International Journal of Minerals, Metallurgy and Materials
Volume 19, Number 8, Aug 2012, Page 679
DOI: 10.1007/s12613-012-0613-3

Production of pig iron from red mud waste fines using thermal plasma technology

K. Jayasankar[1)], *P.K. Ray*[1)], *A.K. Chaubey*[1)], *A. Padhi*[1)], *B.K. Satapathy*[2)], *and P.S. Mukherjee*[1)]

1) CSIR-Institute of Minerals & Materials Technology, Bhubaneswar, India
2) National Aluminum Company Ltd., Bhubaneswar, India

(Received: 2 July 2011; revised: 19 September 2011; accepted: 25 September 2011)

Abstract: Red mud, an insoluble residue produced during alkali leaching of bauxite, is considered as a low-grade iron ore containing 30% to 50% iron. The present paper deals with the use of thermal plasma technology for producing pig iron from red mud waste fines. The smelting reduction of red mud was carried out in a 35 kW DC extended arc thermal plasma reactor. Red mud was properly mixed with fluxes and graphite (fixed carbon, 99%) as a reductant as per stoichiometric requirement. The effect of various process parameters like a reductant, fluxes and smelting time on iron recovery was studied and optimized. An optimum condition for the maximum recovery of iron was obtained. A new thermal plasma process applicable to direct iron making from red mud waste fines that would achieve significant utilization of red mud was proposed.

Keywords: pig iron; waste utilization; red mud; smelting; dolomite; limestone; thermal plasma

1. Introduction

Bauxite is an ore with a high concentration of aluminium compounds which makes it a useful raw material for the extraction of aluminium. Bayer's process is the only process adopted worldwide for the production of aluminum. In this process, aluminium compounds in bauxite are first dissolved chemically, using caustic soda, in an alumina refinery. Red mud is an insoluble residue produced during alkali leaching of bauxite by Bayer's process. It is slurry containing natural substances originally present in bauxite, *i.e.*, the ore residues with a residual amount of alkali are left over from this process. Production of 1 t of alumina is accompanied by generation of about 1.0-1.5 t of red mud. No alternate economic method has yet come to treat bauxite for the production of aluminum, which does not generate red mud. Indian alumina plants have 1.692 million tons of annual capacity [1-2] with metal production of 6×10^5 t per year and generate about 2×10^6 t of red mud every year. It is estimated that nearly 9×10^7 t of red mud is produced annually worldwide, and presently in India, nearly 3×10^6 t of red mud is generated [3]. Alumina producers are facing a serious problem in the disposal of red mud because of the expenses involved in the transportation and pollution abatement. A typical composition of red mud is 30%-50% Fe_2O_3 and remaining Al_2O_3 and SiO_2. It also contains trace amounts of metallic elements such as vanadium, galena, chromium, magnesium and zirconium. Its major mineral constituents include haematite, goethite, anatase, rutile, quartz and sodalite. Clearly, red mud is a potential source of many valuable metals.

In the past, efforts to use red mud in the cement industry for the manufacture of tiles have been successful, but such applications can utilize only a small amount of red mud produced. Over the years, efforts have been made to develop processes for metallurgical as well as non-metallurgical applications of red mud [3-4]. Till date, red mud has found limited commercial utilization in road making, land reclamation and also used as a constituent in making Portland cement. Development of suitable metallurgical processes for metal recovery from red mud is important for bulk utilization, value addition and moving towards zero waste. Two main approaches which have been generally investigated to

---

Corresponding author: K. Jayasankar E-mail: jayasankar_met@yahoo.co.in

© University of Science and Technology Beijing and Springer-Verlag Berlin Heidelberg 2012

recover iron values from red mud are based on: (a) solid-state reduction of red mud followed by magnetic separation to recover iron, and (b) smelting in a blast/electric/low shaft furnace to produce pig iron. Several processes exist to recover metals from red mud, but it is believed that none of these are in commercial operation [5-6]. A new construction material from red mud has been developed by using hardening process [7]. Thermal plasma technology is now an established alternative to be considered for improving the existing metallurgical processes. In the thermal plasma process, high density of ionic charges makes uniform heat transfer to the charge material. The availability of very high temperature, high energy fluxes, and plasma state conditions in the plasma arc allows the reactions to be completed in short duration. They have the advantage of allowing the direct use of fine feed materials [8].

This research article is aimed at utilization of red mud waste fines to recover iron values by using thermal plasma technology. In this paper, we report the use of a 35 kW DC transferred arc thermal plasma reactor, designed and developed at the author's institute, IMMT, Bhubaneswar, India, for making pig iron from red mud. The paper describes in detail the optimization of various process parameters and charge material parameters for pig iron production from red mud waste fines.

2. Materials and methods

Red mud was supplied by NALCO India Ltd. The chemical analysis and size-sieve analysis of red mud are given in Table 1 and Table 2.

Table 1. Chemical analysis results of red mud wt%

Fe_2O_3	Al_2O_3	SiO_2	Na_2O	CaO	TiO_2	Loss of ignition
47.49	21.07	5.72	3.78	1.36	4.86	13.49

Table 2. Size-sieve analysis results of red mud

Size fraction / μm	Percentage / %
−100 +45	25.4
−45 + 38	4.1
−38 + 20	10.8
−20 + 10	17.9
−10	41.8
Total	100.00

Red mud fines were smelted in an extended transferred arc plasma reactor. A brief description of the reactor is as follows.

2.1. Extended transferred arc plasma reactor

Smelting studies were carried out in a 35 kW DC extended transferred arc plasma reactor as shown in Fig. 1. It is a pot type reactor with a zircon coated graphite crucible as the furnace hearth which is thermally insulated by bubble alumina. Graphite electrodes are arranged in a vertical configuration. The bottom electrode (anode) is kept stationary, and the top one (cathode) with an axial hole for passing plasma forming gas is actuated by a rack and pinion mechanism for arc stabilisation. The hearth is provided with a graphite spout to tap both metal and slag. The detailed design specifications of the reactor are available elsewhere [9].

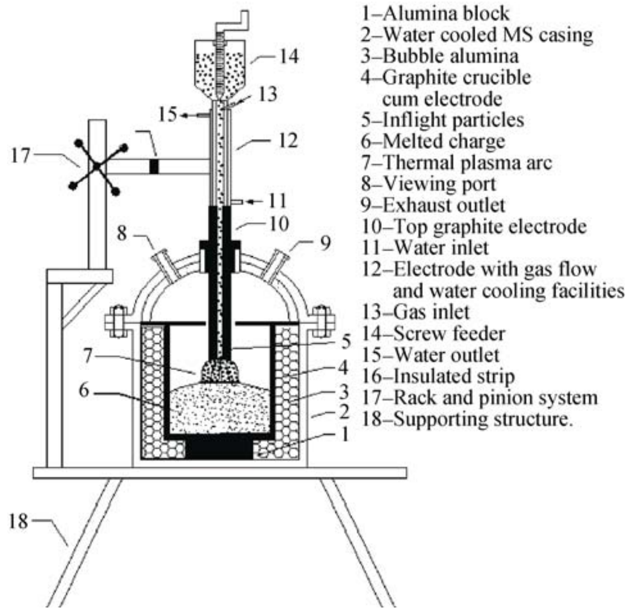


Fig. 1. Schematic diagram of an in-flight DC extended arc plasma reactor.

2.2. Plasma smelting of red mud

Plasma smelting of red mud was carried out in an extended arc plasma reactor. The process of smelting was done by a DC extended arc plasma furnace using graphite powders as a reductant at a constant power of 12.5 kW (current supplied: 250 A; and voltage maintained: 50-60 V). The effect of different parameters, namely, types of fluxes to maintain basicity, reductant (graphite) variation and time, was studied so as to have an optimized set of parameters for production at the cheapest cost. Fluxes like limestone, dolomite, quartz, magnesia, fluorspar, and calcium carbonate were used. Before plasma treatment, all were brought to the same sieve size and uniformly mixed by dry ball milling. Pre-heating was done for 2-3 min to maintain the thermal atmosphere and remove the residual moisture. Then the material was charged with a continuous flow of plasma gas at 1 L/min. For a small scale of raw sample, a 350 g graphite was taken as per stoichiometric calculation and the flux was taken so as to maintain the required basicity (basicity=CaO+MgO/SiO_2+Al_2O_3). The metal and slag were not clearly separated in all cases and chemical analysis was done.

A number of experiments were carried out in the extended transferred arc plasma reactor to study the factors influencing the percentage of recovery of metal from red mud. In reduction test the percentage of recovery of metal in reduction state is defined as below.

The amount of metal iron obtained from the lump is

Metal recovery = weight of iron extracted/weight of iron in red mud fines (raw material)×100%.

3. Results and discussion

CO is a good reducing agent and most stable at above 1000°C. In the plasma furnace, CO reacts with Fe_2O_3. The probable chemical reactions occurring during Fe_2O_3 reduction are the following:

$$Fe_2O_3+CO \rightarrow Fe_3O_4+CO_2 \tag{1}$$

$$Fe_3O_4+CO \rightarrow FeO+CO_2 \tag{2}$$

$$FeO+CO \rightarrow Fe+CO_2 \tag{3}$$

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

$$FeO+C \rightarrow Fe+CO \tag{4}$$

All the equations except (4) are exothermic.

3.1. Physicochemical characterization of raw material

Red mud mainly contains oxides of Fe, Al, Si, Na, Ti and minor amounts of S and P. The typical chemical composition of red mud received is 55.2wt% Fe_2O_3, 16.5wt% Al_2O_3, 6.3wt% SiO_2, 3.1wt% Na_2O, 1.4wt% CaO, 4.5wt% TiO_2, 0.1wt% S, and 0.08wt% P. The loss of ignition is 12.5%. The X-ray diffraction (XRD) analysis is shown in Fig. 2.

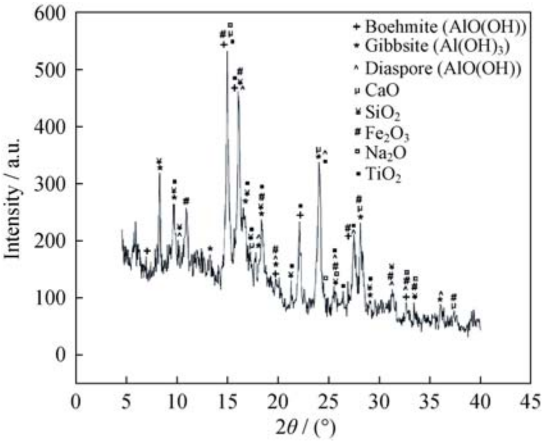


Fig. 2. XRD pattern of an as-received red mud sample.

Fig. 2 shows phases like hematite (Fe_2O_3), anatase (TiO_2), quartz (SiO_2) and different hydrates of Al_2O_3 such as boehmite (AlO(OH)), gibbsite ($Al(OH)_3$) and diaspore (AlO(OH)). Usually ferrohydrite shows a low crystalline character [10], but XRD studies show well-defined peaks corresponding to hematite. The formation of hematite, anatase quartz and gibbsite is very stable from E_h-pH diagram [11-12].

3.2. Effect of smelting time

The charge materials are consisted of red mud, graphite and fluxes at a proportion of 100:11:10 and were smelted in an extended arc plasma furnace, and the smelting time varied between 13 and 17 min for 350 g batch. It can be seen from Fig. 3 that there is a non-linear relationship between each parameter of iron recovery and smelting time, with each parameter of iron recovery achieving peak when the smelting time is about 15 min.

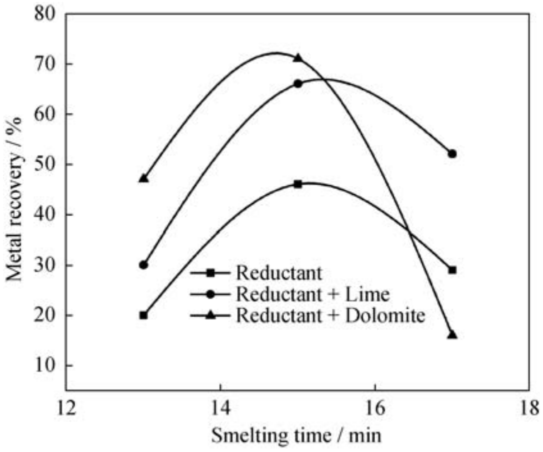


Fig. 3. Effect of smelting time on iron recovery.

It was inferred that the optimum smelting time was about 15 min, during which the reduction reaction of ferrous oxides was stopped as the percentage of iron recovery was not 100% but rather 70%.

3.3. Effect of the reductant

In order to investigate the optimum content of the reductant, different percentages of graphite to red mud were studied, respectively, and other experimental parameters were varied as follows: as shown in Fig. 4, these parameters of iron recovery rise with the increased addition of the reductant to red mud. When the percentage of the reductant to red mud is over 11%, the recovery of iron is decreased. The iron recovery attains a maximum of 45%, when no flux is added when the reductant is used.

3.4. Effect of the flux

The use of lime and dolomite results in significant metal

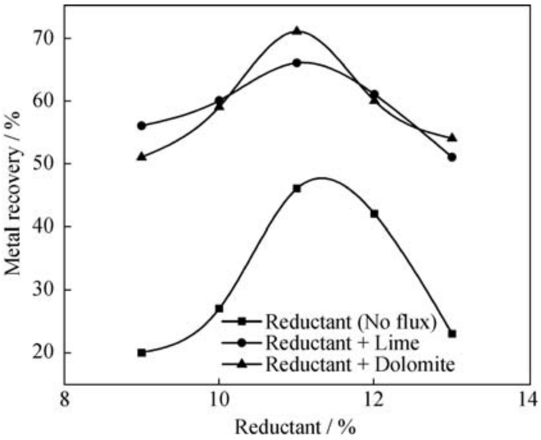


Fig. 4. Effect of the reductant on iron recovery.

recovery, with the maximum metal recovery being 70% at 11% dolomite. There is a sharp decline in the metal recovery when the percentage of the reductant is beyond 11%.

The effect of dolomite on metal recovery was studied. Dolomite was varied from 10% to 16% and the results are shown in Fig. 5. It is observed that an Fe metal recovery of 71% is achieved with 12% dolomite, beyond which the metal recovery is found to decrease. Similar results are seen in case of limestone where its amount is varied between 8% and 14%. It showed a maximum metal recovery of 65% at 10%. With other factors remaining unaltered, increasing dolomite beyond 10%, the metal recovery is found to decrease.

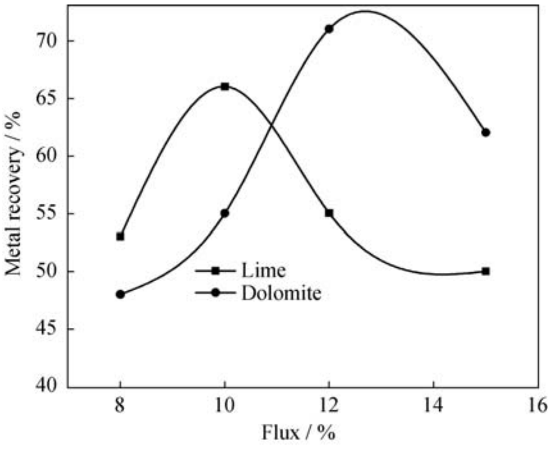


Fig. 5. Effect of fluxes on iron recovery.

The chemical analysis of pig iron and slag produced from red mud is given in Table 3 and Table 4, respectively.

It can be said that plasma smelting is an energy intensive process, which increases the cost of production. But in a plasma smelter, the temperature built-up in the plasma reaction zone is very high. Many oxides, which are not normally reducible by carbon or carbon monoxide in common reactors, are reducible in a plasma reactor. This may be an advantage or disadvantage depending on the product chemistry and microstructure desired. On a rough estimate, the energy conjunction for iron ore reduction in a plasma reactor is as follows: (1) for 350 g scale, the energy consumed is 8.92 kW·h/kg; (2) for 1 kg scale, the energy consumed 5.2 is kW·h/kg.

Table 3. Chemical composition of pig iron wt%

Sample	Fe	C	S	P	Si	Mg
RM-54M	94.81	3.94	0.052	0.211	0.06	—
RM-72M	94.25	4.06	0.023	0.208	1.05	—
RM-97M	94.95	4.10	0.051	0.198	0.07	0.022

Table 4. Constituents of slag wt%

Sample	Fe	FeO	Al_2O_3	SiO_2	Na_2O	CaO	MgO
RM-97S	11.11	8.47	42.06	11.93	2.10	12.57	8.57
RM-54S	5.64	5.03	41.82	13.49	3.94	20.29	5.80
RM-72S	22.13	23.78	38.57	9.75	2.73	11.38	3.25

The alumina-rich slag was found to contain nearly 42% SiO_2, 11%-16% CaO, 10%-20% MgO, 3%-10% metallic iron and 5%-20% unreduced FeO. The XRD analysis of the slag showed the peaks of different compounds as said above.

Apart from the proportion of the reductant (*i.e.* graphite powders) in the charge, the effects of the duration of smelting and the basicity of slag were also evaluated. It may be noted from Fig. 3 that the percentage of recovery improved initially on extending the duration of the plasma smelting operation. But on prolonging the smelting operation, the recovery started dropping.

The effect of time upon metal recovery increases up to a certain level, and after that, it exhibits a reverse trend, *i.e.* the molten iron metal gets into the slag. The other two parameters like the reductant and flux behave in a similar manner, *i.e.*, the metal recovery increasing to a certain level and then falling off gradually. Thermal plasma smelting process has advantages upon other conventional smelting by having a shorter reaction time due to high temperature and heat transfer. Also it is feasible to handle red mud fines without any need of pelletization in case of thermal plasma [13].

3.5. Metallography

The microstructures of the sample were examined in an optical microscope at various magnifications. Most of the samples developed a completely white or mottled cast iron structure. This is to be expected because an external addition of ferrosilicon was not made. Silicon was picked up by way of the reduction of silica in red mud and the quartz added. However, silicon in the metal was inadequate to cause graphitization. Fig. 6(a) shows the microstructure of pig iron produced by smelting of red mud fines with graphite as a reductant and dolomite as a fluxing agent. The as-cast microstructure shows elongated graphitic flakes dispersed in the Fe matrix. Fig. 6(b) shows an interdendritic eutectic mixture of pearlite and cementite in the etched condition.

Most importantly, the titanium balance is not established through such chemical analysis data. In addition, part of the metallic iron could not be separated from the slag because of two reasons. First, the temperature of the small quantity of the metallic charge dropped rapidly on switching off the plasma. This made the slag quite viscous. Secondly the alumina-rich slag itself is viscous in character. The high viscosity of the slag rendered clean slag-metal separation quite difficult. Nevertheless, data presented in Fig. 4 show a clear trend. Initially on increasing the proportion of the reductant, the percentage recovery of iron oxide increases. On further increase of the proportion of the reductant, the iron oxide recovery falls. This trend has been repeatedly observed. The reasons are not clear from the mass balance and chemical analysis data. Hence, further evaluation of the metal and slag characteristics in the SEM-EDS system was considered necessary.

These EDS analysis data (Fig. 7) clearly indicate that the distribution of different elements in 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.

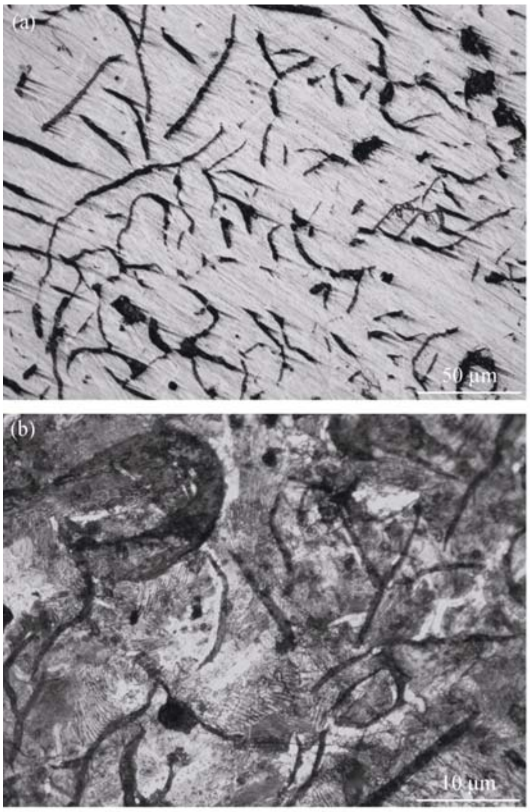
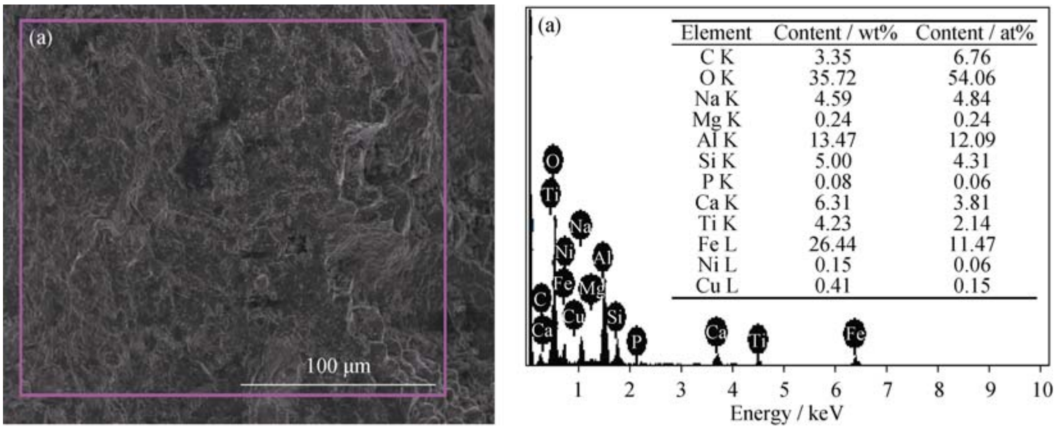


Fig. 6. Typical microstructures of pig iron showing (a) graphite flakes (unetched condition) and (b) eutectic mixture of pearlite and cementite (etched condition).



Element	Content / wt%	Content / at%
C K	3.35	6.76
O K	35.72	54.06
Na K	4.59	4.84
Mg K	0.24	0.24
Al K	13.47	12.09
Si K	5.00	4.31
P K	0.08	0.06
Ca K	6.31	3.81
Ti K	4.23	2.14
Fe L	26.44	11.47
Ni L	0.15	0.06
Cu L	0.41	0.15

Fig. 7. FESEM image (a) and EDS average analysis (b) of a bunch of slag particles.

4. Conclusions

The paper presents an innovative method for the utilization of red mud waste fines. The significant conclusions from the present study are as follows: (1) pig iron was successfully produced by thermal plasma technology from red mud waste fines in one step; (2) the maximum recovery of iron was found to be 71% corresponding to the optimum dolomite of 12% and optimum smelting time of about 15 min for 350 g batch.

Acknowledgements

The authors would like to thank the Director, CSIR-IMMT, Bhubaneswar for giving permission to publish this work and M/S NALCO, India, for their financial support.

References

[1] H.K. Chandwani, V. Vishwanathan, R.N. Goyal, and P.M. Prasad, Recovery of iron and metal values from red mud possibilities in Indian scenario, *NML Tech. J.*, 39(1997), No.3, p.117.

[2] R. Kumar, J.P. Srivastava, and Premchand, Utilisation of iron values of red mud for metallurgical applications, *Environ. Waste Manage.*, 30(1998), p.108.

[3] A. Agrawal, K.K. Sahu, and B.D. Pandey, Solid waste management in non-ferrous industries in India, *Resour. Conserv. Recycl.*, 42(2004), p.99.

[4] M. Andrejcak and G. Soucy, Patent review of red mud treatment-product of Bayer process, *Acta Metall. Slovaca*, 10(2004), No.4, p.347.

[5] E. Erçağ and R. Apak, Furnace smelting and extractive metallurgy of red mud: recovery of TiO_2, Al_2O_3 and pig iron, *J. Chem. Technol. Biotechnol.*, 70(1997), p.241.

[6] S. Kumar, R. Kumar, and A. Bandopadhyay, Innovative methodologies for the utilization of wastes from metallurgical and allied industries, *Resour. Conserv. Recycl.*, 48(2006), p.301.

[7] V.A. Mymrin and A.J. Vazquez-Vaamande, Red mud of aluminum production waste as basic component of new construction materials, *Waste Manage. Res.*, 19(2001), p.465.

[8] K. Jayasankar, S. Mohapatra, S.K. Routray, J.L. Gumaste, and P.S. Mukherjee, Thermal plasma processing for the production of pig iron from various sources, *High Temp. Mater. Process.*, 28(2009), p.1.

[9] R.K. Galgali, H.S. Ray, and A.K. Chakrabarti, A study on carbothermic reduction of ilmenite ore in a plasma reactor, *Metall. Mater. Trans. B*, 29(1998), No.6, p.1175.

[10] U. Schwertmann and R.M. Cornell, *Iron Oxides in the Laboratory: Preparation and Characterization*, 2nd ed, Wiley VCH, New York, 1991.

[11] T. Das, M.K. Ghosh, and G.R. Chaudury, Assessment of the significant parameters influencing the bio-oxidation and bio-precipitation of the iron from industrial leach liquor, *Trans. Inst. Min. Metall. Sect. C*, 114(2005), p.57.

[12] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, National Association of Corrosion Engineers, Pergamon Press, Oxford, 1974.

[13] S.S. Rath, K. Jayasankar, B.K. Satapathy, B.K. Mishra, and P.S. Mukherjee, Kinetics and statistical behaviour of iron recovery from red mud using plasma arc furnace, *High Temp. Mater. Process.*, 30(2011), p.211.