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RECOVERY OF TITANIUM OXIDE FROM UNDIGESTED SAND OF AN INDIAN ALUMINA REFINERY AND PREPARATION OF VALUE ADDED TITANIUM CARBIDE

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Abstract

During the process of alumina production through Bayer's process, around 60% of unwanted gangue is rejected as 'undigested sand' and 'Red Mud'. This industrial waste material poses environmental and disposal problems. Aluminum oxide constitutes only 38 to 60% of bauxite ore. The rest is made up of Fe_2O_3, SiO_2, TiO_2 and some other metallic oxides. After dissolution of alumina in caustic soda, these impurities remain in suspended form which is separated out as undigested sand and subsequently as red mud. Out of these metal oxides, around 8 to 25% of titanium oxide is lost in to this waste. Titanium oxide, present as rutile and ilmenite in the undigested sand, was processed through Wilfley table. A concentrate containing 38% TiO_2 with 47.30% recovery was obtained. This concentrate was subjected to smelting with activated carbon in an extended arc plasma reactor. Titanium carbide was formed as a fused mass within 5 minutes.

Introduction

Around 3 MT of bauxite ore is processed in the alumina refinery employing the time tested Bayer's process, to produce approximately 1 MT of alumina. During the process of alumina production about 60% of unwanted gangue is rejected as 'undigested sand' and 'Red Mud'. Out of total quantity of **200-300** Million tonne per year (Mtpy) of red mud generated in the world, India accounts for about 2Mtpy. This industrial waste material poses tremendous environmental and disposal problems. With the anticipated expansion of alumina Industry in the country, Indian alumina plants have to very soon dispose off over 6 Mt of this red mud every year.

Aluminium oxide from which aluminium metal is extracted, constitutes only 38 to 60% of bauxite ore. The rest is made up of Fe_2O_3, SiO_2, TiO_2 and several other metallic oxides. After dissolution of alumina in caustic soda, these impurities remain in suspended form which is separated out after being washed and then pumped as slurry to the nearby Red Mud pond. During Bayer's process, all alumina content present in bauxite is not recovered and appreciable quantity of alumina goes into the red mud along with other valuable metals. Though some studies have been undertaken by other researchers to recover metal values from red mud, they are not considered economically viable. However, the undigested sand that constitutes around 20% of the refinery rejects is reported to contain between 8-25% TiO_2 and some other metal values which may be recovered in view of their scarcity and significance and processed for value addition. Rao et al [1] have reported the characteristics of undigested sand rejects from the Nalco refinery, Damanjodi, Odisha, India. Limited attempts have been made by the researchers on the characterisation of red mud sludge from this refinery [2-5].

This paper describes the detailed beneficiation technique adopted to recover Titanium value from undigested sand and discusses the processing of Titanium oxide pre-concentrate to smelting in an extended arc plasma reactor for production of value added Titanium carbide.

Materials and Methods

Representative undigested sand sample was collected from an Indian alumina refinery. For processing of undigested sand, around 5 kg (unclassified) of the material was directly treated on the Wilfley Table at different angles. The effect of particle size, classification, wash water, deck length etc. on the Wilfley table was studied during the table operation. Another 10 kg of the same sample was further classified at 100 microns. The operational conditions for tabling of +100 micron fraction were same as the unclassified sample. The operating parameters for tabling of -100 microns fraction on slime table were 10mm stroke length, 1-degree angle and 4 liters per minute of wash water.

Mineralogical analysis was undertaken by Philips XRD and Leitz optical microscope. The micro-chemical composition of feed and processed product was determined by Jeol make Electron Probe Micro Analyser [EPMA, JXA-8100].

The beneficiated Ti-rich concentrate was subjected to plasma smelting with appropriate amount of activated carbon. Before plasma treatment, the concentrate was finely ground and mixed with activated carbon thoroughly for better interaction. Finally, the mixture was pelletized using Poly Vinyl Alcohol as the binder and dried. The plasma treatment was taken up in an indigenously designed 50 kW DC pot type extended arc thermal plasma reactor. The plasma reactor essentially consists of: (i) a top graphite electrode through which the argon gas is introduced to the reactor through the axial holes in the top electrode (ii) a graphite crucible, which forms the bottom electrode.

Results and Discussion

Mineralogy

Megascopically, the undigested sand sample is black to brick red in colour. In view of its appearance like sand sized grains, the sample is termed as undigested sand or plant sand. The constituents of undigested sand are alumina, iron and Ti-rich phases. The mineralogical study of undigested sand sample revealed the presence of 14 volume % of Ti-phase. X-Ray diffraction analysis indicated the undigested sand sample to be composed predominantly of hematite, rutile, goethite (Fig. 1). Hematite and goethite are distributed in all size ranges. Other minor minerals recognized under reflected light microscope and scanning electron microscopes are ilmenite and zircon along with rare sillimanite, mica, goethite and kaolinite booklets. Rutile appears either needle like or platy while ilmenite exhibits a sub-hedral form. Both these crystals exhibit twinning and generally occur in free independent state.

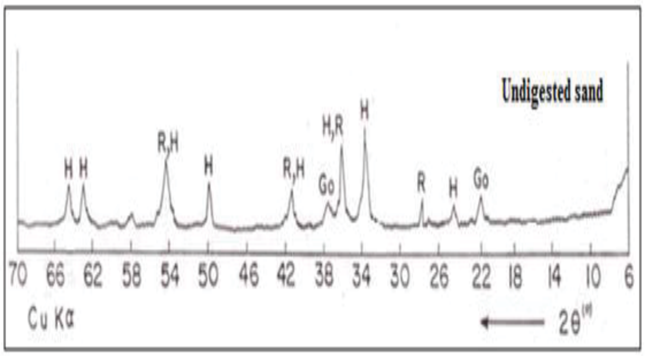

Fig.1: X-ray diffraction patterns of bulk undigested sand [Go: Goethite; H: Hematite; R: Rutile]

Predominance of rutile in -300+100miron size fraction is evident from XRD pattern. As ilmenite in the sample is present in minor amount, no reflection peak appears in XRD pattern. However, presence of both these phases is clearly indicated from their compositional map (Fig.2).

Physical Beneficiation

The bulk feed sample when processed through a Table, a product containing 38.87% TiO_2 with 47.23% recovery was obtained at a deck angle of 3 degrees. Since the sample contains very less amount of finer particles, it was possible to get a good grade material at a deck angle of 1.5 degrees, wash water rate of 2.5 to 3 liters per minute and a stroke length of 10 mm. Table 1 shows the typical result obtained by beneficiating the undigested sand sample using Wilfley table.

Table 1: Tabling studies results (in %) of undigested sand (Deck angle 1.5 degree, % solid 10, wash water 2.5 ltr/min.)

Details	Wt %	TiO_2 %	Fe_2O_3 %	Al_2O_3 %	SiO_2 %	% of TiO_2 Recovery
Heavies	12.54	38.87	56.98	2.45	0.99	47.23
Middling	42.90	8.11	74.75	8.04	1.21	33.90
Tailing	44.56	4.30	71.42	11.93	2.85	18.80
Head	100	10.27	71.04	9.07	1.91	-

In case of classified -100 micron fractions [18.46 wt%] a high weight percent of rougher concentrate was collected followed by cleaning the same to obtain a cleaner concentrate assaying 37.30% TiO_2 having 53.96% Fe_2O_3 with a recovery of 25.79% weight percent. However, in case of +100 micron fractions [81.54 wt%] a concentrate analyzing 41.75% TiO_2 and 53.70% Fe_2O_3 in 29.68% weight recovery was obtained (Table-2). This operation removed not only the associated iron mineral but also the coating of alumina on the surfaces of the intermediates and fines. Overall performance in this route is much superior to that of any other conventional beneficiation techniques.

Table 2: Tabling studies of size classified results (in %) of undigested sand

Size, in µ	Wt %	Details	Wt% w. r. t feed	TiO_2 %	Fe_2O_3 %	Al_2O_3 %	SiO_2 %	% of TiO_2 Recovery
+100	81.54	Heavies	7.30	41.75	53.70	3.28	2.49	29.68
		Middling1	1.50	20.88	69.84	7.52	0.60	3.05
		Middling2	21.00	12.53	71.84	6.91	1.32	22.00
		Lights	51.74	4.18	67.66	17.10	29.00	18.10
-100	18.46	Heavies	7.10	37.30	53.96	3.10	0.94	25.79
		Middling1	2.30	20.63	69.01	5.38	2.16	4.62
		Middling2	6.40	8.27	78.08	8.47	1.66	4.44
		Lights	2.66	5.16	74.02	10.20	1.60	1.20

A high weight percent of rough concentrate was obtained by increasing the deck angle. No significant improvement with respect to titania grade was achieved by cleaning the rougher concentrate and tailings. Similarly, increasing the collection length marked no improvement. Table 3 shows the summary of grade and TiO_2% recovery of Tabling study.

Table 3: Summary of the tabling studies on TiO_2 recovery

		Weight%	Grade%	Recovery %
As received sample		12.48	38.87	47.23
Two step	01	14.40	39.55	55.47
Classification technique	02	18.20	35.62	63.13

The light fraction (tailings) is mostly enriched in hematite, goethite and quartz. The magnitude of XRD peak diagnostic of rutile increases in heavy fraction (concentrate) as compared to the bulk feed sample (Fig.3). The unrecovered Ti values (4 to 5%) in the tailings was due to the presence of some minute ilmenite flakes and rutile needles which got escaped during tabling operation eventually due to their typical morphology.

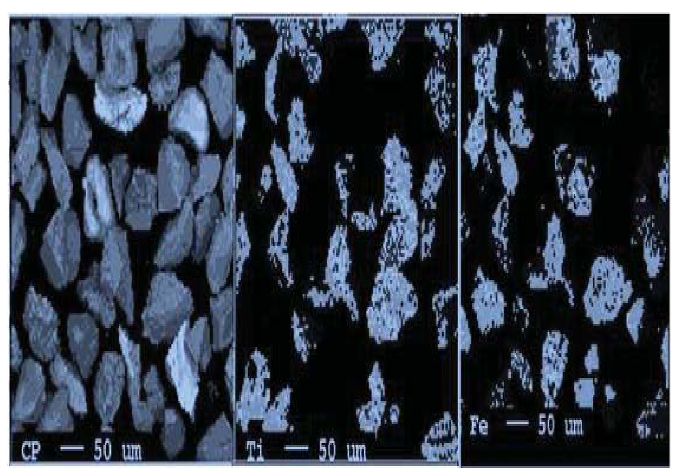

Fig.2: Compositional map of beneficiated plant sand showing Ti-rich minerals

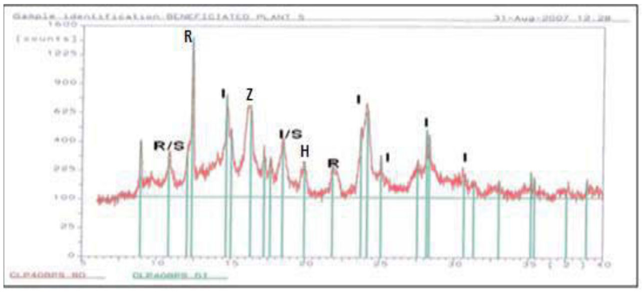

Fig. 3: XRD pattern of Beneficiated Plant Sand
[R: Rutile; S: Silimanite; I: Ilmenite; Z: Zircon; H: Hematite]

Titanium Carbide Preparation

The oven dried Ti-rich pellets were directly charged into graphite hearth of the extended hearth plasma reactor. The plasma processed product was obtained in the form of fused mass and some powder. The polished surface of fused mass show small grains of Ti-C distributed within a homogenous Fe-rich matrix. Theses grains are generally globular in shape, vary in size between 5 and 30 microns, pink in colour and show relatively high relief. X-ray diffraction pattern (Fig.4) and compositional maps (Fig.5) confirm both titanium and Fe-rich phase.

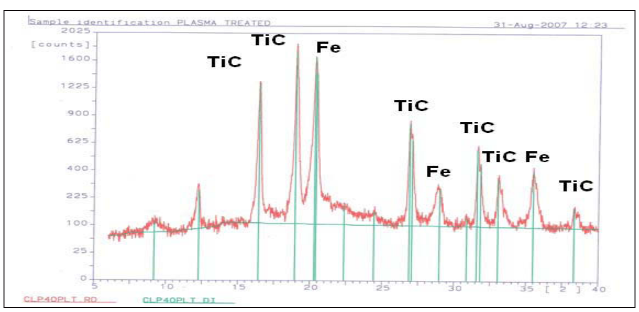

Fig. 4: XRD pattern of Plasma Processed Sample
[TiC: Titanium Carbide; Fe: Iron]

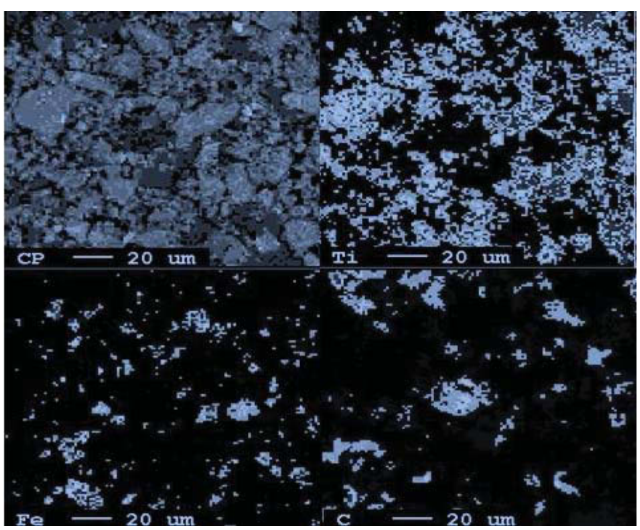

Fig.5: Compositional map of plasma processed sample showing Ti, Fe and C.

The fused mass was ground in the HERZOG Swing Mill Grinder HSM 100 for 5 minutes. The fine powder was then subjected to acid leaching to liberate TiC. The acid leaching has been found effective in removing the Fe from TiC as seen in its XRD pattern (Fig.6) and compositional map (Fig.7). However, the additional carbon shown in XRD can be removed through heavy media separation. The TiC thus produced from undigested sand matches well with the XRD pattern of commercial product.

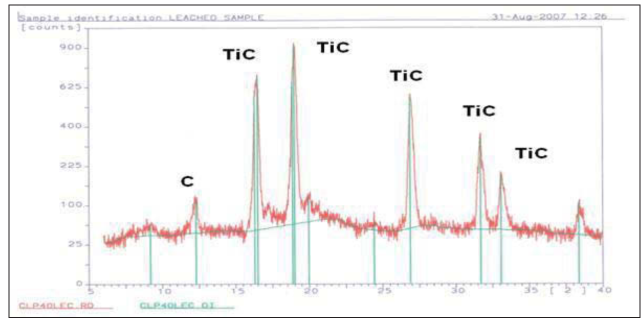

Fig.6: XRD pattern of Acid Leached Sample
[TiC: Titanium Carbide; C: carbon]

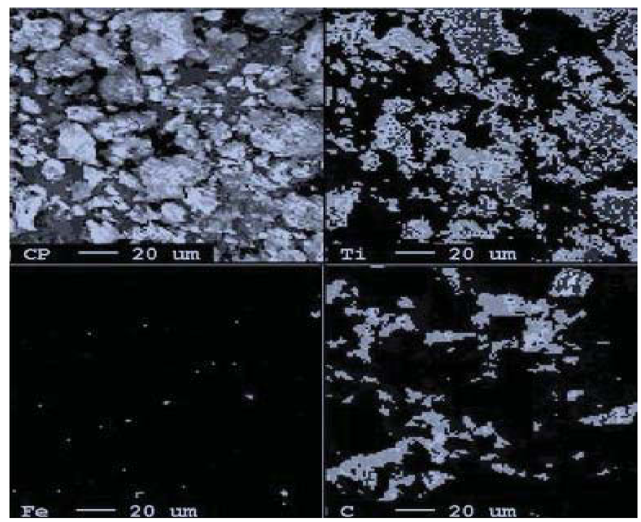

Fig.7: Compositional map of acid leach sample showing Ti, Fe and C.

Conclusions

The undigested sand from an alumina refinery plant contains significant titanium oxide (TiO_2:10%) value, contributed by rutile and ilmenite. The mineral responsible for this significant value do appear in free and independent state. Studies were carried out by gravity separation technique (using Wiffly Table) to recover the Titanium oxide mineral. A concentrate containing 38.87% of TiO_2 with 47.23% recovery was obtained. However, the grade improves in coarser fraction when the bulk sample is classified. The titanium rich concentrate, so obtained through beneficiation, was subjected to plasma smelting with appropriate amount of activated carbon so as to convert it into a fuse mass of Fe- rich titanium carbide (Fe-TiC). Pure TIC was obtained by grinding the mass followed by acid leaching, which matches well with the commercial product.

Acknowledgement

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