REDUCTION ON CAUSTIC CONSUMPTION IN ALUMINA REFINERY

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ABSTRACT

Bauxite is the principal ore for extracting alumina by Bayer Process. Bauxite contains hydroxides of aluminium and small amount of oxides of Iron and Titanium. Silicon is present as SiO_2, either in the form of Kaolinite or in the form of Quartzite. During the high pressure and high temperature digestion for extraction of alumina by Bayer Process, sodalite and cancrinite type of compounds are formed resulting in caustic loss, which needs regular replenishment. Various attempts have been resorted to minimize the caustic loss either by causticization of red mud or by adding lime during digestion. These operations are accompanied by innumerable operational problems. In order to overcome these difficulties, an attempt has been made to achieve low soda loss by adding the oxide of alkaline earth metal. In this paper, details of the experimental results conducted using Burnt Lime (CaO), Magnesite (MgO) and Dolomitic Lime, are discussed.

INTRODUCTION

Bauxite rich in trihydrate of Alumina and Monohydrate (Principally Boehmitic) are used in Alumina Refinery. Silica in the form of Kaolinite and quartzite are unavoidable impurities that accompany it. The Gibbsitic rich bauxite is refined at low temperature and low pressure (140 °C, 10 atm pressure). In this reaction, Zeolitic type compound is formed. Bauxite, which contains both gibbsite and Boehmite to a considerable extent, is treated with caustic at high temperature and pressure (240 °C, 35 atm) for viable extraction, the Kaolinite present in it reacts with caustic to form sodium silicate and sodium Aluminate. These compounds further react to form sodalities and cancrinite depending on the ions present in the liquor. To minimize the formation of these waste products, which eat away, the desilication is resorted prior to digestion. Bauxite is treated with caustic at 95 – 100 °C for nearly 8 hours during which sodium silicates and aluminates combine to form sodalities compound. It is precipitated out thereby preventing from further reaction and reducing the loss.

Some Plants resort to addition of burnt lime prior to digestion to a limited extent (1 – 2% of Bauxite charged). The lime added combines with silica present to form hydrogarnet type compounds (Calcium Aluminum Silicate), but accompanied by the inherent difficulties. The minor impurities like V_2O_5, P_2O_5, F, etc. also take part in the reaction forming respective sodium compounds which on reaching a particular level is removed from the system, as isomorphs in the presence of one another. On addition of lime the equilibrium is disturbed and the concentration of these ions build up in the liquor thereby affecting the purity of the alumina refined. Further, heavy hard cement like scales are formed and deposited on the heat exchangers reducing the heat transfer efficiency.

Causticization is another way of recovering caustic by treating the resultant red mud with lime and filtering off and washing the soda recovered. This needs high quality burnt lime for getting economically viable recovery of caustic. This is a separate unit operation necessitating huge investment. The Sodalite compound contains 4 mole of Na_2O of which three are in the form of sodium aluminum silicate and the fourth mole is adsorbed. This mole is easily removable in the reaction with lime, while for recovering the remaining moles large excess moles of lime is required more than the theoretical amount thus for every mole of Na_2O nearly 4 – 5 moles of lime (CaO) is required.

Various attempts have been resorted to minimize the caustic loss either by causticization of the red mud or by adding lime during digestion. These operations are accompanied by innumerable problems .In order to overcome the difficulties an attempt has been made to achieve low soda loss by adding the oxide of an alkaline earth metal.

EXPERIMENTAL

Bauxite Samples

The chemical analysis and XRD testing results of a four Bauxite samples for experiments are listed in **Table – I.**

Table – I : Chemical And Mineralogical Composition Of Bauxites

Parameters (%)	A	B	C	D
LOI	21.83	22.90	22.72	21.72
SiO_2	3.26	2.64	2.83	3.42
Fe_2O_3	21.22	19.10	19.42	20.87
TiO_2	8.98	8.89	8.92	8.41
Al_2O_3	44.25	45.67	45.09	44.75
Gibbsite	38.12	39.17	37.55	37.28
Boehmite	2.93	2.72	3.78	4.05
Diaspore	1.05	1.03	1.17	0.85
Kaolinite	3.43	4.29	4.03	5.37
Hematite	9.40	8.55	8.16	10.43
Goethite	10.98	10.95	11.66	10.61
Anatase	7.30	8.00	7.86	7.65
Rutile	1.20	0.90	1.02	0.88
Quartz	1.47	0.51	0.76	0.76
Alumogoethite	1.05	0.93	1.34	1.05

Additives Used

a. Burnt Lime (Active CaO – 70%)
b. Burnt Magnesite (MgO – 88%),
c. Dolomite lime (CaO – 52.12%, MgO - 37.35%)

DIGESTION EXPERIMENT PROCEDURE

All the digestion experiments were carried out in an Oil bath bomb autoclave (capacity 150 ml) with a temperature Controller. Four to six bombs digester can be used for every test. The pre-weighed bauxite and additives were mixed with appropriate amount of digestion liquor in the bombs. . Then the bombs were sealed and installed on a rotary frame. The oil bath digester was heated with thermostatically controlled heating mantle. Desilication of bauxite was carried out at 95 ^{0}C for 8 hours holding time and then digestion was done at 240 ^{0}C for 20 minutes. The digestion conditions are given in **Table – II.**

Table –II : Leaching Conditions

Desilication	Temperature	95 °C
	Time	8 hrs.
Digestion	Temperature	240 °C
	Time	20 mts.
Target Molar Ratio	1.55	

When the digestion was completed the bombs were taken out and chilled with water and immediately centrifuge to separate the red mud from the aluminate liquor. The absorbance of Supernatants was measured by Spectrophotometer. The decreases in liquor absorbance are shown in **Table – III.**

Table – III : Effect Of Additives On Liquor Colour

Additives	Additives Dosage (wt % of Bauxite)	% Decrease in Absorbance (At 690 nm)
Burnt Lime (As CaO)	1.0	5.09
	1.5	14.14
Magnesite	1.0	28.03
	1.5	45.67
Dolomitic Lime	2.0	20.34
	3.0	33.90

The solid residue was carefully washed with boiling water, filtered, dried and analyzed. The results of the experiments are shown in **Table - IV.**

Table – IV : Digestion Experiment Results Of Bauxite With Different Additives

S.N.	Bau-xite	Para-meters	Without Additive	Burnt Lime: 1% CaO of Bauxite	Burnt Lime: 1.5% CaO of Bauxite	Magnesite: 1% MgO of Bauxite	Magnesite: 1.5% MgO of Bauxite	Dolomitic Lime: 2% Dolomite (1.04% CaO & 0.75% MgO of Bauxite.)	Dolomitic Lime: 3% Dolomite (1.57% CaO & 1.12% MgO of Bauxite)
1	A	DE	85.41	86.02	86.94	85.83	85.94	86.04	86.81
		SSR	0.81	0.81	0.81	0.80	0.79	0.80	0.79
		BSL	78.99	78.74	78.53	73.16	72.05	76.63	75.42
2	B	DE	85.77	85.45	86.67	85.90	86.32	85.98	86.28
		SSR	0.80	0.80	0.80	0.78	0.77	0.79	0.78
		BSL	65.60	65.02	64.83	59.57	58.22	63.80	62.60
3	C	DE	85.01	85.52	86.52	85.39	85.62	85.54	85.93
		SSR	0.81	0.81	0.81	0.79	0.78	0.79	0.78
		BSL	74.62	73.82	73.55	68.12	66.63	72.44	70.73
4	D	DE	84.29	84.71	85.86	84.60	84.86	84.79	85.23
		SSR	0.80	0.80	0.80	0.79	0.78	0.79	0.78
		BSL	91.66	91.07	90.56	84.08	83.66	89.58	88.66

DE - Digestion Efficiency

SSR - Ratio of Bound Soda and SiO_2 in Mud,

BSL - Bound Soda Loss, Kg NaOH / T Al_2O_3

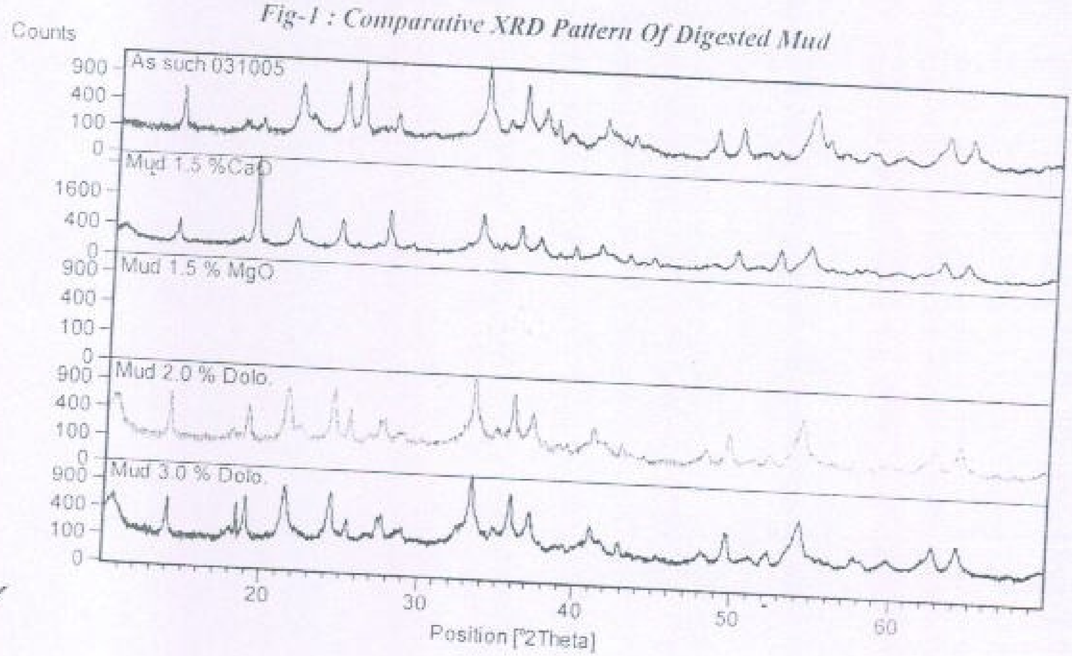
Discussion

The effect of various additives on alumina digestion efficiency of boehmitic bauxite is shown in **Table – IV.** The experimental results show that the additives such as burnt lime, magnesite and the dolomitic lime have catalytic effects and the burnt lime has more favourable effect on the digestion of boehmitic bauxite than the other additives. Increasing the amount of burnt lime, the alumina extraction efficiency is increased.

The calcite or dolomite affects the concentration of Vanadium, Fluorine, Phosphorus salts in the Bayer Liquor. The reaction of lime with phosphorus to form insoluble calcium phosphate and with fluorine in the system to form calcium apatites drastically reduces the phosphate content in the liquor. Reduction in phosphorus concentration results in the stabilization of vanadium salt in the liquor. In the catalytic digestion technology where lime is added as a catalyst to increase the productivity of the process, separation of vanadium salt from the liquor stream to maintain an optimum, desirable salt level becomes difficult.

It can be seen from Table – IV that the Na_2O / SiO_2 ratio in mud produced in digestion is reduced to some extent by adding MgO. One of the reasons obviously is that some amount of Na^+ is replaced by Mg^{++} in MgO due to Mg^{++} entering into the crystal lattice of Sodium Aluminium Silicate during the whole digestion process. In this sense MgO is advantageous to the reduction of caustic soda consumption in digestion process. The major Mg containing compounds in Red Mud produced in Bayer digestion process are $Mg(OH)_2$ and Magnesium Aluminium Silicate. The practice proved that the scaling containing Magnesium is loose and easy to be removed from the heating surface by chemical or mechanical methods. The comparative XRD patterns of the digested Mud obtained with different additives are shown in **Fig. 1.**

Fig-1 : Comparative XRD Pattern Of Digested Mud



From the **Table – III**, it can be seen that the decrease in liquor colour was higher in digested liquor resulted from MgO addition than the lime and dolomitic lime.

The experiment on solubility of magnesite is going on.

Conclusions

1. Ratio of Na_2O / SiO_2 in Red Mud after digestion can be reduced by MgO addition, which may be advantageous to decreasing caustic soda consumption.
2. Magnesite decreases the liquor colour.
3. The scale with MgO content can more easily be removed by chemical or Mechanical process.
4. The techno-economics shall be established before addition of Magnesite.

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