite, Anatase, Rutile, Quartz and sodalite are their major components. So, red mud is a potential source of many metals.

Red mud is used in the cement industry for the manufacture of tiles, but such applications can utilize only small amount of red mud produced over the year. Processes for metallurgical as well as non-metallurgical applications of red mud have been developed. Up till now, red mud has found limited commercial utilization in road making Portland cement. Suitable metallurgical processes for metal recovery from red Mud is important for bulk utilization. Value addition and moving towards zero waste. To recover iron values from red mud two main approaches which have been generally investigated are based on:

1. Iron recovery by solid state reduction of red mud followed by magnetic separation.
2. Pig iron production through smelting in a blast /electric/low shaft furnace.

There are several processes which exist to recover metals from red mud, but unfortunately none of these are practiced in commercial operation. By using hardening process, new construction material from red mud has been developed. Thermal plasma technology is now

an established alternative which is capable enough for improving the existing metallurgical processes. In the thermal plasma process, uniform heat transfer to the charge material occurs due to high density of ionic charges. The reactions are completed in very short duration due to availability of very high temperature, high energy fluxes, and plasma state conditions in the plasma arc. They have the advantage of allowing the direct use of Fine feed materials. [10, 12]

India is rich in mineral resources and has a long history of mining, is a well known body in mineral producing countries of the world. The Indian economy to a great extent depends on the value of the mineral produced. They represent a major portion of raw materials for country's industrial activities. The lack of finance solutions to the problem of red mud allows room for major progression with the current price of metals at record highs. For most important metals, the climate for advancements has never been better. As shown in table below, composition of generated red mud compound and bauxite. Red mud is a concentration of many elements, aluminium mainly. Composition of bauxite and the generated red mud compound as shown in table.

Table 1.1: Composition of bauxite and the generated red mud

SL.No.	Element	Bauxite (%)	Red mud (%)
1	Al ₂ O ₃	56.4	14.7
2	SiO ₂	0.7	2.6
3	CaO	1.2	8.8
4	TiO ₂	4.3	7.2
5	Fe ₂ O ₃	35.1	60.7
6	Na ₂ O	0	1.6
7	Other (P,S,Cr,Mn,Hg,Pb,Zn,Cd)	2.3	

CHAPTER 2
LITERATURE REVIEW

2.1. Natural history of Bauxite:

Bauxite is an abbreviation applied to a naturally occurring mixture of minerals which are rich in hydrated aluminium oxides. Oxides of iron, silicon, and titanium are major impurities while such elements as zinc, phosphorous, nickel and vanadium are found in trace amount. The type of process needed for alumina production is defined by mineralogical characteristics of the bauxite ore. For the case of aluminium containing minerals, it is important to note whether gibbsite, Boehmite, diasporic mineralogy is dominant. This determines the type of leaching operation to be used. The world's metallurgical bauxite production, as per this mineralogy is listed in presence of silica, usually called active. Since, the active silica determines the process required in the same. Because, the production of aluminium is also continuously rising, it can be concluded that production of bauxite is continuously on a high.

Bauxite ore refers to a deposit of the material that contains high levels of aluminium oxide (Al_2O_3) and low levels of hematite (FeO_3) and silica (SiO_2). Bauxite's composition is such that it makes the ore economically mineable in a variety of locations across the globe. Other rich sources of aluminium include a variety of rocks and minerals which includes aluminous shale and slate, aluminium phosphate rock and Kaolites (high alumina clays), etc. [27]. Bauxite deposits are frequently extremely extensive this is due to their method of formation over the geological timeline, and therefore, they are found on almost all continents of the world as shown in Figure 2-3: Locations of Bauxite Mining.

Although, bauxite is found worldwide. The countries with the largest economically mineable deposits, in order of production are Jamaica, Australia, Brazil, Guinea, and India. The largest consumers of aluminium of year 2002 are The United States of America, Japan and Germany. All the three countries do not possess any or very little, bauxite deposits [27].

The only ore currently being used for the production of aluminium is bauxite. Bauxite consists of many hydrous aluminium oxide phases in combination with iron, silicon, titanium oxides and other trace impurities. Main mineral present in bauxite, Gibbsite ($Al(OH)_3$), boehmite ($\gamma-AlO(OH)$), and diasporite ($\delta-AlO(OH)$) a form of boehmite that exhibits a more dense state. Actual hardness of the ore depends on location on the globe where it is found. As friable compacted earth, re-cemented compacted earth, pisolites (small balls), tubulites (twig like hollow material) have been reported across the globe. [10].

2.1.1. Ore preparation and Mineral processing:

Since, each ore requires a unique processing therefore, a lack of published literature in the area of mineral processing and ore preparation is present. To facilitate efficient digestion, at this stage, a function of providing a continuous, consistent and appropriately charged feed to the digesters in the Bayer process is done [10]. Generally, the material is washed first and screened, to remove irrelevant contaminant such as dirt [29]. This procedure is usually completed at the mine. Particle size is regulated/ fixed in the same location where the rest of the Bayer process takes place. A great number of plants now utilize wet grinding mills. Wet grinding mills are charged with the bauxite ore and a portion of the process solution in order to make slurry. In Western Australia Completely autogenously mills with diameters over 25 feet are utilizing approximately 8 inch hard bauxite agglomerates as grinding media [10]. To return the oversize particles to the mill for further grinding Hydro cyclones and screens are used. To utilize abrasion and finalize particle size reduction Research has been done on the effects of holding the ground slurry for extended time periods in mechanically agitated tanks [28].

2.1.2. Bayer processing over view:

Bayer process is an economical solution for producing aluminium oxides from bauxite ore using concentrated NaOH solution (caustic soda) at high pressure and temperature. The Bayer process was invented in 1887 by the Austrian chemist Karl Bayer. Russia, to develop a method for supplying alumina to textile industry as alumina was used as a mordant in dyeing cotton. In 1887, Bayer discovered that the aluminium hydroxide, precipitated from alkaline solution was crystalline and could easily filter and washed. The NaOH selectively dissolves Al_2O_3 from bauxite ore; this produces sodium –aluminium solution from which pure alumina Tri- hydrates. Then, $Al(OH)_3$ precipitation is done, which is than calcined to produce Al_2O_3 , from which metal is recovered.[36]

A few years earlier, hennery Louis le chatelier in France develop a method for making alumina by heating bauxite in sodium carbonate, Na_2CO_3 at 1200 C, leaching the sodium aluminate formed with water. Then, precipitation of $Al(OH)_3$ by CO_2 was done, which was then filtered and dried. This process was abandoned in favour of the Bayer process. Since, the Bayer process is capable of producing huge quantities aluminium oxide and aluminium hydroxide with high – purity aluminium at relatively low – cost. This in fact created opportunity for marketing profitable Bayer plant products outside the aluminium industry. A

breakthrough in the quest for a cost-effective production process for aluminium occurred in 1886. With invention of the electrolytic aluminium process invented in 1886, the process began to get importance in metallurgy. The cyanidation process was also invented in 1887. The Bayer process is the birth of the modern field of hydrometallurgy. Today the process is virtually unchanged and it produces nearly all the world's alumina supply.

The Bayer process is the principal industrial method of refining bauxite to produce alumina. Bauxite is the most important ore of aluminium. It contains only 30-54% alumina, Al_2O_3 . The rest is a mixture of silica, various iron oxides, and titanium dioxide, phosphorous and also zinc, nickel and vanadium, etc. are found in trace amount. The alumina must be purified before it can be refined to aluminium. [36]

A Bayer process plant is basically, a device for heating and cooling a large recirculating stream of caustic soda solution. Bauxite is added at the high temperature point; red mud is separated at an intermediate temperature. Then, alumina is precipitated at the low temperature point.

Bauxite usually consists of two forms of alumina a monohydrate from Tri-hydrate from gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Boehmite requires elevated temperature (above 200c). To dissolve reading in 10% NaOH solution at temperature below 150c. Alumina is produce by Bayer's process through the continuous four stages which can be stated as:

2.1.3. Digestion of bauxite:

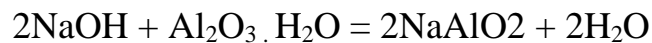
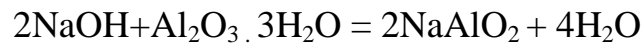
Selective dissolution of alumina from ore.

(a) Grinding: bauxite ore is finely grinded by ball mill to size $< 20\text{mm}$ to allow better solid – liquid contact during digestion, then recycled caustic soda solution is added to produce pump-able slurry and lime is introduced for mud condition and phosphate control.

(b) Desilication: The silica component of the bauxite is chemically reacted with caustic soda this causes alumina and soda losses by combining to solid desilication products. To desilicate the slurry before digestion, it is heated. It is then projected to atmospheric pressure in the pre-treatment tanks. Most desilication products pass out with the mud waste as sodium-aluminium silicate compounds.

(c) Digestion: in digestion bauxite slurry is pumped by high pressure pumps through agitated vertical digester vessels which operate in series. After this, it is mixed with steam and caustic solution. This dissolves the alumina content of the bauxite selectively and then forms a concentrated sodium alumina solution and leaves un-dissolved impurities. Reaction condition to extract the monohydrate alumina are about 250 C and a pressure of about 3500 kPa, achieved by steam generated at 5000 kPa in coal fired Boilers. However, for trihydrate alumina temperature of digestion is < 150 C.

The chemical reactions can be given as:

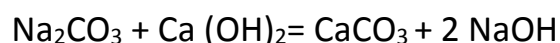


After digestion, about 30% of the bauxite mass remains in suspension as thin red mud as slurry of silicate and oxide of iron and titanium. By flowing through a series of flash vessels, the mud – laden liquor leaving the digestion vessel is flash- cooled to atmospheric boiling point which is then operated at lower pressure.[10]

(2) Clarification of the liquor stream: setting out un-dissolved impurities

(a) Settlers: most red mud waste solids are settled from the liquor stream in single deck settling tanks. To improve the rate of mud settling and achieve good clarity in the overflow liquor stream, flocculants are added to the settler feed.

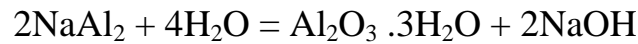
(b) Washers: Here, the mud is washed with fresh water in counter – current washing process to remove the soda and alumina content in the mud before being pumped to large disposal dams, slacked Lime is also added to remove Na_2CO_3 , which is formed by reaction with compounds in bauxite and also from the atmospheric CO_2 . CO_2 reduces the effectiveness of liquor to dissolve alumina and lime regenerates caustic soda, allowing the insoluble calcium carbonate in precipitated form, to be removed with the waste red mud. Following reaction can be shown below:



(C) Filters: settlers overflow liquor containing traces of fine mud which is filtered in Kelly – type constant pressure filters using polypropylene filter cloth.

(3) Precipitation of alumina tri-hydrate:

(a) Crystallization: dissolved alumina is recovered from the liquor by precipitation of crystals. Alumina precipitates as the tri-hydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) in a reaction, which is the reverse of the digestion of tri-hydrate:

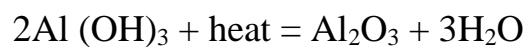


The cooled pregnant liquor flows to rows of precipitation tanks which are seeded with previously precipitated crystalline tri-hydrate alumina. Usually they are of an intermediate or fine particle size to assist crystal growth. The correct particle size is important to smelter operations. So, sizing is carefully controlled. The finished mix of crystal sizes is settled from the liquor stream and separated into their size ranges “gravity” classification tanks.

Caustic liquor which is essentially free from solids overflows from the tertiary classifiers and then it is returned through an evaporation stage where it is re-concentrated, heated and recycled to dissolve more alumina in the digesters. Fresh caustic soda is added to the stream to make up for process losses.

(4) Calcinations of alumina:

Slurry of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ from the primary thickeners is pumped to hydrate storage tanks and then to remove process liquor it is washed on horizontal – table vacuum filters. The resulting filter cake is fed to a series of calcining units and by circulating fluidized bed calciner or rotary kilns the feed material is calcined at 1100c to remove both free moisture and chemically combined water.



The circulating fluidized bed calciner is more energy efficient than the rotary kiln. Finally it produces 90% sandy alumina particles of size +45 micron. To cool the calcined alumina from the rotary kiln, Rotary or satellite coolers are used. Further Fluidised–bed coolers reduce alumina temperature to less than 90c, before it is discharged into conveyer belts, which carry it into storage buildings.[30]

Alumina (aluminium oxide, Al_2O_3) is a fine white material and is the main component of bauxite. The largest manufacturers in the world of alumina are ALCAN, ALCOA, RUCAL, NALCO, Queensland Alumina Limited (QAL) etc.

The residue also contains alumina which is undissolved during the alumina extraction from bauxite. Other components of bauxite Fe_2O_3 , SiO_2 , TiO_2 etc do not dissolve in the basic medium. Some SiO_2 dissolve as silicate $\text{Si}(\text{OH})_6^{-2}$ and are then filtered from the solution as solid impurities (clarification) for various reasons. Most alumina producer adds lime at some point in the process and the lime forms a number of compounds that end up with the bauxite residue. The red mud is the solid impurities remained. The red mud, due to its caustic nature causes disposal problem.

A large amount of the alumina produced is then subsequently smelted in the hall-heroult process, in order to produce aluminium. Metallic aluminium is very reactive with atmospheric oxygen, and then thin passive layer of alumina quickly forms on any exposed aluminium surface. This layer protects the metal from further oxidation due to its passive nature. Through anodizing thickness and properties of this oxide layer can be enhanced. A number of alloys, such as aluminium, magnalium, bronzes are prepared to enhance corrosion resistance. One metal whose growth in the past century has been very fast is aluminium. Its strength and light weight guarantees its demand, especially in transportation where fuel efficiency is of apex importance.

Annual world production of alumina is approximately 45 million tons, over 90% of which is used in the manufacture of aluminium metal. Due to high melting point Al_2O_3 is a refractory material. The major uses of aluminium oxides are in refractory, polishing, ceramics and abrasive applications.

An aluminium oxide is an electrical insulator, but still has a relatively high thermal conductivity. The is $\alpha\text{-Al}_2\text{O}_3$ called corundum, most commonly occurring crystal line alumina. Its hardness makes it suitable for use as an abrasive and also as a component in cutting tools. Bauxite residue (also known as “red mud”) is a by-product of the Bayer process (shown in fig. 2.1) [12]. Its colour is red, due to presence of iron oxides. The amount of residue generated, per ton of alumina produced varies greatly. It depends on the type of bauxite used i.e. from 0.3 tons for high grade bauxite to 2.5 tons for very low grade. The chemical and physical properties of red mud depends primarily on the bauxite used and to a lesser extent the manner in which it is processed. The main solid waste product of alumina industry is Red mud. The world wide annual production of red mud is 70 million tons. Its disposal remains an issue of great importance.

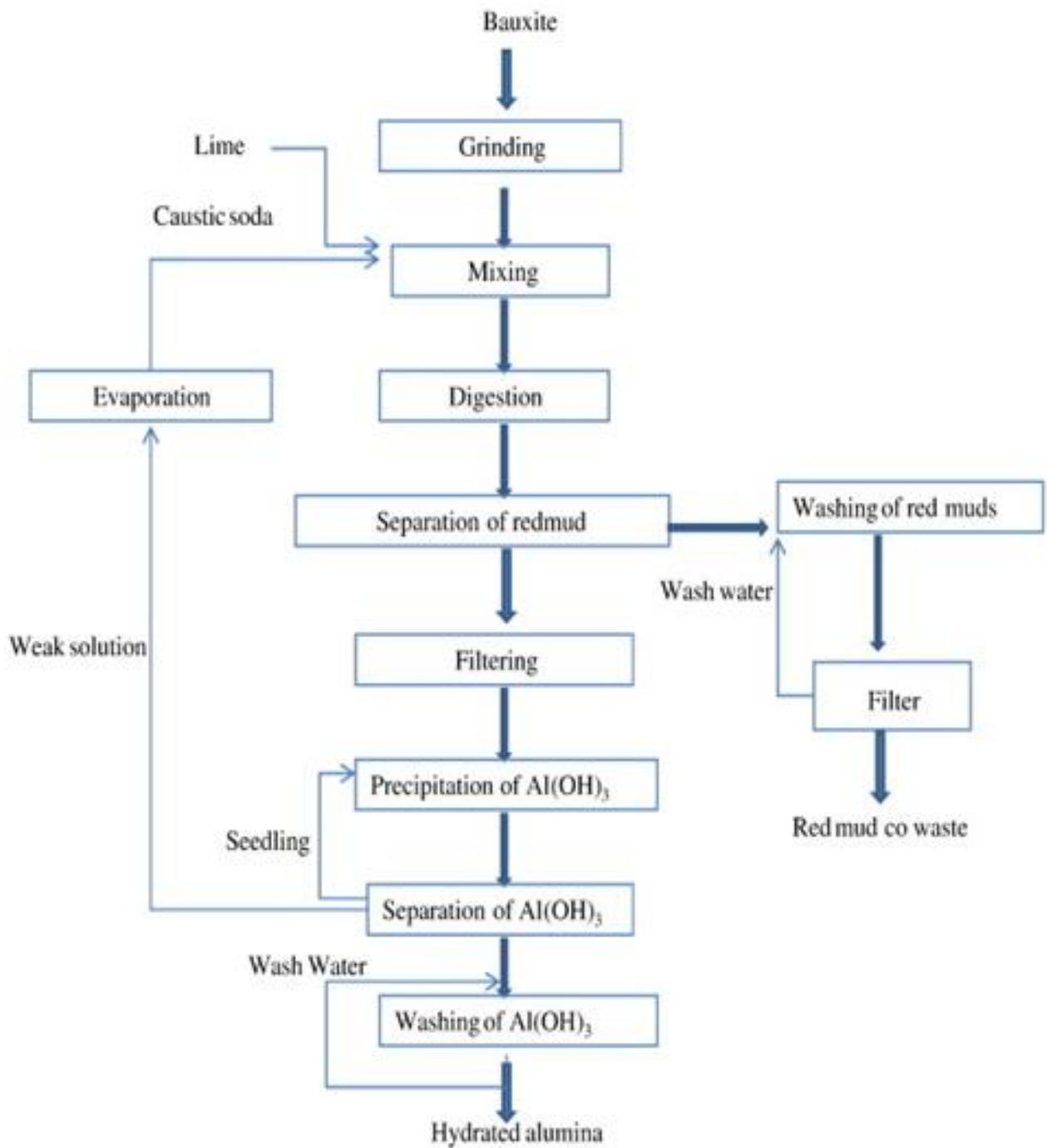


Fig. 2.1: A schematic representation of the Bayer process.

2.2. Nature of Red mud:

A red mud created from the production of alumina using the Bayer process, has proven to be difficult to deal with because of its particular characteristics. The complexity is increased due to the extreme diversity in each red mud product created. There are 22 phases that are typically present in red mud as shown in Table 2.2: Composition of Dried North Coast Jamaican Bauxite and the Generated Red Mud Compound [33] and Table 2-2 [33] shows an overview of the general properties of red mud that make it thixotropic, difficult to settle because of its fine particle size and extreme alkalinity [10]. The major oxides present in red mud and their weight percents are: Fe_2O_3 (25-70%), Al_2O_3 (13-29%) , SiO_2 (3-24%), TiO_2 (4-20%), CaO (0.1-12%), Na_2O (1-10%) with the rest of the 7-13 wt % being made up of V, Ga, P, B, Cd, K, Sr, Ba, Zn, Mg, U, Sb, Bi, Mn, Cu, Ni, Th, Zr, Hf, As, Co, W, Ta, Hg, and Nb. [33]

Table 2.1: Geotechnical properties of red mud

Sl. No.	Properties	Red mud
1	Ph value	11.4
2	Specific gravity	3.34
3	Plastic characteristic	24.75
	Liquid limit (%)	
	Plastic limit (%)	
	Plasticity index (%)	
4	Volumetric Shrinkage (%)	1.6
5	Linear shrinkage (%)	5.26

Table 2.2: Phases present in red mud

SL. no.	Phase	Chemical composition
1	Gibbsite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$
2	Boehmite	$\text{AlO} \cdot \text{OH}$
3	Diaspore	$\alpha\text{AlO} \cdot \text{OH}$
4	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
5	Sodalites	$3(\text{Na}_2\text{AlSiO}_4)_6 \cdot 2\text{H}_2\text{O}$
6	Calcium Aluminate	$\text{CaO} \cdot \text{Al}_2\text{O}_3$
7	Sodium Alumino silicate	$3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot \text{XH}_2\text{O}$
8	Hematite	$\alpha\text{Fe}_2\text{O}_3$
9	Magnetite Goethite	$\gamma\text{Fe}_2\text{O}_3$ $\alpha\text{FeO} \cdot \text{OH}$
10	Maghamite	Fe_2O_3
11	Siderite	FeCO_3
12	Calcite	CaCO_3
13	Calcium alumina silicates	
14	Alumogeoithite	$\alpha\text{FeAlO} \cdot \text{OH}$
15	Anatase	TiO_2
16	Rutile	TiO_2
17	Sodium titanate	Na_2TiO_3
18	Cancrites	$\text{Na}_6\text{CaCO}_3(\text{AlSiO}_4) \cdot 2\text{H}_2\text{O}$
19	Quartz	SiO_2
20	Ca (Mg,Al,Fe) titanate	
22	Magnesite	MgCO_3

2.3. Background of Red mud:

Extensive research was done approximately 20 years ago and further. At that time researcher's focus was on the recovery of aluminium and iron. Attempts were also made to develop a safe material from red mud that could be used for building materials. There has been successful implementation of this in Jamaica with a building constructed of the pseudo-geopolymers created using red mud. It was done almost 20 years ago; this implies that the recycling of red mud has been researched for many years. One possibility for this lack of current research is that, in general, research has moved away from iron and aluminium recycling to things of more values such as precious metals such gold and rare earth element extraction such as platinum.

The reason that previous research did not provide any economic answers to the problem is perhaps the difficulty of working with the red mud, due to extensive silicates and liberation problems.

Because, the modern high grade deposits of the Bauxite ore are no longer in developed countries, they are now being mined in developing countries such as Papua, China, India, Yugoslavia, New Guinea, and Russia. These countries are not as conscious about the environment and thus there is no push for public research to continue. Therefore, most recent research has been completed by the aluminium companies themselves. Because of all this, the research has been at setback and not shared with the academic community thus current information is extremely lacking and inadequate. [9]

There have been various other papers and smaller research projects that can be found on the redmud.org website. This research is primarily focusing on the extraction of rare earth element as well as the development of construction material from red mud.

Although, there have been research and successful applications of construction materials, it is unclear if this is an oversight. Research is being duplicated or if advancements are being made. The goal of this research is to develop a process that will effectively and economically extract the iron and alumina from red mud using plasma technique.

2.3.1. Previous Red Mud Solution Efforts:

Application of red mud has been tried in limited scenario, as a constituent in industrial construction aggregates, road surface material, such as bricks, and cement, in combination

with other waste products such as fly ash. It has also been tried as a soil modifier. For waste utilization after metal extraction, these applications do not add value but can serve as a valid route. Construction material applications consideration is required for addressing the vastness of the problem [14].

One investigator suggests separation of the red mud (in slurry form) using high intensity magnetic separation. The resulting magnetic product can be used as an ingredient for iron making or as a pigment for pottery making. The nonmagnetic portion can be applied in building materials or supplemented back into the Bayer process. The extraction of Fe, the main constituent in red mud has been in focus of several previous research efforts.

Another investigator reduces the Fe with chlorocarbons before magnetic separation and uses the resulting magnetic portion as feed for iron making. [22, 14]. Another research suggests drying the red mud, blending with lime and ground coal and feeding the mixture into a machine that agglomerates it into ½-in. diameter balls. Subsequently, the balls are pre-reduced at high temperatures in a circular grate. The balls are then fed into a submerged arc electric furnace for smelting and transported to a basic oxygen furnace, where high-quality steel is produced. The final product yields about 98-99% pure Fe.7 [23, 24, 14].

Another process entails mixing the red mud with Fe₂(SO₄). This solution removes the Na from the mud, leaving behind material eligible for iron making. Simultaneous recovery of Al and Na is performed by mixing the red mud with a solution of caustic soda and lime at 300C at pressures of 4-9MPa. This solution is supplemented into the Bayer process for increased alumina recovery.

One approach utilizes the amphoteric characteristics of Al by extracting it via treatment with sulfuric acid. It also attempts to extract the Al through biological leaching using sewage sludge bacteria. [10]

An additional process that emphasizes Ti recovery converts the red mud into sodium-aluminium fluoride compounds. The red mud is mixed with hydrochloric and hydrofluoric acid to obtain a silicic acid, which is then separated out [14]. Evaporation leaves behind a material close to cryolite. The remaining material is mixed with the residual liquor, which dissolves the Fe and Al. The Ti-rich solid remaining can be further processed via chlorination. [8] Synchronous recovery of Al, Fe and Ti is investigated by a number of researchers. One method utilizes chlorination combined with fractional distillation to extract

Fe and Ti from red mud. The red mud can be leached prior to this to retrieve Al. [7] a novel technique is being investigated where the red mud is carbothermically reduced in an electric arc furnace to produce pig iron and a fiberized wool material from slag. [9]

After looking at the previous creative attempts made to deal with red mud there are many limitations that must be addressed and solved before anything useful can be made. Red mud is generated and currently stored where processing for alumina recovery from bauxite ore (Bayer process) is done. Any recovery process from red mud that would require the transport of red mud (fine material with 20-30% water) to far distances, iron making operations, will likely be cost prohibitive. Thus, any conversion scheme that is adopted needs to be located near the bauxite processing facility. Whether an electric arc furnace or a rotary hearth type of process is used, it must be collocated. Solid-state carbothermic reduction of red mud to recover Fe and its separation from the remaining oxides via any physical means is difficult due to the mineralogy of red mud where fine iron oxide is intimately associated with other oxides and does not allow the separation of reduced Fe in a concentrated form. This is a major limitation which forces the carbothermic smelting of red mud. A solid Fe-rich product, such as direct reduced Fe, is unlikely. However, a solid product with reduced metallic Fe amenable to steelmaking remains a possibility. Injection of red mud, with or without pre-reduction, into a blast furnace through the tuyeres, is an interesting concept. However, the high alumina content is a problem for the slag fluidity and volume in the blast furnace and the high alkali content is not compatible with the refractory and alkali accumulation. While lime, silica and Titania additions from red mud are acceptable to the blast furnace, alumina and alkali oxides must be removed before any injection. This concept will also require transportation adding to commercialization challenges. Removal of alumina via soda-ash roast and water leaching can produce liquor that can be reverted back to the Bayer process, thus generating a residue that will be very low in alumina and alkali metals material now suitable for Fe production by any viable process. Alumina can be a recoverable commodity at this stage. Once alumina and alkali metals are removed by soda-ash roast and Fe is reduced by carbon, the resulting material may be smelted to produce pig-iron and a slag now rich in calcium titanate. Titanium could be considered a product from this slag stream. However, the process suitable for Ti recovery is the sulfation method developed by the US Bureau of Mines¹⁴. The Kroll process is unsuitable due to the high lime content of the slag. Based on these considerations.

2.3.2. Current Methods of Treatment, Storage and Associated Problems:

Limited advancements have been made due to the unusual chemical and mineralogical complexities associated with red mud investigations for treating, disposing of and utilizing red mud. With no environmentally friendly and economical way of disposing of red mud, companies are forced to figure in disposal fees in their final bottom line, a cost that is passed down to the end consumer. In an era where low costs and environmental friendliness are crucial, economically viable options of treatment are imperative [10].

Space requirements for storage of red mud are one of the largest constant problems facing the aluminium industry to date. There are two current methods of storage. The first is to simply pump the red mud into holding ponds. However, this method takes up a considerable amount of land. The other way to store the mud is to first dry it and then dry stack it upon a special liner. Once there is sufficient red mud the dry stack is then covered with topsoil. This method still alleviates some of the issue of land use however; the land cannot be used for farming or to live on. Farming cannot occur due to the fact that red mud is extremely basic in chemical nature due to the large amounts of sodium used in the original processing of aluminium that is left in the by-products. Although there have not been any reports of leaching from the red mud through the liners there is still the risk of caustic soda leaching into groundwater. Another risk is leaching of heavy metal into the groundwater such as lead, cadmium and mercury. [1, 3, 6, 10, 12]

Perhaps one of the most well documented tragedies associated with red mud occurred on October 4, 2010 in Hungary. The dam wall of the Ajka refinery collapsed and approximately one million cubic meters of red mud flowed into the surrounding countryside. [1] Nine people were killed in the disaster, 122 people were injured and the contamination included 40 square kilometres. The nearby Marcal River was reported to have suffered a loss of all living organisms, and within days the contamination had reached the Danube River as well. [4, 6]

This is hardly the only incident of contamination caused by red mud. Table 2.3 discusses 17 other incidents in the past 10 years. It appears that aside from the direct contamination of the red mud, the next largest concern has been the dust that is produced from the drying of the red mud. [1, 5] a vast majority of the red mud is 10microm, and this material is too fine to ever completely settle out. Also, this tiny particle size means that any slight breeze will easily disrupt the dry stacks if they are not properly covered after each addition. [1, 6]

Table 2.3: Incidents in the past 10 years

Sl.no.	Date	Company	Country	Incident
1.	1966-present	Rio tinto	France	Red mud discharge into ocean.
2.	6-may-2002	Alcoa	Australia	Disposal of red mud on to local farm land.
3.	14-may-2006	Alcoa	Australia	Poisonous dust emission.
4.	6-april-2007	Rio Tinto	Canada	49 tonnes released into saguenay river.
5.	21-feburry-2008	KAP Aluminium	Montenegro	Fine dust contamination.
6.	20-aug-2008	Rio Tinto	Canada	Red mud disposal into river.
7.	27-apr-2009	Norsk Hydro	Brazil	Red mud discharge into murucupi river.
8.	1-feb-2010	Rusal	Jamaica	Clouds of toxic dust.
9.	27-june-2010	Vedanta	India	Fine dust contamination.
10.	16-may-2011	Vedanta	India	Pollution after heavy rain.
11.	26-may-2012	Guangxi Huayin	china	Leaking of disposal pond.

2.3.2.1 Closed cycle disposal:

As the most prominently used method for storage this method consists of first washing red mud in order to remove as many water soluble elements as possible including caustic and sodium aluminate. Even after effective washing is completed in a counter current decantation apparatus the liquid contained in the solid fraction still can have a pH of 12 or higher [28]. Due to this, the slurry (10-30% solids) cannot come in contact with ground water. It must be pumped to impoundment ponds outfitted with special liners to inhibit contamination [33]. Once the material is in the ponds it is subjected to two types of treatment, settling using flocculants or the drying and evaporation of water (DREW) process. DREW greatly reduces

the time needed to ensure settling has occurred using perforated drain pipes at the bottom of the ponds under layers of sand and gravel. Even though the process improves the probability of a high density stabilized mud field forming the high cost of construction can be prohibitive? [10]. Numerous problems are associated with this process as outlined below [33]

High cost of land: 0.2 square meter per year per ton of aluminium oxide capacity is required by a typical alumina plant utilizing traditional CCD methods as red mud can only effectively be dewatered to 37% solids at a depth of 1.5m [35] resulting in large amount of water storage. High cost of construction, maintenance, and constant monitoring of the impoundment ponds and dikes Seepage of caustic soda and other hazardous elements, as a multitude of alkaline and toxic elements have the potential to seek through the membranes lining the ponds thus contaminating soil and possibly ground water.

High cost of recycling pond water, due to the low amount of solids in the slurry large amounts of water must be recycled back into the Bayer process Difficulty to reclaim and rehabilitate land used. Both due to aesthetic damage to the surrounding areas due to dust and because of the caustic toxic nature of red mud make re-vegetation difficult [10]

2.3.2.2. Dry Stacking Methods or Thickened Tailings Disposal (TTD):

This process involves the removal of excess water from the red mud until water content below 45% is reached typically being done using drum filtration systems. Dewatered material then needs to be transported to its final destination typically at higher costs [35]. Once at the final location, one of two final dewatering techniques are used; either solar drying or sloped stacked TTD methods. In the solar drying method, the partially dewatered slurry is spread to a height of approximately 3 inches on a slight grade. Sloped stacked methods consist of pumping the material and allowing it to form a conical shape that will use gravity to flatten. In both of these methods the mud is then allowed to dry and harden until heavy equipment can be used to level the area, usually taking two to three weeks depending on environmental conditions. [10, 33] .These methods decrease the land usage by up to four times when compared to the CCD method, and create a storage bed with a stable base and excellent compressive strength. The downside however is that any rain water must be collected as it can leach through the stack and dissolve the soluble substances; also this area cannot support plant life without considerable modifications [28]. To prevent dust hazards, common soils are spread on top and plant life can begin re-vegetation of the areas after organic fillers and fertilizers are added. [10, 35]

2.3.2.3. Sea disposal: Environmental irresponsibility and potential catastrophic effects make this method practically extinct. Only done as a last remaining option this procedure is closely monitored by the environmental governing body. [10]

Table 2.4: Plant capacity and dumping procedure

SL.NO.	NAME OF THE PLANT	PLANT CAPACITY	RED MUD OF ALUMINA T/T	DUMPING PROCEDURE
1.	INDAL,MURI	72,000	1.35-1.45	This refinery adopted the closed cycle (wet slurry) disposal system (ccd).this disposal ponds have not been provided with any liner.
2.	INDAL, BELGAUM	2,20,000	1.16	The plant switched over to dry disposal mode from wet slurry disposal mode in 1985.
3.	HINDALCO,RENUKOOT	3,50,000	1.4	Traditional CCD method of impoundment was used.
4.	BALCO,KORBA	2,00,000	1.3	Residue after setting, counter currently washed in four stages and filtered.
5.	NALCO,DAMONJODI	800000	1.2	A method modified CCD method is used for disposal.

2.3.3 Sources of red mud: As a by-product of the aluminium industry, red mud is a worldwide problem as shown in Figure 2.2. [10]



Fig. 2.2: worldwide red mud generation

2.3.4. Application of red mud:

Currently there are no effective uses for red mud. As shown in the section Motivation for Project, if red mud is stored in retention ponds it risks the dam breaking and contaminating and destroying anything nearby. Efforts have been made to utilize dry stack tailings however the small particle size has created a dust problem. Any small gust has been reported to send a toxic cloud of tiny red mud particles into the air, thus decreasing the quality of life for residents around the area.[10]

2.3.5. Properties of red mud:

Although a by-product, there are still enough value added constituents present to warrant research into extraction of the valuables. The most abundant metal is iron, as seen in Table 2-4 which is almost five times as high as the next element, aluminium. The oxides of iron and aluminium make up almost 80% of the present material as seen in Table 2-5. Because of that the focus of this thesis's research was in the extraction of metal.

Table 2.5: wt% of element in red mud

SL.no.	Element	Weight%
1.	Aluminium	7.630
2.	Cadmium	0.011
3.	Calcium	6.315
4.	Carbon	1.085
5.	Cerium	0.077
6.	Chromium	0.165
7.	Dysprosium	0.009
8.	Iron	35.450
9.	Magnesium	0.163
10.	Manganese	0.913
11.	Mercury	1.000
12.	Silicon	1.470
13.	Sodium	1.065
14.	Terbium	0.003
15.	Thorium	63.000(mg/kg)
16.	Thulium	0.001
17.	Titanium	3.655
18.	Zinc	0.080
19.	Ytterbium	0.005
20.	Yttrium	0.087

CHAPTER: 3
MATERIALS AND METHODS

3.1. Material:

3.1.1. Red mud: In this work red mud was supplied by NALCO India Ltd. The chemical analyses of red mud are given in Table 3.1. Red mud is classified by EC as a non hazardous waste (commission decision 2000/532/EC) however its small particle size (dust like, mean particle size 0.49 micro meter), high alkalinity and large amounts (30 to 35 million tons per year on dry basis world).



Fig. 3.1: Red mud

Table 3.1: Chemical analysis of red mud

SL.NO.	COMPOUND	Wt.%
1.	Fe ₂ O ₃	47.49
2.	Al ₂ O ₃	21.07
3.	SiO ₂	5.72
4.	Na ₂ O	3.78
5.	CaO	1.36
6.	TiO ₂	4.86
7.	LOI	13.49

3.1.2 Aluminium powder: Aluminium powder was provided by DISIR LAB, RAJGANGPUR.



Fig. 3.2: Aluminium powder

3.1.3 Coke: 100 mesh size, carbon powders were added in stoichiometric amounts for the reducible oxides.



Fig. 3.3: Coke

3.1.4 Lime: Lime (CaCO_3) is also provided by DISIR LAB, RAJGANGPUR.



Fig. 3.4: Lime

3.2 HOMOGENISATION: All the ingredients are mixed and homogenised in pulveriser taking the mixes in Tungsten Carbide crucible with Tungsten carbide balls.



Fig. 3.5: Pulveriser

3.3 Work plan:

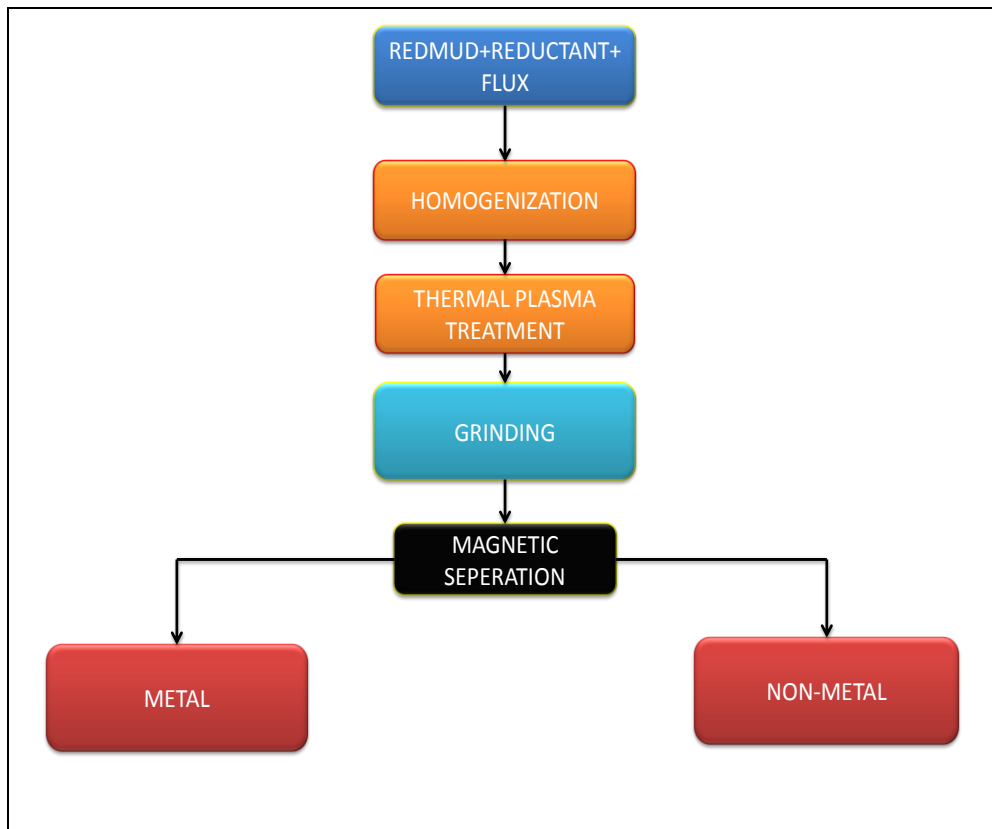


Fig. 3.6: Work plan for experiment

3.4 Material preparation:

The homogenised mixes as per compositions given in Table no 3.2, 3.3 and 3.4 are mixed with distilled water (10-12 parts) in a 5kg mixer for 20 minutes. Pellets having diameter 10-15mm are made by hand rolling. The pellets are dried in an air oven for 2 hours to remove the moisture. Now the samples are ready to feed in the crucible of plasma furnace. Argon was used as ionising gas. Flow rate of Argon gas was 2.5 LPA.

Table 3.2: Composition of sample A

SL.NO	Compound/Material	Wt.%	Wt in gram.
1.	Red Mud	85	360
2.	Coke	15	40

Table 3.3: Composition of sample B

SL.NO	Compound/Material	Wt.%	Wt in gram
1.	Red Mud	75	562.5
2.	Coke	10	75
3.	Lime	10	75
4.	Aluminium dross	5	37.5

Table 3.4: Composition of sample C

SL.NO	Compound/Material	Wt.%	Wt in gram
1.	Red Mud	65	650
2.	Coke	15	150
3.	Lime	15	150
4.	Aluminium dross	5	50

3.5. Plasma arc reactor:

The crucible where fusion was done made of graphite which worked as Cathode. The crucible was put inside a rounded metallic pot lined with 60 % Alumina cast able. The annular space between the graphite crucible and metallic pot was filled with bubbled Alumina which works as a heat insulator. The Anode which runs vertically from the top towards the cathode was made of Graphite with a 5mm coaxial hole runs throughout facilitating to pass ionising gas. The gas flow was regulated with a flow meter. Both the electrodes were connected with 20 KW generators which feed in 440 V AC. This device was an export arc plasma reactor where initial arc was generated and plasma arc length was controlled by moving the anode upward fitted with a rack and pinion system. The power was controlled with a potentiometer fitted with the generator. Schematic diagram was given in Fig.[15]

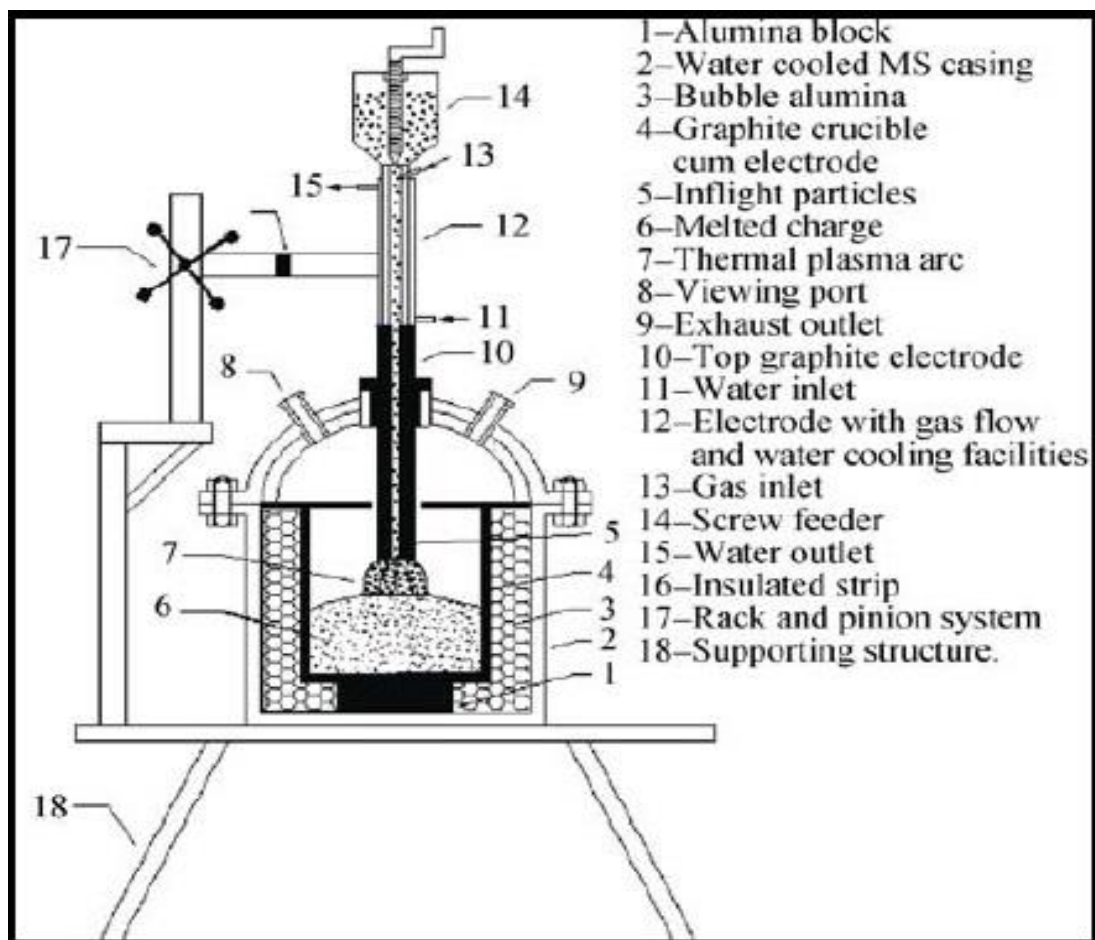


Fig. 3.7: Schematic diagram of plasma arc reactor

3.5.1. Smelting process:

Initial arc was made and pellets were fed slowly. Gradually the power was increased and total mass was brought into molten condition. The process parameters were as under.

Voltage: 30-60V

Ampere: 200-330A

Gas flow rate: 2.5L/M

Process time- 40 Minutes

After the process was over the furnace was cooled down naturally. The sample was removed from the graphite crucible for characterisation. The gangue materials were separated. Further the samples were crushed and ground. The metallic and non metallic parts were separated for characterisation.



Fig. 3.8: Smelting process in plasma furnace



Fig. 3.9: Smelting process

3.6. Material characterization:

3.6.1. Phase analysis by XRD: Phase analysis of Magnetic and non magnetic parts were done by X -ray diffractometer using Panalytical Xpert pro system. Different parameters were as under.

Table 3.5: Parameters of XRD

X-ray	ceramic
Anode material	copper
window	beryllium
Filter	Nickel
$K\alpha_1$	1.54060 Å
$K\alpha_2$	1.54443
Voltage	45kv
Current	40mA
Detector	proportional
Scanning start position (2θ)	10.0090
Scanning end position(2θ)	59.9890
Scanning step size (2θ)	0.02
Scanning step time (2θ)	0.4
Scanning type (2θ)	continuous

It is a very compact unit where the x-ray generator, goniometer optics and recording system are all encapsulate together. The goniometer is a precision one and facilitates rapid measurement with high angular accuracy.

It is possible to do the measurement of powder samples in small quantity without any shaping because of almost horizontal position of the sample holder surface. Therefore the vertical goniometer has its own advantages in measuring these samples in addition to having advantage of loading of the samples.

The ease of operation to select the scanning speed ranging between 60deg/min to 120deg/min in six steps of constant speed is also an advantage in this equipment. This helps in selection of operating conditions when the overall picture of an x-ray diffraction profile in an angular range profile or full scale measurement is required.

3.6.1.1. Sample preparation:

Representative samples of slag were made by coning quartering and taken in pulveriser for grinding below 20 micron. 0.71 gm of the ground slag sample was put on a aluminum disc having a groove of 15mm diameter, leveled and pressed with a glass slide. Operating condition was maintained as mentioned earlier. Phases were identified using high score plus software.

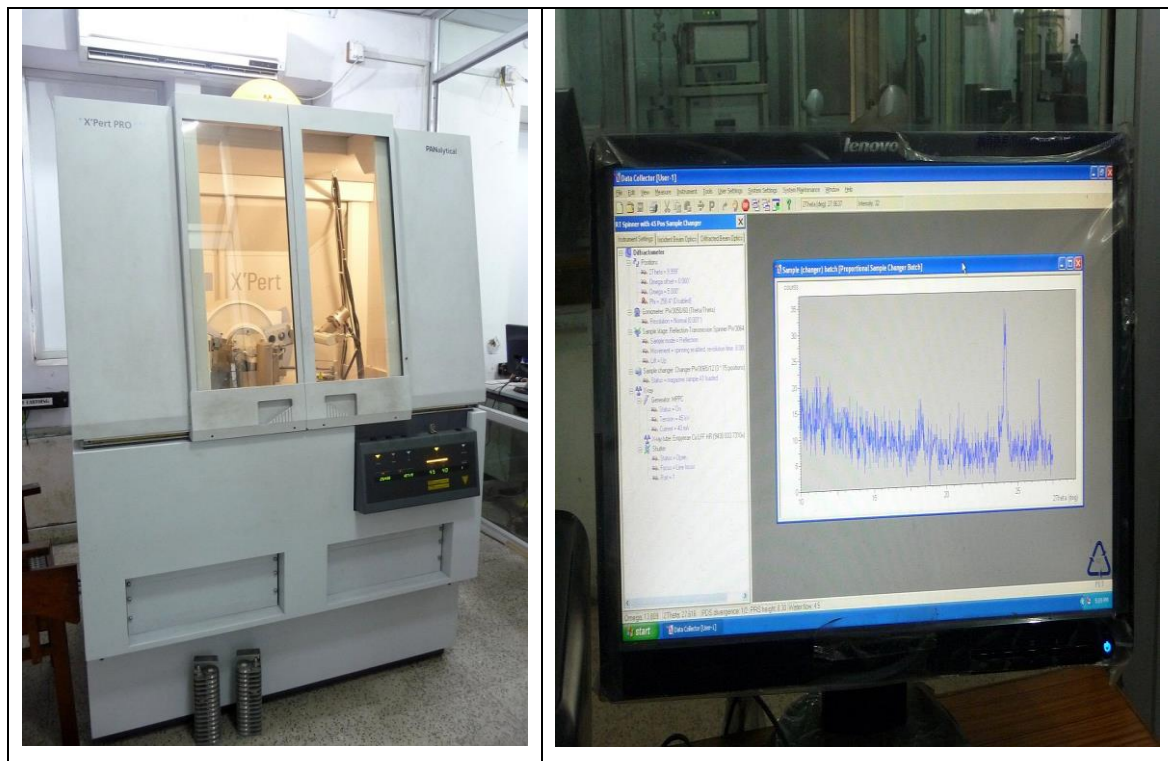


Fig. 3.10: XRD machine

3.6.2. Micro structural Analysis by Optical Microscope:

Microstructural studies of Magnetic and non magnetic parts were done on polished section under reflected light in a universal microscope. (Carl Zeiss, Axio Universal Research Microscope with Image analyser.).

3.6.2.1. Sample Preparation:

Polish sections were prepared as per the standard methods. The samples were impregnated with cold resin (Araldite and Hardener in 9:1 ratio) and evaluated in Vacuum desiccators for 30 minutes. Then the mounted samples were kept overnight to get hardened. The preliminary polishing was done with carborundum paper of 120, 400 and 600 designations. The final polishing was done on a special micromax polishing cloth attached to a rotating wheel where alumina powder in water medium was used as the polishing medium. Finally the samples were polished with 0.1 micron diamond paste on paper. The polish sections were examined under reflected light.



Fig. 3.11: Optical microscope

CHAPTER: 4

RESULT AND DISCUSSION

Operating condition during plasma processing shown in below table:

Table 4.1: Operating condition during processing

Sample no.	Process time in Min.	Power consumption KW	Power consumption/kg in units KW
A	40	12	40
B	30	10	31
C	26	8	25

4.1. Sample A (15% coke + 85% red mud):

Table 4.2: Result of sample A after processing

SL.no.	Total materials fused	Recovery	Magnetic part	Non Magnetic part
1.	400 grams	300 grams	250grams	50 grams

4.1.1. XRD:

(a) Magnetic:

Table 4.3 XRD analysis of sample A

Sample no.	Major phases	Minor phases
Sample A (Magnetic)	Fe ₃ C (Cohenite), Fe (Iron), Tic (Khamrabaevite)	Fe ₂ Ti (Iron Titanium)

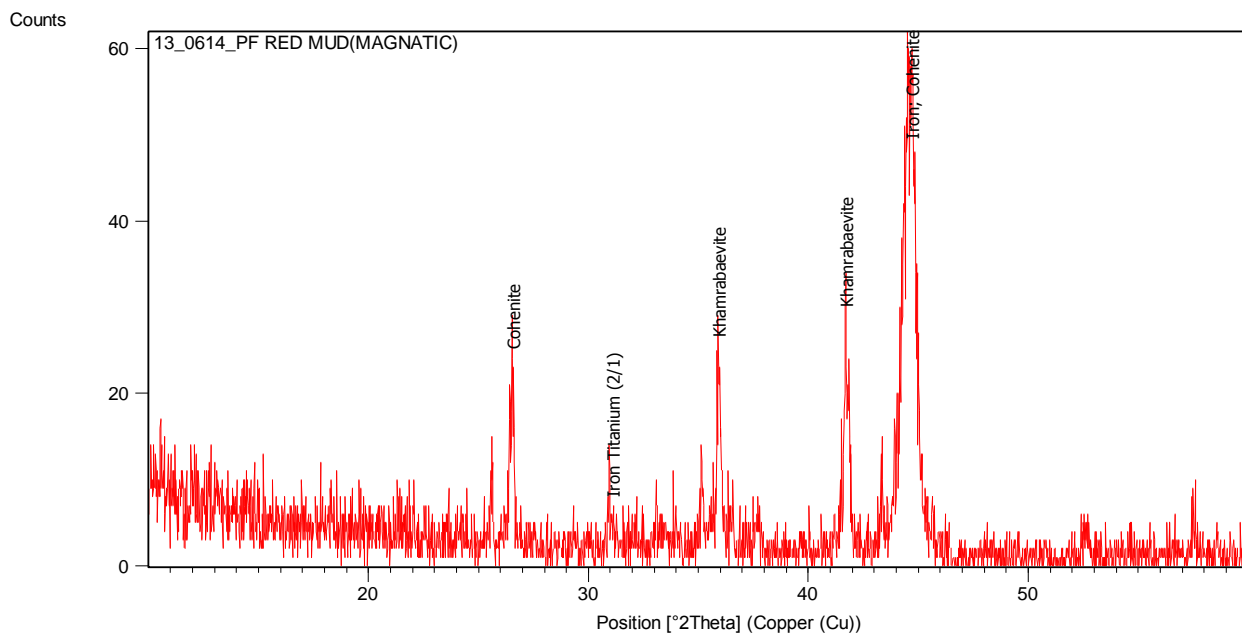


Fig. 4.1: XRD pattern of sample A

(b) Non-Magnetic part:

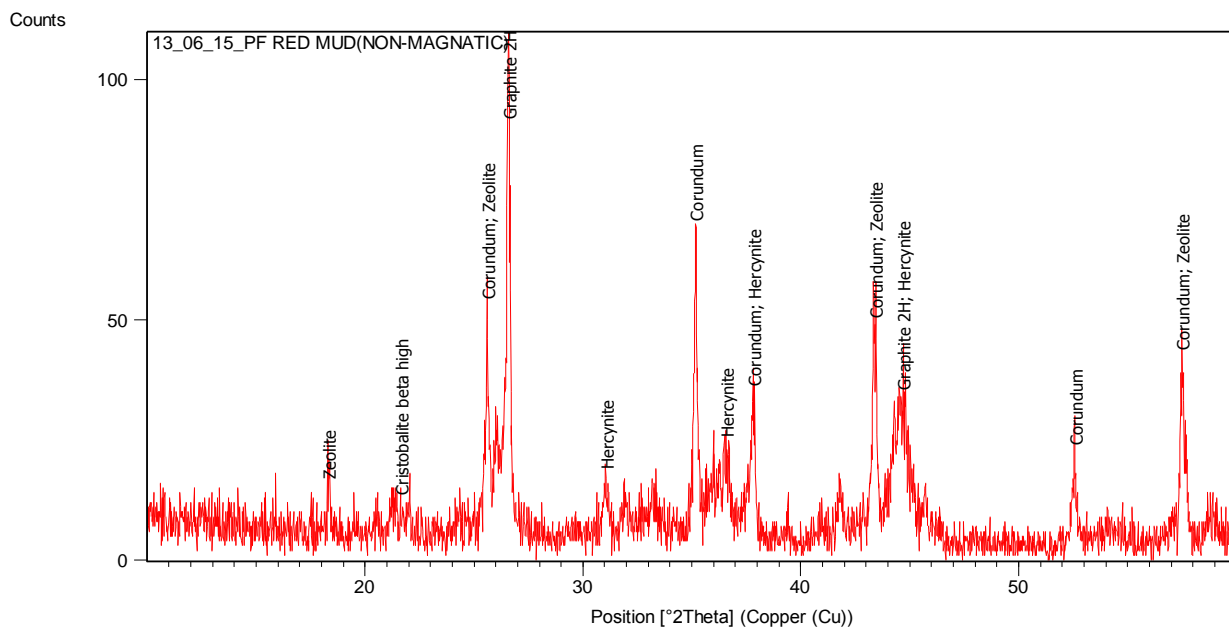


Fig. 4.2: XRD pattern of sample A

Table 4.4: XRD analysis of sample A

Sample no.	Major phases	Minor phases
Sample A (Non-Magnetic)	Al ₂ O ₃ (Corundum), C (Graphite)	Al _{1.994} Fe _{1.006} O ₄ (Hercynite), SiO ₂ (Zeolite),

4.2. Sample B (75% red mud + 10% coke + 10% lime + 5% aluminium powder):

Table 4.5: Result of sample B after processing

SL.no.	Total material fused (gram)	Recovery (grams)	Magnetic part (grams)	Non-Magnetic part (grams)
1.	500	380	310	70

4.2.1. XRD

(a) Magnetic part:

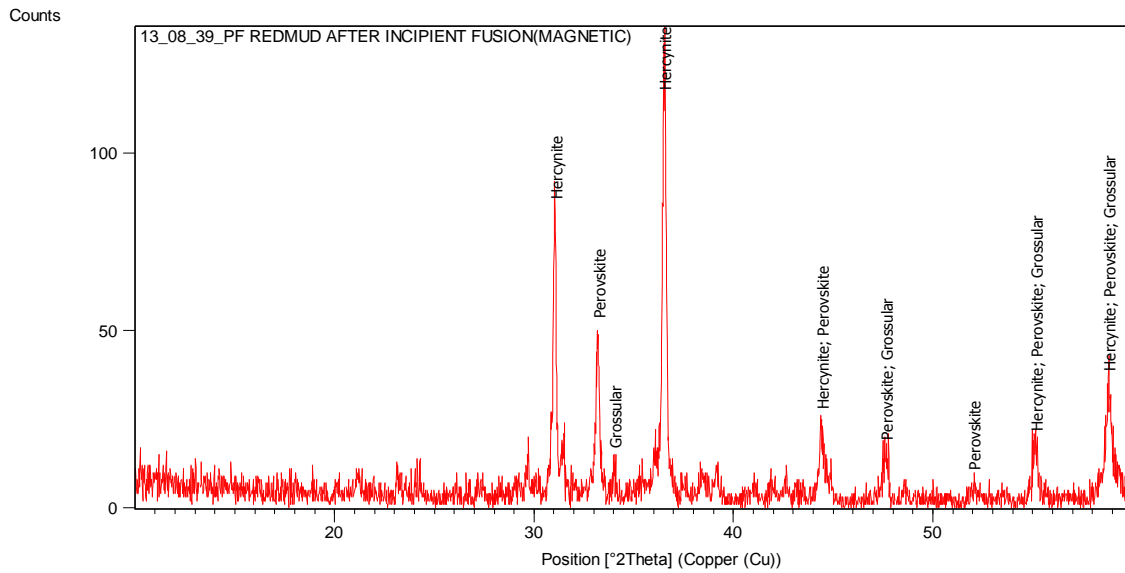


Fig.4.3: XRD pattern of sample B

Table 4.6: XRD analysis of sample B

Sample no.	Major phases	Minor Phases
Sample B (Magnetic part)	Al_2FeO_4 (Hercynite), TiO_3Ca (Perovskite)	$\text{Al}_2\text{Ca}_3\text{O}_{12}\text{Si}_3$ (Grossular)

(b) Non –Magnetic part:

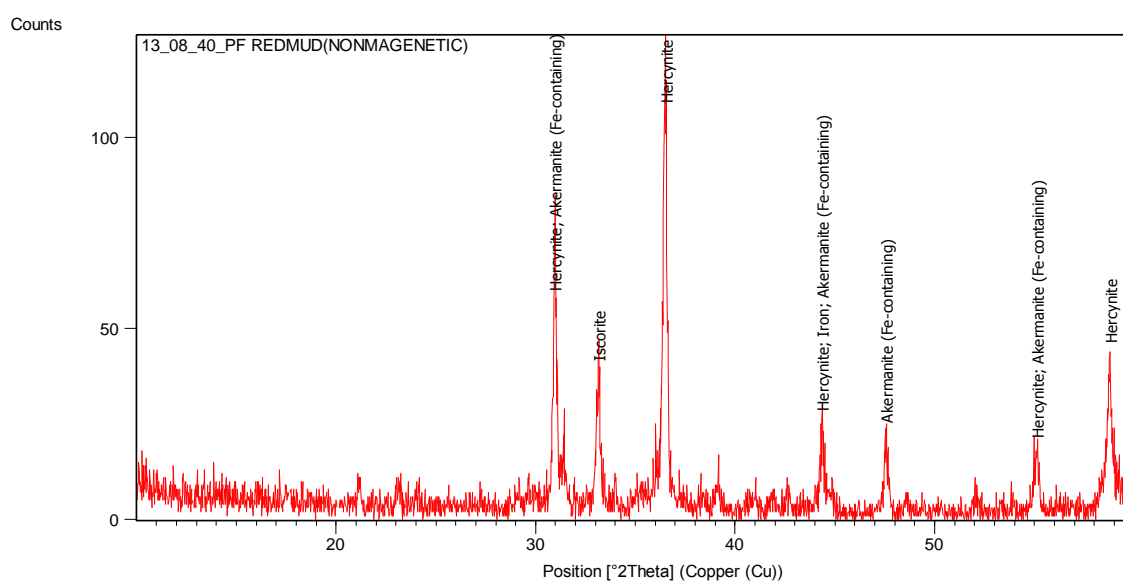


Fig 4.4 XRD pattern of sample B for non magnetic material

Table 4.7: XRD analysis of sample B

Sample no.	Major phases	Minor phases
Sample B(non-Magnetic part)	$\text{Al}_{1.1993}\text{Fe}_{0.996}\text{O}_4$ (Hercynite)	$\text{Fe}_7\text{O}_{10}\text{Si}$ (Iscorite), $\text{Ca}_2\text{Fe}_{0.45}\text{Mg}_{0.55}\text{O}_7\text{Si}_2$ (Akermanite Fe-containing)

4.3. Sample C (Result of 65% red mud + 15% coke + 15% lime +5% aluminium powder):

Table 4.8: Result of sample C after processing

Sl. No.	Total material fused in gram	Recovery in gram	Magnetic part in gram	Non-magnetic part in gram
Sample C	1000	820	600	220

4.3.1. XRD:

(a) Magnetic part:

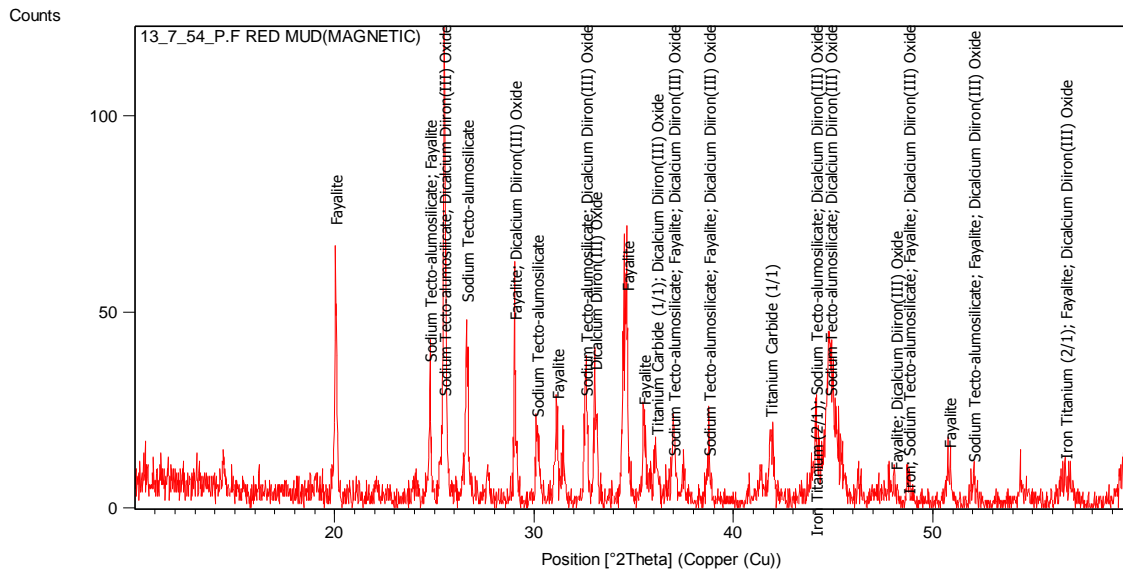


Fig. 4.5: XRD pattern of sample C for magnetic material

Table 4.9: XRD analysis of sample C for magnetic materials

Sl.no.	Major phases	Minor phases
Sample C (magnetic part)	TiC(Titanium carbide),Si ₂ O ₆ NaAl (Sodium Tecto-alumosilicate)	Fe ₂ Ti (Iron Titanium), Fe(Iron),Fe ₂ O ₄ Si (Fayalite),Ca ₂ Fe ₂ O ₅ (Dicalcium diron oxide)

(b) Non- Magnetic part:

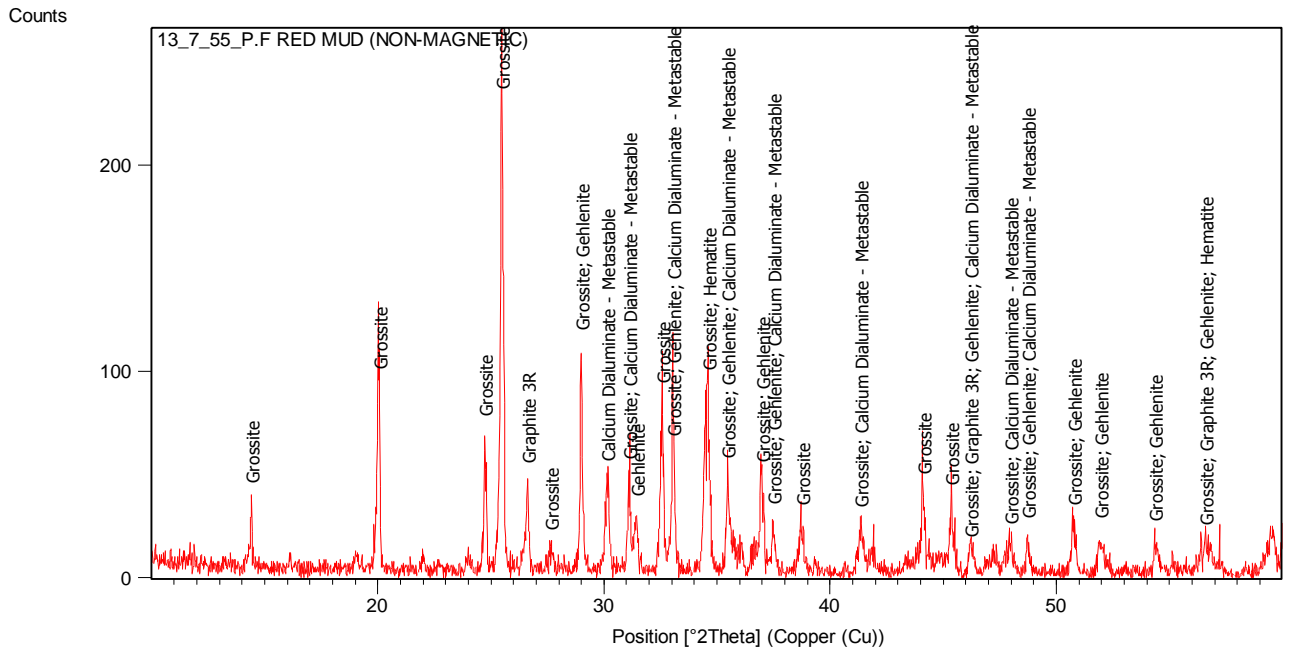


Fig. 4.6: XRD pattern of sample C for non magnetic materials

Table 4.10: XRD analysis of sample C for non magnetic materials

Sl.no.	Major phases	Minor phases
Sample C (Non- Magnetic part)	Al ₄ CaO ₇ (Grossite),C (Graphite 3R),Al ₂ Ca ₂ O ₇ Si (Gehlenite)	Al ₂ CaO ₄ (Calcium dialuminate- metastable),Fe ₂ O ₃ (Hematite)

4.4. Microscopic result:

4.4.1. Sample A (85% red mud + 10% coke):

(a) Metal Part:

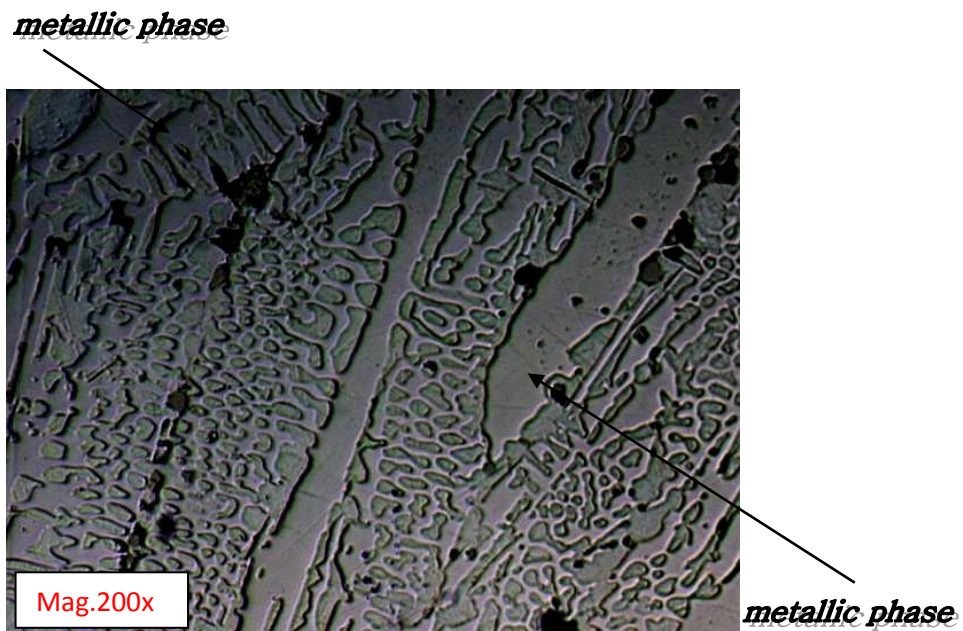


Fig: 4.7: microstructure of sample A for metal part

(b) Non-Metal part:

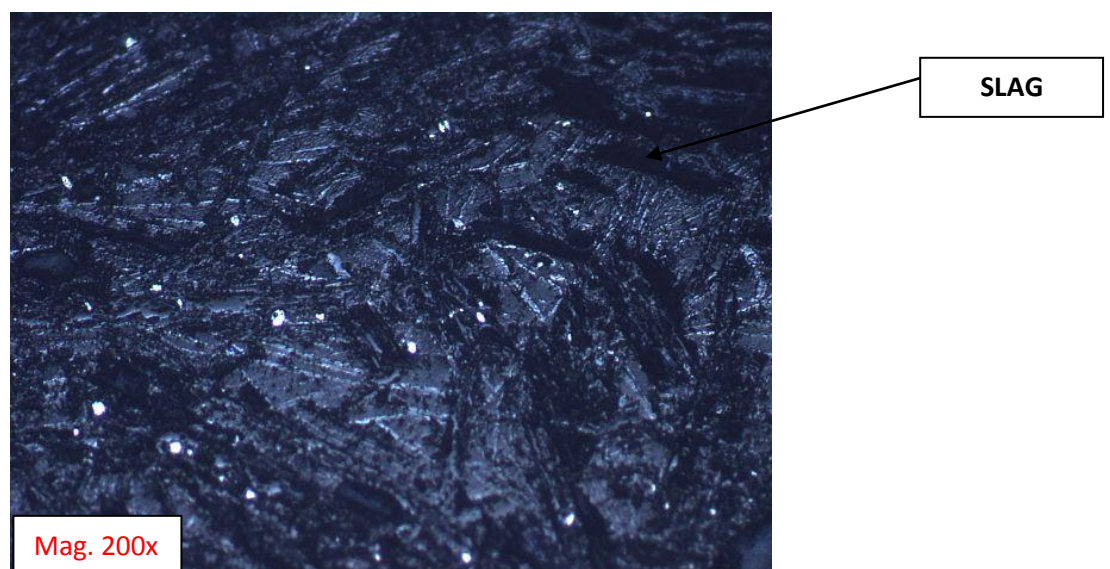


Fig.4.8: Microstructure of sample A for non metallic part

4.4.2 Sample B (75% red mud + 10% coke+ 10% lime +5% aluminium powder):

(a) Metal Part:



Fig. 4.9: Microstructure of sample B for metallic part

(b) Non- Metal part:



Fig. 4.10: Microstructure of sample B for non metallic part

4.4.3. Sample C (65% red mud + 15% coke+ 15% lime +5% aluminium powder):

(a) Metal Part:

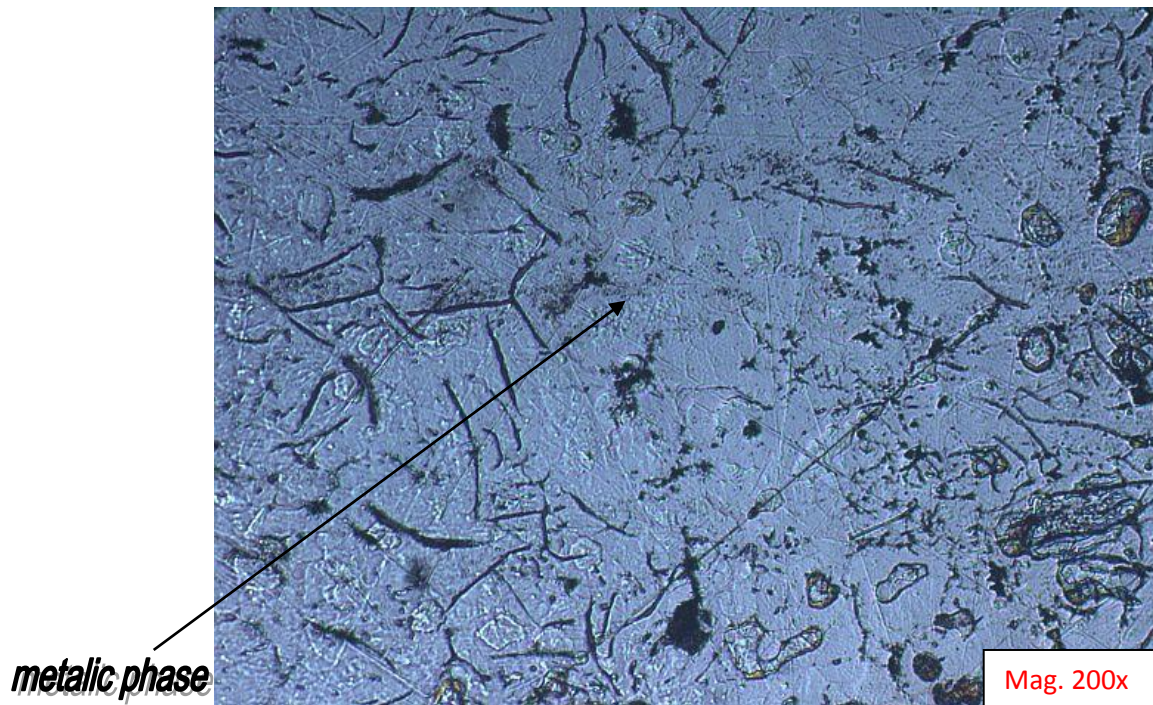


Fig. 4.11: Microstructure of sample C for metallic part

(b) Non-Metal part:

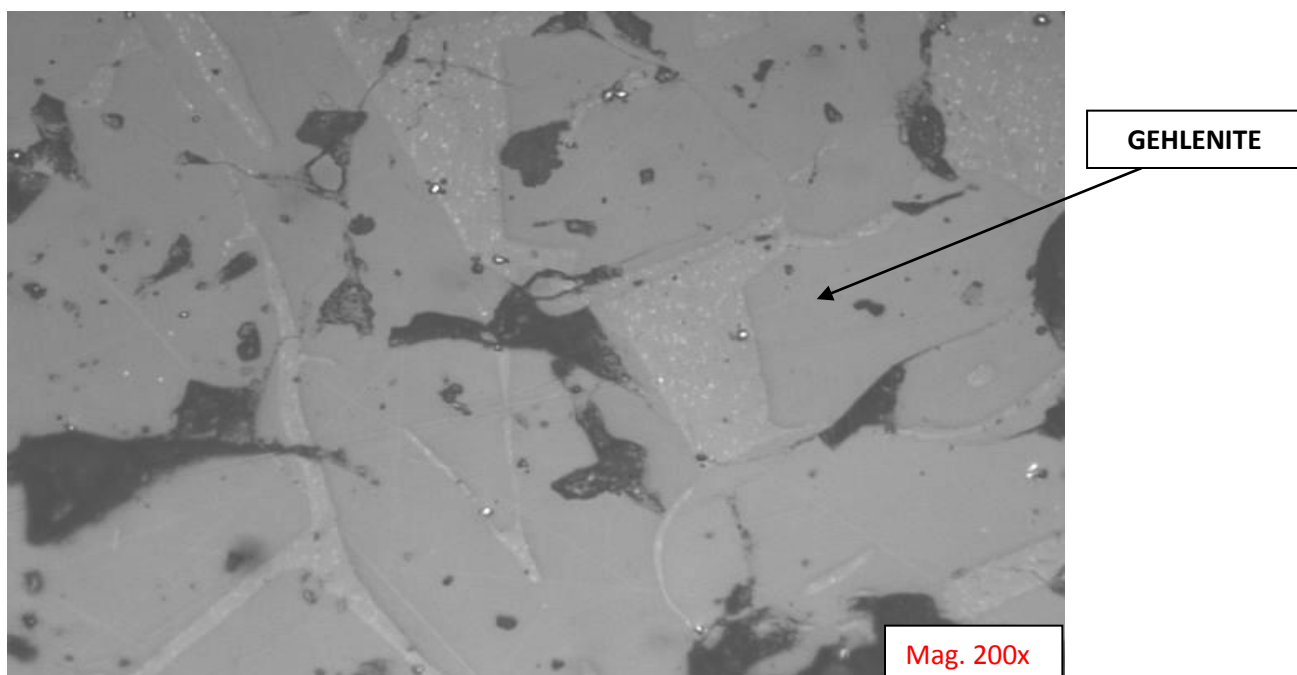


Fig. 4.12: Microstructure of sample C for non-metal part

4.5 Discussion:

CO is a good reducing agent and most stable at above 1000 C. in the plasma furnace, CO reacts with Fe₂O₃[15]. The probable chemical reactions occurring during Fe₂O₃ reduction are the following:



However, some direct reduction of FeO by solid carbon may also occur according to the reaction:



Following inference was made from these experiments:

1. Fusion time of red mud added with coke only is comparatively higher than Sample B and C which contains lime. In Sample C power consumption is least as it contains less amount of carbon.
2. Sample A contains higher amount of slag phases due to comparatively higher melting temperature.
3. In Sample B and C Magnetic material contains fewer amounts of slag phase because addition of lime converts the slag phase to Gehlenite having a melting temperature of 1590°C.
4. In Sample C, Fe₃C and TiC is comparatively less because composition of sample contains lesser amount of carbon.
5. In Sample B and Sample C Ferro titanium and Fe content is higher and TiC is less as aluminium dross was also added as a reductant.

CHAPTER: 5
CONCLUSION

5.1. Conclusion:

This process seems to be viable for extraction of Iron and Ferrotitanium from red mud which is a potential threat for its disposal. Also the slag generated from this process which is Gehlenite can be used for making refractories or can be used in Port land slag cement after granulation.

5.2. Scope for Future work:

1. Although alkali was removed from the red mud with the addition of warm water but alkali could not be removed completely. This alkali can be recovered completely before fusing these materials.
2. Also illemanite can be blended for better recovery of ferrotitanium.
3. Bigger trial can be done in a continuous plasma furnace for better separation of slag
And metal and having better cost economics.

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