PRODUCTION OF PIG IRON FROM NALCO REDMUD BY APPLICATION OF PLASMA SMELTING TECHNOLOGY

Parth Sarathi Mukherjee[1], Bhagyadhar Bhoi[2], Chitta Ranjan Mishra[3], Ramani Ranjan Dash[4], Bijaya Kumar Satapathy[5], Kalidas Jayasankar[6]

[1,2,6] Institute of Minerals and Materials Technology, Bhubaneswar 751 013, Orissa, India
[3,5] National Aluminium Company Limited, NALCO Bhawan, P-1, Nayapali, Bhubaneswar 751 013, Orissa, India
[4]Gandhi Intitute of Engineering & Technology, Gunupur, Rayagada, Orissa, India

Keywords: Bauxite[1], Redmud[2], Plasma Smelting[3], Pig Iron[4], Slag Cement[5]

Abstract

Red Mud, a by-product generated from the caustic leaching of bauxite to produce alumina in the Bayer Process, causes serious environmental problems and is considered as a hazardous industrial waste. A novel process has been developed for production of Pig Iron from NALCO Red Mud by employing Plasma Smelting Technology. Red Mud containing 15-40% Fe_2O_3 was subjected to Thermal Plasma Smelting by use of Extended Arc Plasma Reactor at a temperature of 1600°C for a period of 30 minutes and high quality Pig Iron was produced. Effect of various process parameters like basicity, amount of reductant, plasmagen gas, input electric power and reduction time for recovery of Pig Iron has been studied and optimized. Basicity of 0.3, reduction time of 25 minutes at 12.5 kW power was found to be optimum for maximum recovery of pig iron (70%) from Red Mud in 1kg scale.

Introduction

During digestion of bauxite with caustic soda employing Bayer Process, Red Mud, a hazardous waste material is generated at the rate of two tons of Red Mud per one ton of alumina. NALCO, a Navaratna Company under Government of India, has set up Asia's largest integrated Alumina- Aluminum complex in the state of Odisha, India and produces 15,75,000 MT of alumina per annum. In the process about 31,50,000 MT of Red Mud is generated which is preserved in a nearby pond specifically made for the purpose which contains around 30-50 % iron.

One among the top ten alumina refineries in the world, NALCO's energy efficient alumina refinery utilizes time tested Bayer's process technology of atmospheric pressure digestion at lower temperature.

Utilization of Red Mud for production of cement, tiles, bricks and blocks etc has been tried by many researchers. However these efforts have resulted in partial utilization of Red Mud and the problem of bulk utilization of Red Mud still remains a challenge. Since Iron is a major constituent of Red Mud, it was thought prudent to extract iron values in the form of Pig Iron utilizing the novel Plasma Smelting Technology. By employing this technology, techno-economic feasibility for bulk utilization of Red Mud can be established.

Raw Materials

The raw materials used for the present work are NALCO Red Mud, Limestone , Quartz and Fluorspar. The chemical analysis of these raw materials are presented in Table-1 and Table-2. The chief constitute of Graphite is carbon of 99%.

Table-1 : Chemical Analysis of NALCO Red Mud (wt%)

Red Mud	Fe_2O_3	SiO_2	TiO_2	Al_2O_3	Na_2O	K_2O	LOI	MgO	CaO
Batch-I	53.6	18.9	2.20	4.88	8.29	-	9.30	0.21	0.54
Batch-II	47.60	4.10	5.60	14.36	-	-	12.51	0.27	0.62
Batch-III	48.8	2.25	7.20	16.68	-	-	12.80	0.31	0.67

Table-2: Chemical Analysis of Limestone, Quartz and Fluorspar

Constituents	Wt. %		
	Limestone	Quartz	Fluorspar
CaO	45.59	2.50	60.00
SiO_2	4.04	96.50	-
MgO	7.10	0.50	-
Al_2O_3	0.26	-	-
CaF_2	-	-	40.00
Other Oxides	1-5	-	-

Experimental

Experimental Set up:

Schematic diagram of 50kW DC Plasma reactor is shown in Fig.1. It is a pot type of rector where two graphite electrodes are arranged in the vertical configuration. The graphite crucible is used as the hearth of the reactor and is connected to the bottom graphite anode. The crucible assembly constitutes the anode. The top graphite electrode known as cathode is having an axial hole to pass the plasma forming gas. The bottom electrode and the crucible are kept fixed. The formation and stabilization of the plasma arc is done by the movement of the top electrode, with simultaneous application of power supply which is actuated by a rack and pinion mechanism. The hearth is thermally insulated by the bubble alumina in a mild steel casing. Graphite spout is connected in the hearth for tapping of both metal and slag. The water cooling system is provided at the end of the top and bottom electrode to avoid the over heating of electrical terminals. A graphite lid is provided with ceramic insulation to promote free travel of the electrode without electrically shorting the body. The lid is thermally insulated with magnesia and opened for the exhaust gases. The electrical power to the plasma reactor is supplied by a DC 50 kW power source.

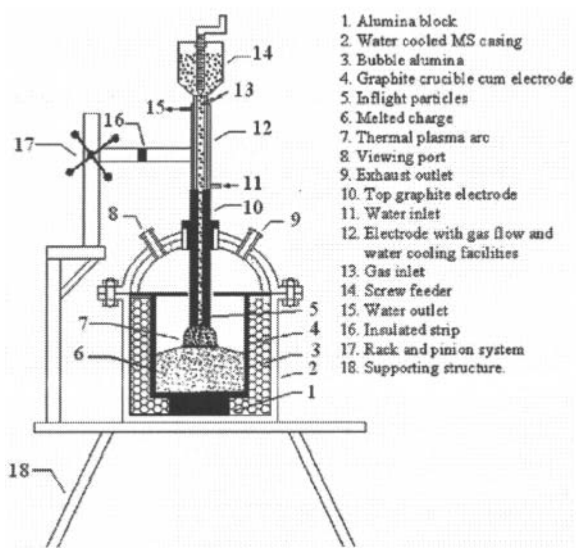

Fig.1 Schematic diagram of indigenously developed extended arc plasma reactor

Plasma Smelting of Red Mud:

Initially Red Mud, coke and dolomite / limestone/ fluorspar (flux) powder of required composition were thoroughly mixed and charged inside the graphite crucible. Argon gas was used as plasmagen gas and was passed through the top electrode at a rate of 1.0 LPM. The arc was struck and the current of 250 amperes was maintained with an arc voltage of about 60 volts. The plasma arc was continued for 20 to 30 minutes to complete the chemical reaction. The temperature of the molten bath was measured by using Minolta Optical Pyrometer. At the end of the smelting, the tap hole was opened and the molten pig iron and slag were allowed to pour in to the graphite mould. The experimental conditions are furnished in Table-3.

Table-3 Experimental conditions optimised

EXPT. NO.	Raw material	Current (I)	Volt-age (v)	Time (m)	% of metal
1. (Red Mud + 11% Graphite + 5% Quartz)	Redmud=200gms Graphite=20gms Quartz=10gm	250	50	11	32.81
2.(Red Mud + 11% Graphite + 10% Limestone + Quartz) [Basicity: 0.15]	Redmud=1kg Graphite=110gms Quartz=40gm Lime stone=100gm	250	50	25	67
3. (Red Mud + Graphite + Fluorspar) Fulorspar is added before tapping. [Basicity: 0.23]	Redmud=1kg Graphite=110gms Quartz=50gm Flourspar=94gm	250	50	25	69.26
4. (Red Mud + Graphite + Flurospar + Limestone) Fluorospar is added before tapping. [Basicity: 0.33]	Redmud=1kg Graphite=110gms Quartz=50gm Lime stone=50gm Flourspar=47gm	250	50	25	60

Results and Discussions

The red mud along with graphite and flux (Limestone/ Flourspar) were smelted in 35kW extended arc plasma reactor. The main aim and objectives of the work was to find out higher recovery of Pig Iron. To achieve this, the process parameters like basicity and reduction time were studied.

The probable chemical reactions occurring during Fe_2O_3 reduction are the following:

$3\ Fe_2O_3+CO=2Fe_3O_4+CO_2$ (1)
$Fe_3O_4+CO=3FeO+CO_2$ (2)
$FeO+CO=Fe+CO_2$ (3)

$Fe_2O_3+3CO=2Fe+3CO_2$ (4)

Carbon content in graphite reacts with atmospheric O_2 to form:

$C+O_2=CO_2$ (5)
$CO_2+C = 2CO$ (6)

$2C+O_2= 2CO$ (7)

CO is most stable at above 1000°C. It is a good reducing agent and reduces Fe_2O_3.

In plasma furnace, CO reacts with Fe_2O_3. The reaction steps are as follows:-

$Fe_2O_3+CO=Fe_3O_4+CO_2$ (8)
$Fe_3O_4+CO=FeO+CO_2$ (9)
$FeO+CO=Fe+CO_2$ (10)

However some direct reduction of FeO by solid carbon may also occur according to the reaction (11). All the equations except (11) are exothermic.

$FeO + C = Fe + CO$ (11)

The experimental parameters like effect of basicity, reductant and reduction time have been studied and a typical metal and slag analysis are given in Table 4 and Table 5.

Table-5 Typical analysis of Pig Iron

Basicity	Test Parameters (wt%)				
	Fe	C	S	P	Si
0.25	94.95	4.10	0.051	0.198	0.07

Table-6 Slag Analysis

Test Parameters (wt%)						
Fe(Metal)	FeO	Al_2O_3	SiO_2	CaO	Na_2O	MgO
5.64	5.03	41.82	13.49	20.29	3.94	5.80

The Effect of Basicity on the Recovery of Pig Iron:

Basicty plays an important role in the production of Pig Iron from Red Mud. The basicity ranging from 0.07 to 1.50 has been studied. It is observed that the maximum recovery of 71.10% achieved with the basicity of 0.25. With further increase of the basicity, the metal recovery decreases (Table-7). This may be due to the fact that presence of alumina makes the slag more viscous. This is substantiated by the metallographic and EDS studies (Fig. 5).

Table-7 Effect of Basicity [Red Mud (RM),Limestone(LS), Graphite(G), Quartz (Q), Dolomite (D)]

Sl No	Raw Materials	Basicity	Metal Recovery (%)
1	RM=350g,G=11%, $CaCO_3$=6%,MS=6%, Q=5%	0.07	62.00
2	RM=350g,G=11%, LS=10%, Q=5%	0.20	65.64
3	RM=350g,G=11%, Q=5%, F=10%	0.23	70.00
4	RM=350g,G=11%, Q=5%, D=12%	0.25	71.10
5	RM=350g,G=11%, Q=5%, D=14%	0.29	62.60
6	RM=350g,G=11%, Q=5%, D=16%	0.32	60.00
7	RM=350g,G=11%, Q=5%, LS=87g	0.40	61.50
8	RM=350g,G=11%, Q=5%, LS=110g	0.50	50.40
9	RM=350g,G=11%, Q=5%, LS=229g	1.00	55.00
10	RM=350g,G=11%, Q=5%, D=795g	1.50	40.70

The Effect of Reductant on the Recovery of Pig Iron:

The effect of reductant on the recovery of Pig Iron was studied in the range of 9 to 14% of the charge mix. In this case graphite is acting as the reductant. The results are shown in Table-8. From the results obtained, it is observed that the recovery of metal is increasing with increasing the amount of reductant from 9 to 11% and thereafter, a decrease in trend is observed. The reasons are not clear and needs further in-depth investigation.

Table-8 Effect of Reductant (graphite)
[Experimental Conditions : time= 15min, Power= 12.5 kW and Basicity=0.2];

Sl. No	Material Charged	Reduc-tant (%)	Metal Weight (g)	Metal Recovery (%)
1	RM=350g, LS=10.0%, Q=5%	9.00	64.50	55.60
2	RM=350g, LS=10.0%, Q=5%	10.00	69.50	60.00
3	RM=350g, LS=10.0%, Q=5%	11.00	76.00	65.54
4	RM=350g, LS=10.0%, Q=5%	12.00	71.00	61.24
5	RM=350g, LS=10.0%, Q=5%	13.00	60.00	51.72
6	RM=350g, LS=10.0%, Q=5%	14.00	49.00	42.20

The Effect of Reduction time on the Recovery of Pig Iron:

The recovery of Pig Iron production depends on the reduction time. The time range from 11 to 17 min have been studied. The results are shown in the Table-9. It is observed that there is increase in the recovery of Pig Iron up to 15 min and thereafter it decreases. This may be due to evaporation of metal values during prolonged smelting operation period. This may be due to the reverse reaction of iron to form complex failite slag. Further investigation in this line is being carried out.

Table-9 : Effect of Time: [Power 12.5 kW and Basicity= 0.2]

Sl. No	Material Charged	Time (min)	Metal	
			Wt.(g)	(% Recovery)
1	RM=350g LS=10.0%, G= 11.0%, Q=5%	11	37.00	31.89
2	RM=350g LS=10.0%, G= 11.0%, Q=5%	12.00	35.00	30.17
3	RM=350g LS=10.0%, G= 11.0%, Q=5%	13.00	35.00	30.17
4	RM=350g LS=10.0%, G= 11.0%, Q=5%	14.00	60.50	52.15
5	RM=350g LS=10.0%, G= 11.0%, Q=5%	15.00	76.00	65.51
6	RM=350g LS=10.0%, G= 11.0%, Q=5%	16.00	61.00	52.58
7	RM=350g LS=10.0%, G= 11.0%, Q=5%	17.00	60.00	51.70

Statistical Design of Experiments:

The experimental parameters like basicity, reductant, time and power have been optimesed by statistical design of experiments and extrapolation of results which indicates that basicity of 0.3, reduction time of 25 minutes at 12.5 kW power was found to be optimum for maximum recovery of pig iron (70%) from Red Mud in 1kg scale.

Process Flow Sheet:

Thermal Plasma Technology offers a unique process for the production of Pig Iron from Red Mud- an industrial waste from Alumina Refineries. By employing this technology, a process flow sheet has been developed for extraction of Pig Iron from NALCO Red Mud which is shown in Fig. 2.

The appropriate quantities of raw materials viz. Red Mud, reductant and flux are mixed properly in a dry ball mill and then the charge mix was subjected to Thermal Plasma Treatment. The charge mix was smelted in the Thermal Plasma Reactor and the metal and slag were tapped separately. The tapped metal can be alloyed with Fe-Si, Mg which yields S.G. Iron. The slag produced can be utilized for the manufacture of tiles/cement.

Flow Chart

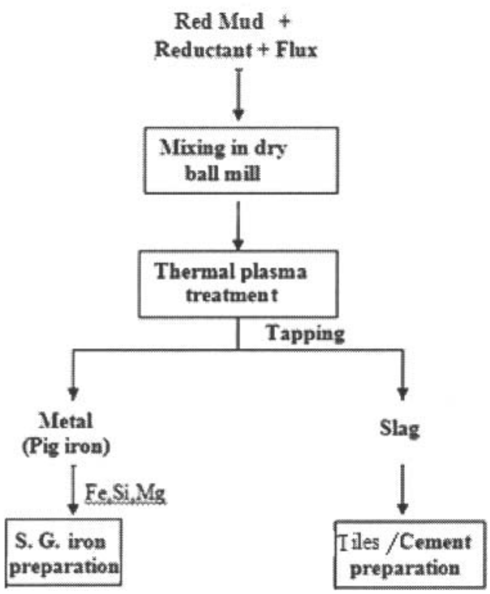

Fig.2 : Process Flow Diagram

Metallographic Studies of Red Mud, Pig Iron and Slag

(a) Red Mud:

The Red Mud sample was subjected to metallographic studies. The microstructure as well as the EDS analysis are shown in the Fig.3. EDS analysis data clearly indicate that the distribution of different elements in the Red Mud is not uniform. However many trace elements which remained undetected during bulk chemical analysis of red mud and slag were easily detected during EDS analysis. These data indicate the complex composition of Red Mud and consequently that of the smelter slag.

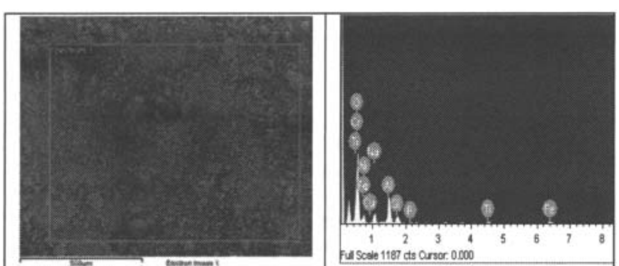

Fig.3 The Microstructure and EDS analysis of Red Mud

(b) Pig Iron

The Pig Iron produced by above method was subjected to metallographic studies. The microstructures of the sample were examined in a light microscope at various magnifications. Most of the samples developed a completely white or mottled structure.

This is to be expected because Silicon was picked up by way of reduction of the silica in the red mud and the quartz added. However, the silicon in the metal was inadequate to cause graphitization. The secondary electron micrograph of a plasma smelted Pig Iron and EDS analysis are shown in Fig.4.

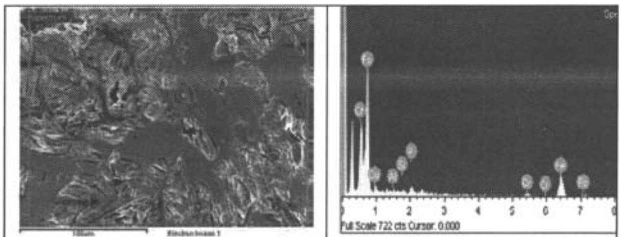

Fig.4 The secondary electron micrograph of a plasma smelted pig iron and EDS analysis

From this study it is observed that high concentration of Cr, Cu and P are found to be present in the particular spot analysed. The minor quantities of Cr_2O_3, P_2O_5 and CuO present in the Red Mud are completely reduced in the plasma smelter and are picked up in the Pig Iron.

It is interesting to note that Al has been picked up. Normally Al_2O_3 is so refractory that it is never reduced in the blast furnace or electric arc furnace. But the high temperature in the plasma reaction zone apparently favoured reduction of Al_2O_3 and pick up of Al in the metal, presumably as complex Fe-Al-carbide.

Titanium is also picked up most likely as a complex carbonitride, since the typical cuboidal precipitates of TiC could not be detected even after thorough scanning of the microstructure. Apart from reduction of iron oxide and silica, the reduction of other oxides also consumed the reductant. Naturally, such undesirable reduction reactions increased on prolonging the trial. Evidence of reduction of other oxides has been obtained through EDS analysis.

(c) Pig Iron Slag

The metallographic and EDS analysis of slag samples collected from the plasma reactor is shown in Fig.5.

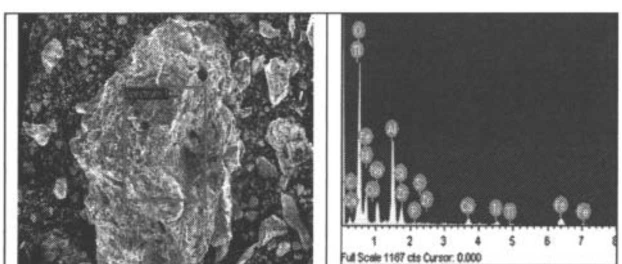

Fig.5 The Metallographic and EDS analysis of a Pig Iron slag

From this study it is observed that the Pig Iron slag is rich in Al_2O_3 along with SiO_2, MgO , FeO , CaO, TiO etc .

Conclusion

Thermal Plasma Technology offers a unique one step process for processing of Red Mud. Red Mud will be an important source of iron for the steel industry in future with appropriate technology. Present work takes a critical look into an innovative method for utilization of Red Mud-an industrial waste. The Thermal Plasma process has been developed for recovery of metal values from Red Mud as high value pig iron by optimizing process condition.

Optimised results shows that a basicity of 0.3 with a reduction time 25 minutes at plasma power 12.5 kW are optimized at which maximum recovery of pig iron to the extent of 70% can be achieved.

Acknowledgement

The authors are grateful to the Chairman-cum-Managing Director, NALCO, Bhubaneswar, Orissa, India for sponsoring the project work and Director, Institute of Minerals and Materials Technology (IMMT-CSIR), Bhubaneswar for kind permission for undertaking the work in the Laboratory.

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