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RECOVERY OF METAL VALUES FROM RED MUD

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Abstract

In processing bauxite for production of alumina by the conventional Bayer process, huge quantities of so called red mud are generated which are disposed of as a waste product. The red mud is normally contains caustic soda and therefore poses pollution hazardous and requires storage in specially made large size ponds. This waste material at present does not find any use, hence, in addition to the pollution hazard, considerable expenditure and wastage of land is involved in disposal of this waste material. Therefore, in view of the increasing problem of waste disposal, it is desirable to recover the oxides of iron, titanium and aluminum from red mud.

The process applies to the recovery of alumina, titania and ferric oxide from red mud which comprises the following steps (i) Roasting of red mud in presence of alkali (ii) Extracting the salts produced in step (i), (iii) Precipitation of hydroxide salt and (iv) Converting the hydroxide salt into oxides. Balco's red mud contains 45-47% Fe_2O_3, 18-20% TiO_2 and 16-25% of undigested alumina .Many methods have been tried by others to recover the metal values and it is proposed in the laboratory on bench scale. The present papers provide an alternative and more environmentally acceptable process for the recovery of iron, titanium and aluminum from Balco's red mud.

Introduction

To produce every ton of the aluminum metal 5 to 5.5 tonnes of bauxite ore has to be treated by the well known Bayer process. On digestion with caustic soda, bauxite leaves behind about 50% of its own weight of an insoluble residue known as Red Mud. Disposal of such huge quantities of this solid waste by their impoundment in mud lakes causes problems of increasing land cost, storage and pollution. The application of any red mud depends on its Physico-chemical properties. The red mud is highly complex material containing largely the following six oxides namely ferric oxide, Aluminum oxide, Titanium dioxides, Silica, Sodium Oxide and Calcium Oxide in varying quantities besides minor amount of traces of other elements as oxides.

Furthermore, it is alkaline, fine sized and poor in settling. Dumping of red mud is certainly an environmentally unfriendly activity. However the solid waste, red mud is a store house of wealth because it contains the metal values of Iron, Aluminum and Titanium. Perhaps the best way would be to convert this waste into the corresponding metal values. However, there is a very strong argument against this in the countries with large availability of Iron ores, Titanium ores and Aluminum ores. However, the time is not very far off when depletion of mineral resources will make it viable to convert these wastes into useful products. The growing awareness of environmental pollution and concern for protecting ecological balance has created alternative ways of its utilization converting the waste into wealth. The successful use of red mud as a raw material source for metal production depends on the recovery of each metal value present in the particular red mud.

Besides the undissloved alumina, red mud contains the alkali insoluble oxides like Fe_2O_3 and TiO_2.The alkali aluminosilicate is formed due to the reaction between combined silica of bauxite with caustic soda. Various formulae have been proposed to represent this desilication compound. Bayer gave the formula for this desilication product as $Al_2O_3.Na_2O.3SiO_2.9H_2O$.Though the composition of these silicates has not been definitely ascertained, it is certain that it depends upon the content of the reactive silica and digestion conditions adopted.

It has been indicated earlier that the alumina is present as an alkali aluminosilicate with minor amounts of undissloved (diasporic) aluminium oxyhydroxide.

Experimental

The possible method for treating red mud for the recovery of metal values comprises of the following steps:

(i) Roasting the red mud with soda ash and lime
(ii) Extracting the fused mass
(iii) Digestion and precipitation of hydroxide salt
(iv) Conversion into appropriate oxide

The red mud sample of Bharat Aluminum Company Limited, Korba (India) was in the form of cakes having pale reddish color. This was easily friable and could be crushed with ease. The major constituents of red mud are analyzed by XRF (PW-2440 Philips, Netherland). The sample analyzed as follows as shown in Table 1:

Tablel: The Major Constituents of Red Mud

Constituents	Weight %
LOI	10.48
SiO_2	5.45
Fe_2O_3	37.33
TiO_2	18.88
Al_2O_3	18.38
Na_2O	5.89
CaO	2.71

XRD analysis was carried out using PANalytical X'Pert Cubix Pro Series diffractometer equipped with a copper target tube, X'celerator detector and operated at 40kV and 30mA.The dried sample were scanned within 2θ range from 10-70^0. Diffraction data were analyzed using PANalytical X'Pert High Score Plus Version 2.1.The main crystalline phase of red mud were Hematite (Fe_2O_3) ,Calcite ($CaCO_3$), Goethite (FeOOH), Gibbsite ($Al(OH)_3$), Boehmite (AlOOH), Cancrinite ($3NaAlSiO_4.NaOH$), Quartz(SiO_2), Anatse (TiO_2). The X-ray diffractogram of red mud is shown in Fig.1.

The method adopted for the recovery of Al_2O_3, TiO_2 and Fe_2O_3 from red mud is presented in Fig.2. The process for the recovery of metal values from red mud is briefly outlined below:

(i) Crushed red mud was thoroughly mixed with burnt lime and soda ash in the different weight ratios and then roasted at the desired temperature, ranging from 900-1100^{0}C.The roasted mass was crushed and extracted with hot water and filtered.

(ii) The Filtrate, sodium aluminate can be accommodated by recycling into the aluminate solution in the Bayer process.

(iii) The residue is light and can be treated for the recovery of Iron and Titanium. The residue is digested with concentrated sulfuric acid.

(iv) The digested slurry was dissolved in water and filtered. The residue containing high silica was separated.

(v) Titanium hydroxide was precipitated from the filtrate by hydrolysis. The Titanium hydroxide was filtered and calcined to get pure TiO_2.

(vi) The Filtrate was evaporated to obtain $FeSO_4$.

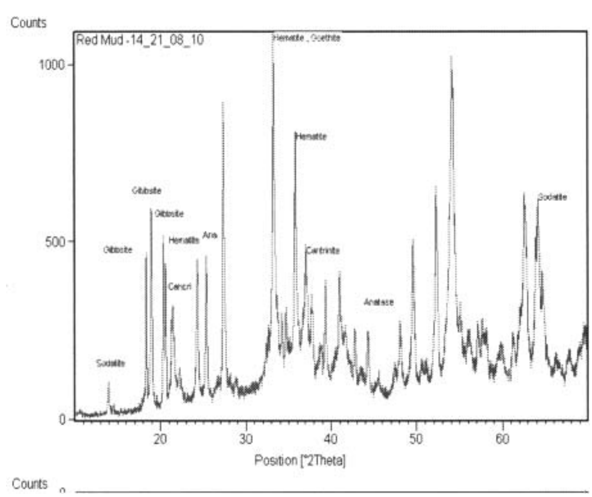


Fig.1. XRD Pattern of Balco's Red Mud

Results

In the roasting experiments burnt lime was used to immoblize the SiO_2 of the red mud. A burnt lime containing 85% of total CaO was used. The effect of the different variables on the recovery of Al_2O_3 was studied.

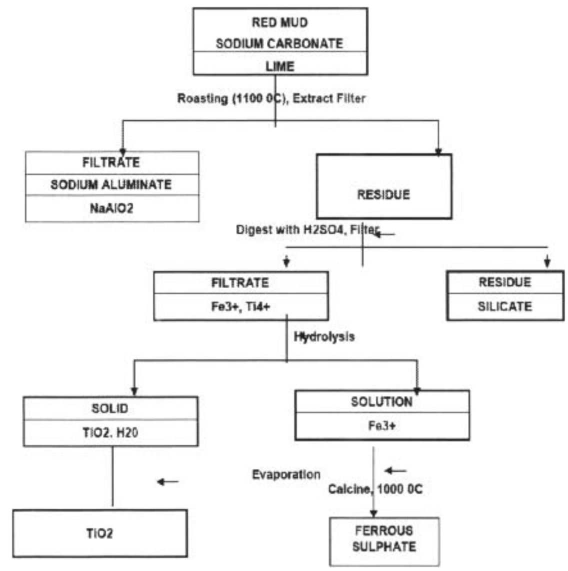


Fig. 2. Schematic diagram for recovery of metal values from Red Mud.

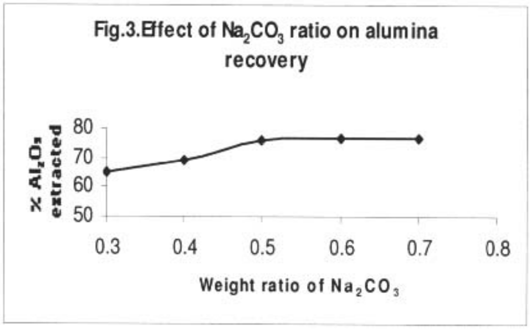
Effect of Soda ash on Alumina Recovery:

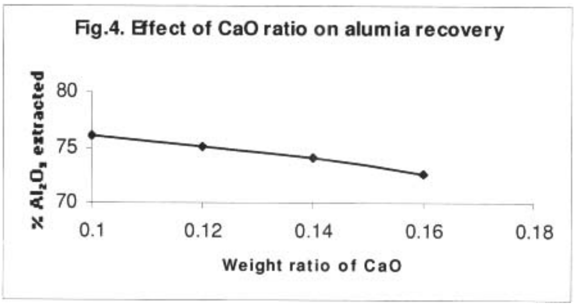
The red mud mixture containing burnt lime and soda ash was roasted at 1100^{0}C for 3 hours and subsequently leached. Lime was added to the mixture so that the mass contained $CaO:SiO_2$ in the molar ratio of 1.5:1.The Na_2CO_3 weight ratio was varied from 0.3 to 0.7 by the addition of varying quantities of soda ash and the alumina recoveries are indicated in Table 2 and Fig. 3.

It is observed that on addition of increased quantities of soda ash, the sinter becomes hard and has a tendency to absorb moisture thereby making dry grinding difficult and wet grinding has to be employed.

Table 2. Effect of varying sodium carbonate ratio

Weight Ratio (Mud:Na_2CO_3:CaO)	% Al_2O_3 Extracted	Sinter Characteristics
1:0.3:0.1	64.98	Easily extract
1:0.4:0.1	69.09	Easily extract
1:0.5:0.1	76.17	Slightly hard
1:0.6:0.1	76.32	Slightly hard
1:0.7:0.1	76.47	Slightly hard





From Table 2 and fig.3 it is observed that the alumina recovery increases from 64.98% to 76.17% as the Na_2CO_3 weight ratio increases from 0.3 to 0.5 and no appreciable increase is observed thereafter. This may be attributed to the side reactions taking place during the roasting operation itself, such as the formation of sodium ferrites and sodium titanate. The presence of Fe_2O_3 & TiO_2 affects the alumina recoveries. It was observed that use of Na_2CO_3 and red mud in the weight ratio of 1:0.5, 76.17% Al_2O_3 could be recovered and further roasting tests were carried out using this quantity and the effect of other variables.

Effect of CaO on alumina recovery:

Varying quantities of burnt lime were used for roasting red mud with sodium carbonate in the range of 1:0.5 and the alumina recoveries are indicated in Table 3 and Fig.4 were studied. It is observed from the Table 3 and Fig.4 that as the CaO content is increased, the alumina extraction is decreased and this can be attributed to the formation of a complex compound of lime and alumina.

Effect of temperature of roasting on recovery of alumina:

In order to determine the effect of roasting temperature mixtures containing red mud, sodium carbonate and burnt lime were heated in the weight ratio of 1:0.5:0.1 for 3 hours at temperature ranging from 900^0C to 1150^0C.

Table 3. Effect of varying lime quantity on alumina recovery

Weight Ratio Mud:Na_2CO_3:CaO (inclusive of lime in mud)	%Al_2O_3 extracted	% Mole ratio of SiO_2:Al_2O_3 dissolved in solution
1:0.5:0.10	76.03	1.08
1:0.5:0.12	75.12	0.97
1:0.5:0.14	74.05	0.89
1:0.5:0.16	72.66	0.83

Table 4. Effect of roasting temperature

Temperature of roasting,^{0}C	%Al_2O_3 Extracted	%Mole ratio of SiO_2:Al_2O_3 dissolved in solution
900	71.12	1.01
1000	74.34	1.09
1100	76.30	1.11
1150	78.09	1.23

It is observed in figure 6 that on increasing the roasting temperature from 1 hour to 3 hour, the Al_2O_3 recovery is increased from 70.25% to 75.95%. Further roasting for 4 hours and 5 hours decreases the Al_2O_3 recovery to 74.14%. A retention time of 2 to 3 hours is sufficient at this roasting temperature.

Discussion

When the red mud is roasted with sodium carbonate and lime, the alumina is converted into a sodium aluminate while silica is converted to an insoluble dicalcium silicate as follows:

$Na_2CO_3 + Al_2O_3 = 2\ NaAlO_2 + CO_2$

$SiO_2 + 2CaCO_3 = (CaO)\ 2SiO_2 + 2CO_2$

The soda besides reacting with Al_2O_3 reacts with $Fe_2O_3.TiO_2.SiO_2$ as follows:

$Na_2CO_3 + Fe_2O_3 = Na_2O.Fe_2O_3 + CO_2$

$Na_2CO_3 + TiO_2 = Na_2O.TiO_2 + CO_2$

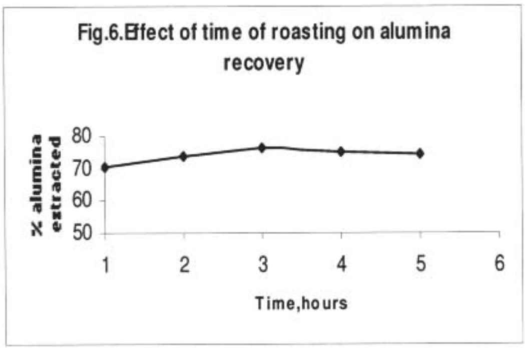
$Na_2CO_3 + SiO_2 = Na_2O.SiO_2 + CO_2$

During leaching, the sodium ferrite and part of the sodium titanate decompose to Fe_2O_3 and TiO_2.

$Na_2O.Fe_2O_3 + H_2O = 2NaOH + Fe_2O_3$

$Na_2O.TiO_2 + H_2O = 2NaOH + TiO_2$

The sodium silicate dissolves in water and thus enters the solution.



The residue resulting from the lime soda roasting process is very light, fine and can be treated for the recovery of Iron and titanium values.

The following observations were found on roasting of red mud with Na_2CO_3 and lime in the weight ratio of 1:0.5:0.1 at 1100^{0}C for 3 hours:

(i) The alumina extraction efficiency was 76%.
(ii) Recovery of Iron as Fe_2O_3 was 74.81%
(iii) Recovery of Titania as TiO_2 was 72.13%

Conclusion

It was observed that 76% of the Al_2O_3 could be extracted by roasting the red mud with Na_2CO_3 and CaO (weight ratio 1:0.5:0.1) at 1100^{0}C for 3 hours. About 0.8-1.1% mole ratio of SiO_2 dissolved simultaneously in solution. The aluminate liquor obtained is unsuitable for precipitation of desired grade of aluminium hydroxide. It will thus be necessary to adopt a separate desilication step. It is suggested that if this silica containing solution from the lime soda process is added, the resulting pregnant solution will contain low SiO_2 concentrations suitable for subsequent precipitation of aluminium hydroxide. The proposed method provides more environmentally acceptable process for the extraction of Aluminium oxide,Iron Sulphate and Titanium dioxide from red mud.

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