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Utilization of iron values of red mud for metallurgical applications

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ABSTRACT

A brief overview on the utilization of iron values of red mud is presented along with the results of some recent investigations conducted at National Metallurgical Laboratory. Red mud from Nalco, characterized by high iron content, is used in the studies. Two different strategies are explored : (a) extraction of iron and other metal values from red mud using a patented process, named as Elgai process, available for the removal of alumina from iron ores; and (b) use of red mud as an additive in the iron ore sintering. The second approach has particularly yielded interesting results. Sinter with acceptable physical properties and reducibility could be produced with red mud addition from 50 to 125 kg/tonne of sinter. Red mud addition leads to the dilution of the iron content of sinter. It is suggested that this problem can be circumvented with addition of blue dust, a waste material, along with red mud.

Keywords : Iron ore sintering, Metal recovery, Mineralogical characterization, Red mud.

INTRODUCTION

Red muds (bauxite tailings) are the residues generated in Bayer process during production of alumina from bauxite [1]. Red mud may contain as much as 63% Fe_2O_3, 43% Al_2O_3, and 24% TiO_2 depending upon chemical and mineralogical make up of bauxite and bauxite treatment technology [1-4]. About 0.5-2 tonne of red mud is generated for each tonne of alumina produced. The Indian bauxite processing industries contribute over 1.9 million tonnes of red mud in about 40 million tonnes/year of red mud produced globally (Fig.1). Disposal of red mud is a formidable environmental problem due to its production in massive quantities, high caustic content and slimy and sludgy character. There is growing interest in the processing and utilization of red mud for various metallurgical as well as nonmetallurgical applications (Table 1) [1-5].

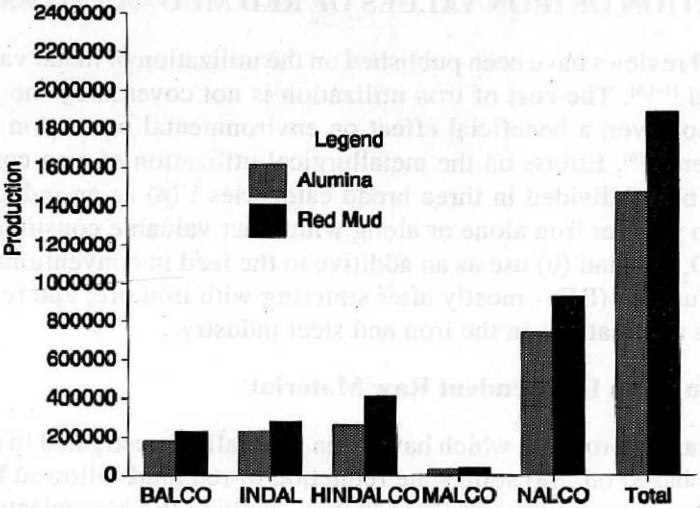


Fig. 1 : Alumina production and generation of red mud by Indian aluminium plants (in tonnes).

Table I. Utilization of red mud

I. *NONMETALLURGICAL APPLICATIONS*

A. *Pollution Control* - waste water treatment, stripping of SO_2

B. *Materials* - Building industry, additive to cement, rubber filler, pigments, zeolite/naphelite, insecticides and fertilizer carrier

II. *METALLURGICAL APPLICATIONS*

A. *Iron and Steel* - production of pig iron, additive to iron ore sinter

B. *Complete Recycling* - lime-soda-sinter process, smelting slag-disintegration process

C. *Recovery of Minor Constituents* - for example recovery of TiO_2

Since iron as oxides/oxyhydroxides is usually the largest component of red muds, iron recovery from red mud has attracted major attention [3,4,6]. In this paper we present results of some recent studies at NML on the extraction of iron and other metal values from red mud, and prospects of red mud utilization as an additive in the iron ore sintering. A brief overview on utilization of iron values of red mud is presented as a prelude to the results presented.

UTILIZATION OF IRON VALUES OF RED MUD - AN OVERVIEW

Several reviews have been published on the utilization of metal values present in red mud [1-4,6]. The cost of iron utilization is not covered by the price of the product, however, a beneficial effect on environmental protection should also be considered [6]. Efforts on the metallurgical utilization of iron content of red mud may be subdivided in three broad categories : (a) as an independent raw material to recover iron alone or along with other valuable constituents such as Al_2O_3, TiO_2 etc; and (b) use as an additive to the feed in conventional iron making blast furnace (BF) - mostly after sintering with iron ore; and (c) other miscellaneous applications in the iron and steel industry.

Utilization as an Independent Raw Material

Two main approaches which have been generally investigated to recover iron values are based on : (a) solid state reduction of red mud followed by magnetic separation to recover iron; and (b) reduction smelting in a blast/electric/low shaft furnace (with or without prereduction) to produce pig iron. The former had limited success but the smelting technology appears to have been standardised on bench/pilot scale, for example the work done at McDowel Wellman Engg. Co.,USA, and Giulini GmbH, Germany [2-4,7].

Red mud cannot be considered as competitive raw material for iron and steel making because the Fe_2O_3 content of the red mud is much lower (typically 30-50%) than the conventionally used iron ores (>60%). Presence of other components and physical characteristics are the additional drawbacks of red mud. Based on these considerations, processes for the simultaneous recovery of all the major constituents, namely Al_2O_3, Fe_2O_3 and often other constituents such as Na_2O, TiO_2 and V_2O_5, have been developed [2,4,7-11]. Notable technologies, developed at the laboratory as well as pilot plant scale, include Complex Separation Melting Process developed in Hungary, Smelting Slag Disintegration Process (Yugoslavia) and Soda-Lime-Carbon Sinter Process of US Bureau of Mines [2-4,6-9]. Ziegenbalz [10] has described electrothermic processing of red mud which permits the recovery of soda and high quality pig iron [10]. A carbonyl process has been reported for deironing red mud and bauxite, and for the preparation of a raw material for the alumina industry and of iron carbonyl suitable for use in iron metallurgy [11]. None of the reported processes could be developed on an industrial scale due to unfavourable energy economics and high capital cost.

In India, know how for the recovery of Fe, Al_2O_3, V and Cr from red mud has been developed by Regional Research Laboratory (RRL), Bhubaneswar [3,12,13]. National Metallurgical Laboratory (NML), Jamshedpur has evaluated technical feasibility of Al_2O_3 extraction, along with vanadium oxide, from Muri red mud by Soda-Lime sinter process [3]. Prasad and coworkers [3] have explored the production of ferrotitanium to utilize both iron and titanium values of Indian red muds.

Use in Conventional Blast Furnace and Sintering

The metallurgical utilization of red mud as additive to the blast furnace feed was carried out first in Federal Republic of Germany and Hungary in forties and fifties. However, as a result of its low Fe_2O_3 content, the red mud diluted the feed and its Na_2O content had adverse effect on the lining of the blast furnace [7]. Commercial scale trials in erstwhile Soviet Union have indicated that addition of up to 3% red mud in sinter mix increased sinter strength, reduced dust content, improved productivity and reduced coke consumption in blast furnace operation [6]. Horwath and Parlag [14] studied the effect of 3, 5 and 10% red mud on the properties of sinter and found that addition of 5% red mud has a favourable effect on a sinter mix containing mainly magnetite. Use of red mud with hematite ore in sinter mix enhanced productivity of blast furnace due to improved reducibility of the sinter, improvement in the desulphurisation capacity of the slag and decreased coke consumption [7,15].

Other Applications in Iron and Steel Making

Thakur and Das [4] have described several miscellaneous uses of red mud in iron and steel making. For example, use of red mud as an effective desulphurisation and dephosphorization agent for steel, as an additive to bring down the viscosity of steel making slag and to accelerate slag formation in BOF steel making. Red mud along with carbon has also been used as an agent for the treatment of blast furnace slag.

RECENT STUDIES AT NML

Recent studies at NML has focused primarily on the utilization of iron values of red mud. Two different approaches are explored : (a) extraction of iron and other metal values from red mud through the Elgai process [16]; and (b) use of red mud in iron ore sintering. The Nalco red mud is used in the studies because of its high iron content. Nalco, the largest producer of alumina in our country, contributes over half of the red mud generated (Fig. 1) [17-19]. Chemical composition and phase analysis of the red mud used in the investigation are given in Table 2.

Extraction of Iron and Other Metal Values from Red Mud

The 'Elgai Process' is a patented process for the removal of alumina from

Table 2 : Chemical composition and phase analysis of the Nalco red mud

A. CHEMICAL COMPOSITION (AFTER DRYING AT 120°C)

Chemical composition, wt.%						
Al_2O_3	Fe_2O_3	TiO_2	SiO_2	CaO	Na_2O	LOI
Red mud used in the metal recovery tests						
20.4	47.4	2.8	7.4	3.2	5.2	13.0
Red mud used in the sintering studies*						
12.0	65.0	2.4	6.0	-	2.8	10.5

* refered to as red mud sand

B. PHASE ANALYSIS

Components	Major Minerals	JCPDS File
Al_2O_3	Gibbsite (Al_2O_3, $3H_2O$)	33-0018
Iron	Hematite (Fe_2O_3)	33-0664
	Aluminogoethite [α - (Fe,Al) OOH]	29-0713
Silica	Quartz (α - SiO_2)	33-1161
	Kaolinite [$Al_2Si_2O_5(OH)_4$]	29-1488
	Sodalite ($Na_4Si_3Al_3O_{12}Cl$)	20-0495
TiO_2	Anatase (TiO_2)	21-1272
	Rutile (TiO_2)	21-1276

aluminous iron ores (Fig. 2) [16]. The flow sheet of the Elgai process is quite similar to the Soda (or Soda-Lime)-Carbon sinter process except that sintering is avoided during roasting using a lower temperature. The process is claimed to offer several advantages, for example, almost complete recovery of alumina, high purity of magnetic fraction resulting in considerable savings in flux and energy during smelting, and prospect of simultaneous recovery of other minor elements. Since the chemical composition of the iron ore treated in Elgai process resembled Nalco red mud, the process has been tested for its applicability to Nalco red mud. The details of experimental procedures followed are given below.

Red mud, charcoal and soda were mixed in a rod mill and pelletized using a laboratory pelletizer. The pellets were roasted between 700°-925°C and water leached. The variables studied include amount of soda addition (excess over stoichiometric requirement), milling time, roasting temperature and time, effect

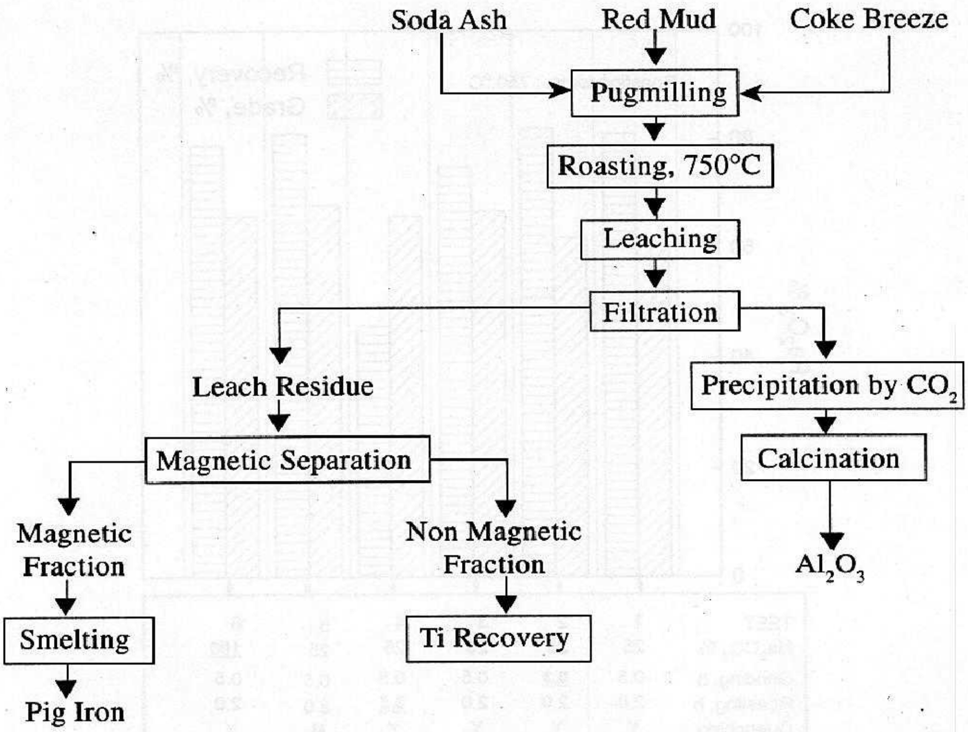
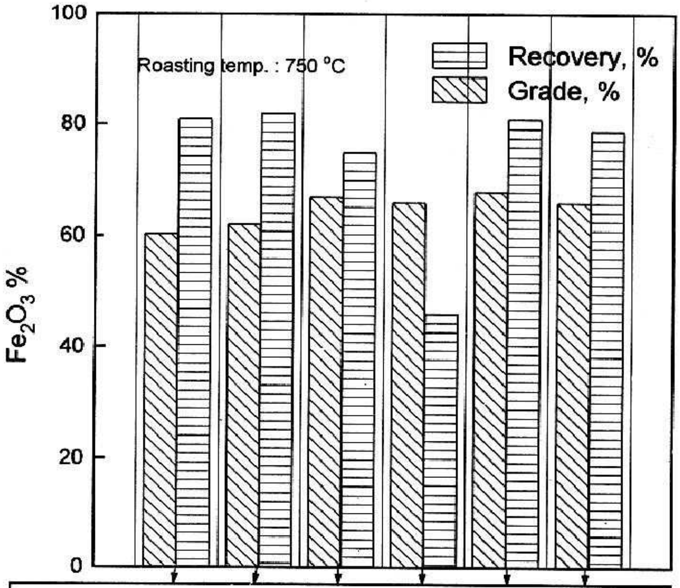


Fig. 2 : 'Elgai Process' - a process for the removal of alumina from aluminous iron ores

of water quenching of the roasted product and leaching temperature and time. The Al_2O_3 recovery was calculated from the Al_2O_3 content of the leach liquor. The leach residue was dried and subjected to magnetic separation by wet process in a Davis tube using a fixed magnetic field of 2400 gauss and water-flow rate of about 1 litre/min. The weights of magnetic and nonmagnetic fractions were taken and these were analysed for Al_2O_3, Fe_2O_3, SiO_2 and TiO_2 contents. The solid samples at the different stages of the process were characterized by XRD (Model : SEIMENS D500 diffractometer) and SEM-EDS (JEOL840A SEM with a KEVEX EDS detector) to know the behaviour of iron bearing constituents during the process.

The results presented in Fig. 3 are for the tests in which roasting was carried out at the temperature recommended in the Elgai process (750°C) and other parameters, such as grinding/mixing time or conditions of roasting and leaching, were varied. About 80% Fe_2O_3 could be recovered in the magnetic fraction in most of the tests. Test involving prolonged roasting upto 3.5 h (Fig. 3)



TEST	1	2	3	4	5	6
Na_2CO_3 %	25	25	25	25	25	**100**
Grinding, h	0.5	**0.3**	0.5	0.5	0.5	0.5
Roasting, h	2.0	2.0	2.0	**3.5**	2.0	2.0
Quenching	Y	Y	Y	Y	**N**	Y
Leaching						
Temp., °C	65	65	**75**	65	65	65
Time, h	1.5	1.5	**2.0**	1.5	1.5	1.5

Fig. 3 : Effect of various experimental conditions on the magnetic separation of iron phases from the leach residues. The experimental conditions used in Test 1 are similar to the Elgai process and condition(s) varied in other tests are indicated in bold. Na_2CO_3% represents excess over stoichiometric requirement. Carbon (added as charcoal), (1/4)th the weight of iron, is same in all the tests.

resulted in lower recovery of iron oxide minerals in the magnetic fraction because of the formation of greater amount of nonmagnetic wustite (FeO) phase. Figure 4 shows the results of tests in which roasting temperature was varied between 700° to 925°C and all other conditions were kept same as in the Elgai process. Iron recovery (expressed as Fe_2O_3 %) varied between 73-82% and higher recoveries (~ 80%) are obtained in the tests involving roasting at 750° and 925°C. The grade of magnetic fraction (Fe_2O_3 %) is about 60% in all the tests conducted upto the roasting temperature of 750°C (Figs. 3 and 4). Grade increases upto about 72% at or above 800°C roasting temperature (Fig. 4).

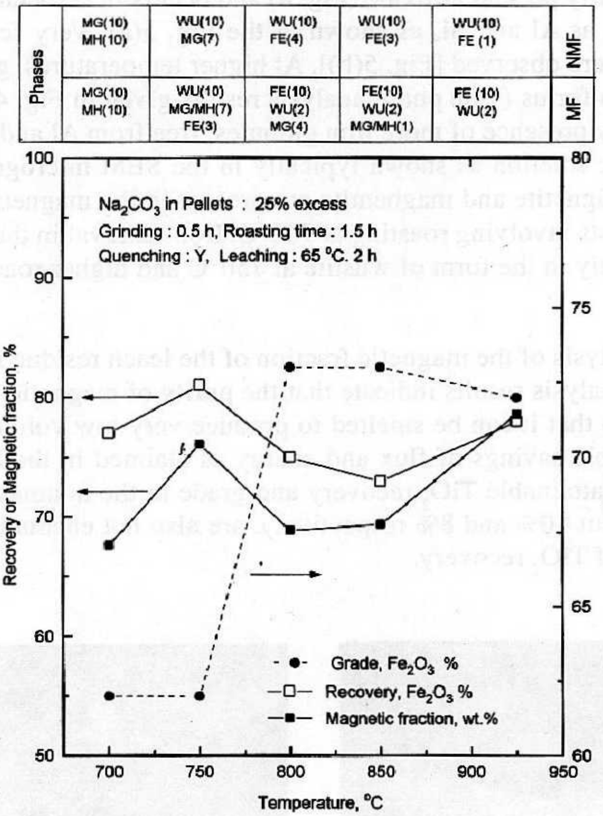


Fig. 4 : Effect of roasting temperature on the magnetic separation of iron phases from leach residue. Phases separated in the magnetic fraction (MF) and nonmagnetic fraction (NMF) are indicated along with the relative peak intensity for the strongest line in the XRD pattern. MH - Maghemite, MG - Magnetite, WU - Wustite, FE - Alpha iron

XRD analysis of magnetic and nonmagnetic fractions was carried out to explain the results of iron separation. Iron bearing phases formed at different roasting temperatures are superimposed in Fig. 4 showing the effect of temperature on the separation of iron phases. Formation of maghemite/magnetite at 700°C and gradual increase in the formation of metallic iron at higher temperatures through Fe_2O_3-Fe_3O_4-FeO-Fe transitions is in broad agreement with the thermodynamic stability of various iron oxides in the presence of carbon [20]. Superior grade of magnetic fraction at higher temperatures is linked with greater amount of metallic iron formation and its separation in the magnetic fraction (Fig. 4). At 750°C, iron is dominantly present as oxide (Fig. 4) and occurs in association with other elements, such as Al and Si, as shown in the Fig. 5(a). Very few globules of metallic iron were observed [Fig. 5(b)]. At higher temperatures, greater amount of metallic iron forms (vide phase analysis results given in Fig. 4). This is also corroborated by presence of more iron globules, free from Al and Si impurities, in the magnetic fraction as shown typically in the SEM micrographs given in Fig. 6. Both magnetite and maghemite are present in the magnetic fraction obtained in the tests involving roasting at 700°C. Iron removal in the nonmagnetic fraction is mostly in the form of wustite at 750°C and higher roasting temperatures.

Typical analysis of the magnetic fraction of the leach residue is presented in Table 3. The analysis results indicate that the purity of magnetic fraction is not high enough so that it can be smelted to produce very low volume of slag and with considerable savings of flux and energy as claimed in the Elgai process. The maximum attainable TiO_2 recovery and grade in the nonmagnetic fraction (at 925°C), about 40% and 8% respectively, are also not encouraging from the point of view of TiO_2 recovery.

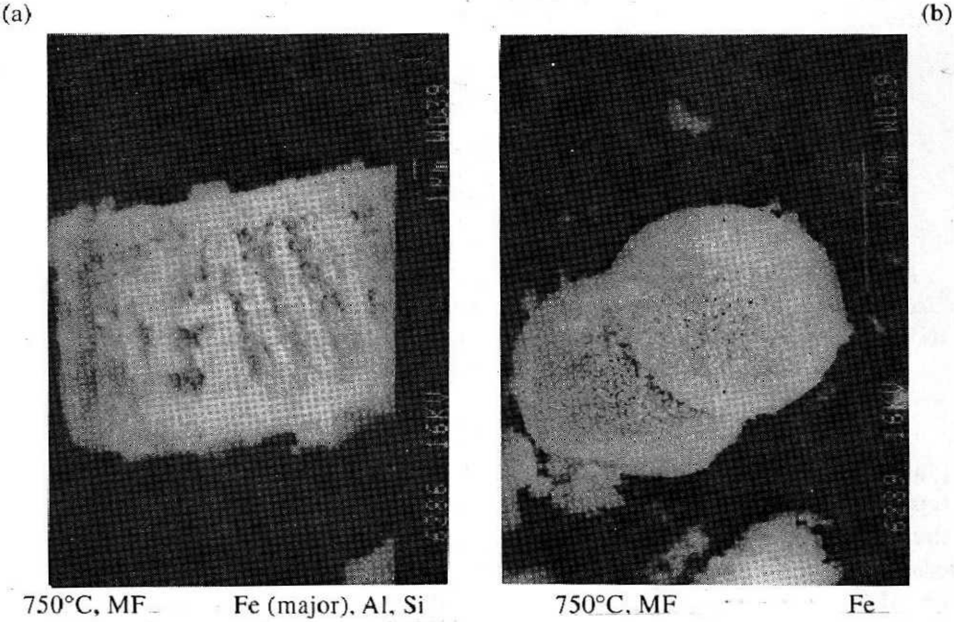
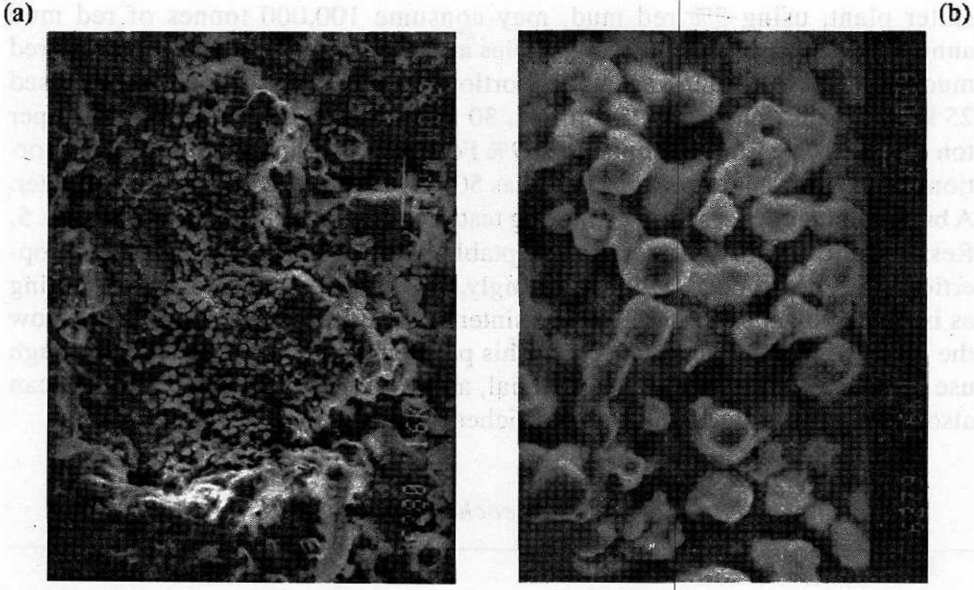


Fig. 5 : SEM micrographs of typical iron bearing particles in the magnetic fraction of leach residue [roasting temperature 750°C].



925°C, MF Fe

925°C, MF Fe

Fig. 6 : SEM micrographs of typical iron bearing particles in the magnetic fraction of leach residue [roasting temperature 925°C].

Table 3 : Chemical composition of magnetic and nonmagnetic fractions

Constituents	Roasting*	Chemical Composition (wt. %)			
	Temperature, °C	Fe_2O_3	Al_2O_3	SiO_2	TiO_2
Magnetic fraction	750	62.3	13.5	6.4	-
	925	72.0	10.5	9.8	-
Nonmagnetic fraction	750	43.7	18.5	8.5	3.1
	925	75.7	0.8	9.5	8.4

* Other conditions same as in the Elgai process (Test 1, Fig. 3)

Red Mud Addition during Iron Ore Sintering

Use of iron oxide containing red mud by introducing it to the blast furnace through sinters of acceptable quality is an attractive proposition from the point of view of large scale utilization. It is estimated that a 2 million tonnes/year sinter plant, using 5% red mud, may consume 100,000 tonnes of red mud annually. Pre-feasibility sintering studies are being conducted at NML using red mud sand from Nalco in various proportions with iron ore fines. The tests used 25 kg MgO (as dolomite), 25 kg lime, 30 kg mill scale and 15 kg flue dust per ton of sinter. The iron ore contained 59% Fe, 9.6% SiO_2 and 2.3% Al_2O_3. Proportions of red mud added to sinter mix was 50, 75, 100 and 125 kg per ton of sinter. A brief summery of results of sintering tests conducted are given in Tables 4& 5. Results indicated that sinters with acceptable physical and physicochemical properties could be produced [21]. Interestingly, alkali was removed during sintering as indicated by chemical analysis of sinters. The iron content of sinter is below the required level of about 48% Fe. This problem can be circumvented through use of blue dust, another waste material, along with red mud. The problem can also be minimized by using iron ore richer in iron content.

Table 4 : Physical and physicochemical properties of sinters

Red mud sand (kg/ton sinter)	Return fines generated, %	Sinter properties, %		
		Tumbling index	Abrasion	Reducibility index
50	25.9	72.9	5.6	63.6
75	28.3	72.6	5.8	58.5
100	29.0	70.7	5.8	61.2
125	26.6	73.7	5.5	-

Table 5 : Chemical analyses of the sinters

Constituent	Red mud sand (kg/ton sinter)			
	50	75	100	125
Fe	42.8	43.8	44.7	42.9
FeO	6.7	5.8	5.5	6.4
SiO_2	9.4	8.2	8.1	8.9
Al_2O_3	3.8	3.0	3.5	3.8
CaO	22.8	23.0	21.3	22.8
MgO	3.2	3.5	3.5	3.6
Na_2O	NF	NF	NF	NF

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