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Formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ Salts During Thermo Chemical Leaching for Extraction of Alumina from Red Mud by Lime Soda Ash Sinter Process

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ABSTRACT

Impurities like V_2O_5, SiO_2 and MnO_2 present in sodium aluminate liquor during thermo chemical leaching has a detrimental effect on the efficiency of alumina extraction from red mud. The objective of this study was to obtain information on the immobilisation of above impurities from red mud followed by formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts. During thermo chemical leaching alumina is extracted by sintering using Na_2CO_3 and Lime grit waste material of Alumina refinery plant. During extraction of alumina from Bauxite by Bayer's process, cationic impurities like Si, V, Mn of Bauxite and anionic impurities of liquor like chloride, sulphate and carbonate form Sodalite or Cancrinite resulting in soda and alumina loss (Sod or Can, ideal formula Na_8 $(Al_6Si_6O_{24})$ X_2. YH_2O; X^-=Cl^-, OH^-,1/2CO_3^{2-},1/2SO_4^{2-}, $Al(OH)_4^-$). In order to minimise the loss, a novel economic method was studied using lime soda sinter process. During sintering Sodalite or Cancrinite content of red mud form CaV_2O_6, $CaSiO_3$ and $CaMnO_3$, salts which enhance the alumina extraction. These impurities form CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts, which confirm the decomposition of Sodalite or Cancrinite by X-Ray Diffractometer (XRD) & Scanning Electron Microscope (SEM) and discarded with leached red mud. The effect of Na_2CO_3 and CaO additive, sintering temperature, time and leaching of alumina extraction study was carried out. Studies show that it was possible to extract alumina from red mud with maximum alumina extraction by immobilisation of impurities and formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts.

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Keywords: Red Mud, Thermo chemical leaching, Immobilisation, Sodalite, Cancrinite;

1 INTRODUCTION

Red mud is a by-product in the manufacture of alumina; it contains mainly iron oxide (54-65%) with significant amounts of silica, alumina, calcium oxide and titania, dispersed in a highly alkaline and caustic liquor (Ngygen et al.1998 and Alvarej et al., 1999). The treatment and disposal of bauxite residue is a major operation and may account for 30-50% of operations in an alumina refinery (Ngygen et al.1998). Red mud has been accumulated at the rate of 140 million tonnes annually throughout the world (Mohapatra et al., 2000). For a given aluminum production rate, the quantity of the red mud generated during the alumina extraction process varies significantly depending on the original properties of the bauxite and the operating conditions of the Bayer's process, and in particular, the process temperature (Li et al., 2001). As red mud contains a substantial amount of alumina, it is necessary to develop methods to extract this alumina as the important raw material for production of aluminium (Mohapatra et al., 2000). Several methods for extracting alumina as well as for recovery of other metal values from alumina-bearing materials have been studied (Mehrotra et al., 1979). The United States Bureau of Mines has been evaluating possible alternatives to the use of bauxite for several years. These include acid leaching processes and sintering processes applied to clays and anorthosites. Fly ash from burning regular coals has also been investigated extensively as a potential source for alumina. The processes studied for the extraction of alumina from fly ash include variations of existing sintering and leaching processes.

The present process involves immobilisation of sodium soluble impurities like SiO_2 V_2O_5 and MnO, by sintering of red mud using soda ash in presence of lime grit ($CaO+CaCO_3$) an intermediate waste material generated during processing of bauxite. The waste red mud, lime grit and soda ash mixture is sintered at temperatures above 900 ^oC –1100 ^oC to convert the alumina content to form solid sodium aluminate. SiO_2, V_2O_5 and MnO_2 in red mud react with calcium content of lime grit to form the relatively inert di-calcium oxy-anion insoluble salts in presence of soda ash. The sodium and the oxy-anion impurities present in red mud react with sodium carbonate to form the corresponding sodium salts.

$$Na_2CO_3 \rightarrow Na_2O+CO_2 \quad (1)$$
$$Al_2O_3 + Na_2O \rightarrow 2NaAlO_2 \quad (2)$$
$$SiO_2 + Na_2O \rightarrow Na_2SiO_3 \quad (3)$$
$$V_2O_5 + Na_2O \rightarrow 2NaVO_3 \quad (4)$$
$$2MnO + Na_2O \rightarrow 2NaMnO_2 \quad (5)$$
$$Fe_2O_3 + Na_2O \rightarrow 2NaFeO_2 \quad (6)$$

The ground-sintered products were then leached with an aqueous solution of sodium hydroxide. During leaching, sodium aluminate is dissolved in sodium hydroxide to form sodium aluminate, and the impurities like the oxy-anions (i.e.V_2O_5, MnO_2, SiO_2) are immobilized to form a complex insoluble oxides of calcium, which remains associated with the hydrolyzed mass of sodium ferrite and subsequently forms ferric oxide with a minimum sodium ion inclusion in the residual mass shown in the reaction mechanism Eqn-7.

$$NaAlO_2+NaVO_3+NaMnO_2+NaFeO_2+Na_2SiO_3+CaO+NaOH(aq) \rightarrow NaAlO_{2(aq)}+[Ca_2SiO_4+CaMnO_3+CaV_2O_6 + Fe_2O_3]_{(s)} \quad (7)$$

To achieve high alumina extraction, the decomposition of di-calcium silicate must be as low as possible. In practise the amount of silica recovered in the leaching step is too high as the Ca_2SiO_4 is not sufficiently stable under the leaching conditions (Hartsborn et al., 2000) and silica extraction of around 15-20% (Wanchao et al., 2009) occur during leaching, tying up sodium and aluminium with the formation of TCA, Hydro garnet and DSP.

There exists an opportunity for a process for treating red mud along with lime grit and soda ash by sintering to separate aluminium and sodium from sodalite (DSP), thus producing an adequately stable insoluble phase during leaching and therefore increasing the extraction vis-à-vis the yield.

These wastes were not investigated yet in any industrial process or used for material production as an additive. The aim of this study was to extract alumina from red mud with high extraction efficiency as well as formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts followed by impurity immobilisation. The treated leached red mud can be suitable for filling of land for vegetation and development of land for forestation.

2 EXPERIMENTAL DETAILS

The red mud and lime grits used in experimental studies were from National Aluminium Company limited, Damanjodi, Koraput. The Na_2CO_3 used in experimental studies was from Merck, Bombay. 100g of red mud, mixed with different ratios of sodium carbonate and lime grit grinded in a pulveriser, and then the mixtures were sintered at temperatures of 900, 1000, 1100 °C in a ceramic crucible in high temperature muffle furnace for 1 to 4 hrs. After sintering the sinter products were pulverised and leached with 80 gpl caustic at 105 ^{o}C for 1 hour using a 2.5 litre capacity Autoclave. The leached red mud was filtered after the leaching. The amount of Al_2O_3 in leach solutions was determined by using titrimetric method. The analysis of impurities like SiO_2, V_2O_5 and MnO_2 were carried out using UV-VIS Spectrophotometer and Atomic Absorption Spectrometer. The leached residues were analysed using X-Ray Fluorescence Spectroscopy (Model PW 2400) and the different phases were characterised by using X-Ray Diffraction (Dmax-2200, Rigaku, Japan). The formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts were studied by SEM (Model Leo Electron Microscopy, 430, United Kingdom).

3 RESULTS AND DISCUSSION

3.1 EFFECT OF Na_2CO_3 ADDITIVE

The extraction of alumina from sintered mud by leaching with 80 g/l of sodium hydroxide solution does not significantly change without addition of Na_2CO_3 in the sintered mass. The XRD of red mud and leached sintered red mud are shown in figure 1 and figure 2, respectively.

The extraction efficiency of alumina increases from the sinter red mud products with increasing lime grit, sintering temperature and time with fixed quantity of Na_2CO_3 as shown in the Tables 1 & 2. However, a sharp increase in alumina extraction and formation of

CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts were observed at sintering temperature of 1100 ^oC by increasing sintering time from 1 hr to 4 hrs as well as by increasing Na_2CO_3 from 10g to 25g as compared to red mud 100g.

Tables 1 & 2 show that the extraction efficiency increases with addition of lime grit as well as with increasing of temperature and sintering period in presence of different amount of soda ash.

Table 1. Chemical analysis of sintered red mud using lime grit ($CaO+CaCO_3$) and Na_2CO_3

Conditions	Al_2O_3	Fe_2O_3	TiO_2	SiO_2	CaO	V_2O_5	MnO	Na_2O
RM+CaO+Na_2CO_3 (in gm)	**%**	**%**	**%**	**%**	**%**	**%**	**%**	**%**
Red Mud (RM)	16.07	53.75	4.24	8.25	0.146	0.148	0.157	3.82
100+10+20, 900 ^oC, 1hr	14.00	46.85	3.70	7.20	8.850	0.129	0.137	16.84
100+15+25,1000 ^oC, 3hrs	14.40	48.15	3.80	7.40	8.960	0.133	0.141	14.53
100+20+25,1100 ^oC, 4hrs	13.55	44.90	3.54	6.89	12.53	0.124	0.131	16.14

Table 2. Chemical analysis after leaching of sintered red mud using lime grit ($CaO+CaCO_3$) and Na_2CO_3

Cond.*	Al_2O_3	Fe_2O_3	TiO_2	SiO_2	CaO	V_2O_5	MnO	Na_2O	LOI	Extraction efficiency
	%	%	%	%	%	%	%	%		%
1	13.45	61.64	4.94	5.11	1.67	0.091	0.141	1.84	11.05	16.25
2	5.34	54.06	3.64	6.16	6.72	0.100	0.106	2.16	21.54	61.79
3	4.80	54.24	2.94	6.58	6.94	0.095	0.102	1.99	22.16	66.66
4	0.32	54.37	3.76	6.94	10.7	0.086	0.101	2.15	21.51	97.64

**1: Red Mud (RM); 2: RM+CaO+Na_2CO_3 (in gm) = 100+10+20, 900 ^oC, 1hr; 3: RM+CaO+Na_2CO_3 (in gm) = 100+15+25, 1000 ^oC, 3hrs; 4: RM+CaO+Na_2CO_3 (in gm) = 100+20+25, 1100 ^oC, 4hrs.*

During lime soda ash sinter process the sodalite and cancrinite present in red mud form CaV_2O_6 (d value =2.67 Å, 2.70 Å), $CaSiO_3$ (d value =2.70 Å) and $CaMnO_3$ (d value =2.67 Å) salts during sintering which formation were confirmed by XRD of sinter red mud at 1100 ^oC after leaching as shown in Fig. 3 and Fig. 4. It can be generally said that increasing the amount of Na_2CO_3 additive and the calcinations temperature increased the extraction of alumina and impurities immobilization due to formation of above salts during the process of leaching as shown in SEM (Fig. 12). The rate of the alumina extraction at 1100 °C is higher than at 900-1000 ^oC. High amount of Na_2CO_3 addition is not necessary. In order to get high alumina efficiency followed by impurities immobilization, only 25% (wt) Na_2CO_3 addition is enough.

3.1.1 EFFECT OF CaO AND Na_2CO_3

When Na_2CO_3 addition is increased from 15g to 20g in 100g of red mud, at 900 ^oC the alumina extraction was enhanced from 51.8% to 61.79%. However the alumina extraction efficiency was reached to 66.66% with 15% (wt) CaO and 25% (wt) Na_2CO_3 addition to this mixture in place of 10% (wt) CaO. But the alumina extraction was reached to 97.64% (Fig.-5) and formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts with 20% CaO and 25% (wt) of Na_2CO_3 addition to this mixture. The reason for increasing alumina extraction and impurities immobilization was the occurrence of insoluble dicalcium silicates (Fig. 3 & Fig.4) and formation of CaV_2O_6 (d value =2.67 Å, 2.70 Å), $CaSiO_3$ (d value =2.70 Å) and $CaMnO_3$ (d value =2.67 Å) salt, because of CaO addition and soluble sodium aluminate (Fig.3), and of Na_2CO_3 addition in solid state. Increasing CaO addition from 10% (wt) to % (wt) the alumina extraction efficiency increased from 38.35% to 97.64%. Increasing the amount of CaO more than 20 wt% decreased the alumina extraction efficiency. It was understood from this result that the excess of CaO reacted with a little amount of alumina in the solution and insoluble Calcium Aluminium Silicates Hydrates was formed. It was expressed in the literature that the formation of insoluble calcium aluminium silicates was occurred due to excessive sintering temperature/time and presence of excess of limestone (Banerjee et al., 1989). It was clarified that the addition of CaO more than 20g was not necessary to recover high alumina ratio from the red mud. The addition of more than 20g leads to only wasting of CaO. The amount of optimum soda was determined as 25g in 100g of red mud (17.24% (wt) Na_2CO_3 of the red mud) for solving enough alumina in the red mud. Since the addition of Na_2CO_3 in between 15g to 25g gives significant recovery of alumina.

3.1.1.1 EFFECT OF Na_2O/Al_2O_3 AND CaO/SiO_2 MOLAR RATIO

The optimum range for alumina extraction and formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts corresponds to soda/alumina ratios of 1.2 to 1.3. The ratio greater than 1.3 is not necessary, and in fact they seem to be harmful. This is believed to be due to the formation of some insoluble compounds between soda and alumina. These data correspond to a constant value of Na_2O/Al_2O_3 = 1.3. We can see that, with an increase in the CaO/SiO_2 ratio, extraction increases up to CaO/SiO_2 =1.75 to 1.8 and then decrease thereafter. Here it is also seen that ratio equal to the stoichiometric values are not the optimum values as reported previously in the literature. From these results, it is known that the extractions of alumina as well as impurities immobilization are best with the soda / alumina and lime / silica to obtain 1.3 and 1.8, respectively. Therefore, these ratios were adopted as standard for the subsequent experiments.

3.1.1.1.1 EFFECT OF CALCINATIONS TEMPERATURE AND TIME FOR EXTRACTION OF ALUMINA

The alumina extraction efficiency increased from 38.35% to 45.13% by increasing sintering temperature from 900 ^oC to 1000 ^oC with sintering time of 2 hrs. But there is no significant change in alumina extraction by increasing sintering temperature from 900 ^oC to 1100 ^oC with soaking time of 2 and 3 hours. The alumina extraction efficiency was increased from 61.11% to 97.64% by increasing amount of lime grit as well as sodium carbonate and sintering temperature 900 ^oC to 1100 ^oC with soaking time 4 hours (Fig. 5). Hence the optimum condition for formation of sodium aluminate is maximum during sintering of red mud with 20% of CaO along with 25% Na_2CO_3, 1100 °C for soaking period of 4 hours time. The leaching time 1 hr with 80 gpl caustic at 105 °C, under these optimum conditions, the highest extraction efficiency of alumina was obtained as 97.64% and impurities immobilisation more than 90% (Fig. 6 to Fig. 8) as well as formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts.

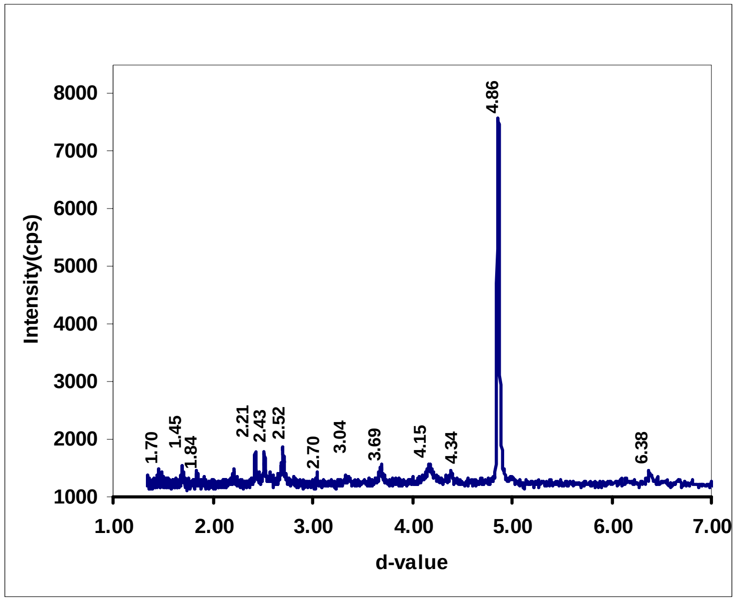

Fig. 1. XRD of Red Mud

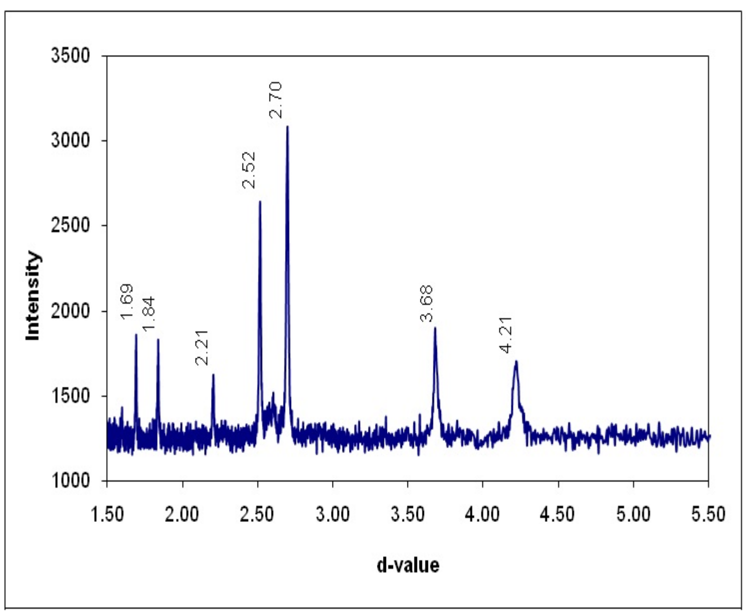

Fig. 2. XRD of sintered Red Mud after leaching

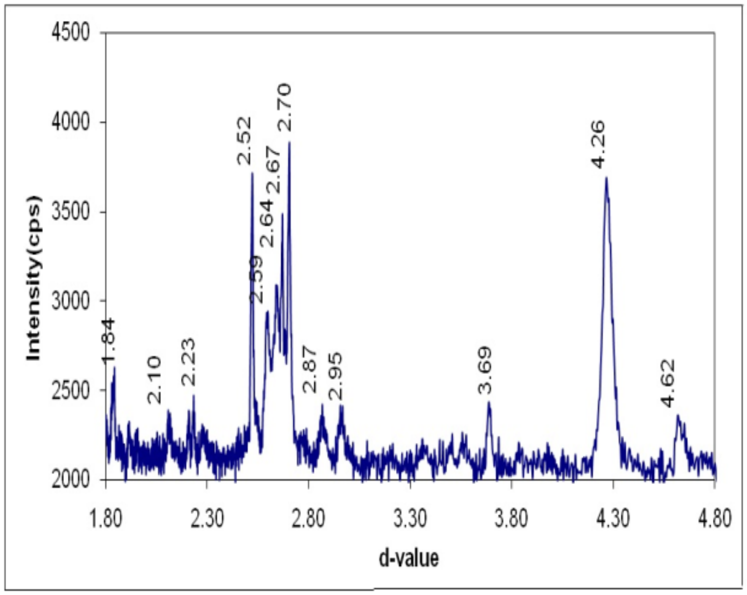

Fig. 3. XRD of sintered Red Mud at 1100 °C

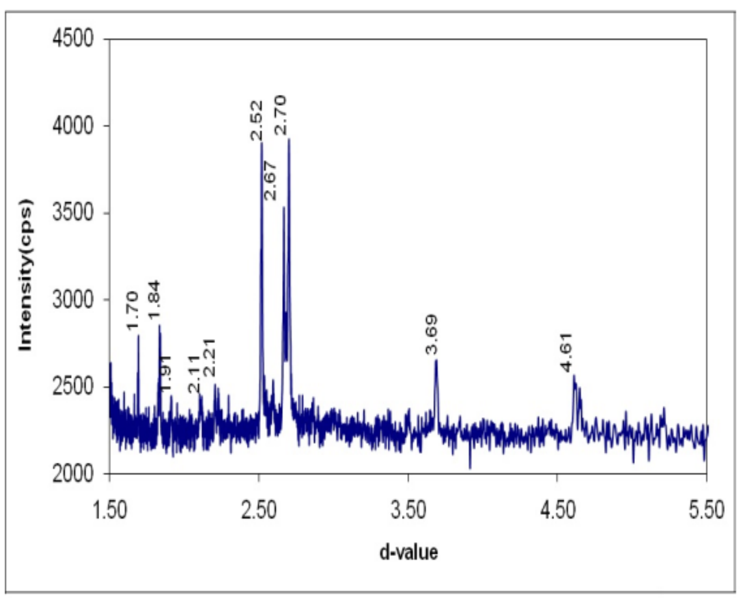

Fig. 4. XRD of leached sintered Red Mud at 1100 °C

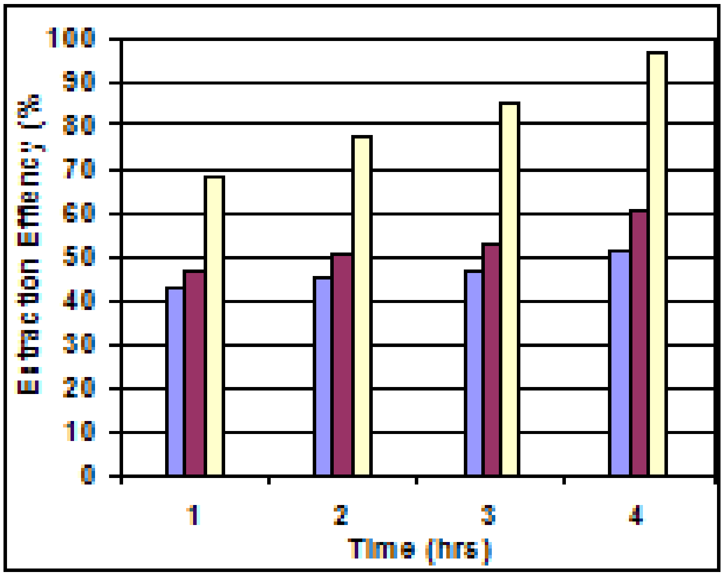

Fig. 5. Alumina Extraction Efficiency

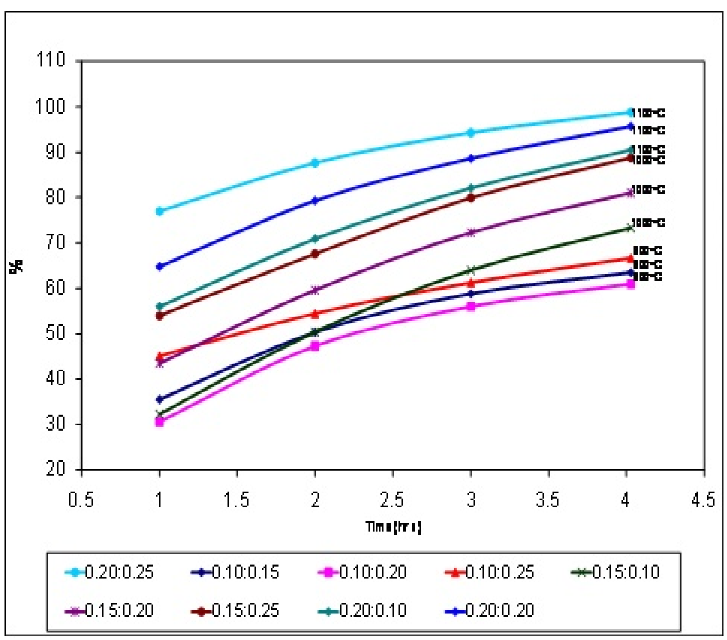

Fig. 6. Retentation of SiO_2 in leached mud

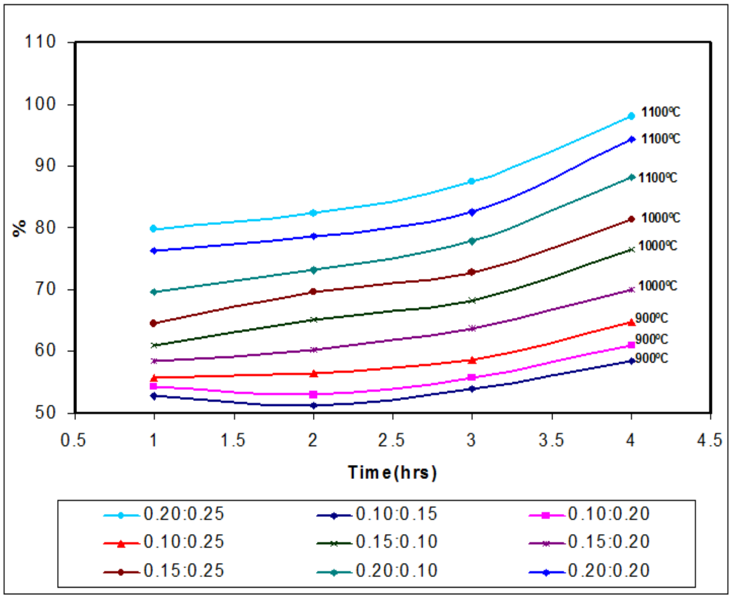

Fig.7. Retentation of V_2O_5 in leached mud

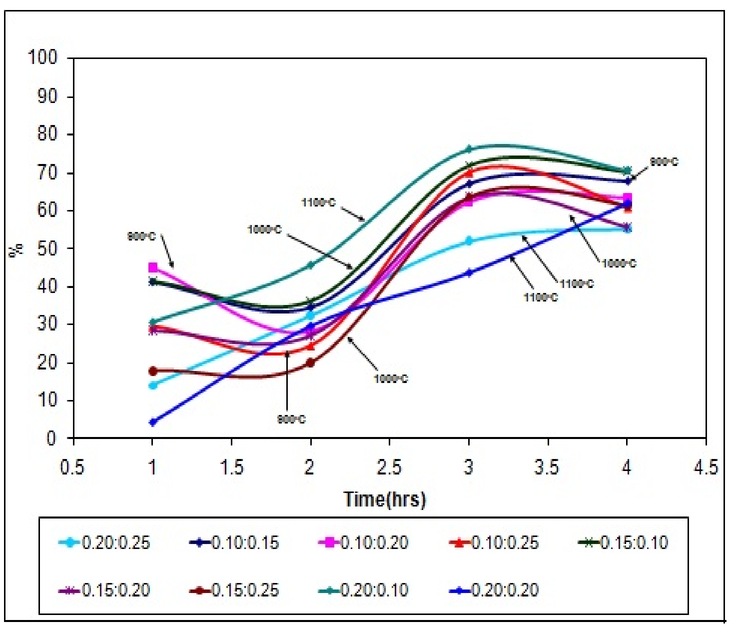

Fig. 8. Retentation of MnO_2 in leached mud

SEM of red mud shows the particles are in lumpy form (Fig. 9), whereas after sintering the red mud at 1100 ^{o}C the particles are agglomerated with each other as shown in Fig. 10. During sintering of red mud with lime grit and sodium carbonate the red mud forms sodium aluminate (d value=2.23 Å, 2.52 Å, 2.59 Å, 2.64 Å, 2.95 Å), sodium calcium silicate (d value=2.64 Å), di-calcium silicate (d value=2.21 Å) and calcium ferrite (Fig. 11) that is confirmed from the XRD of sintered products shown in Fig. 3.

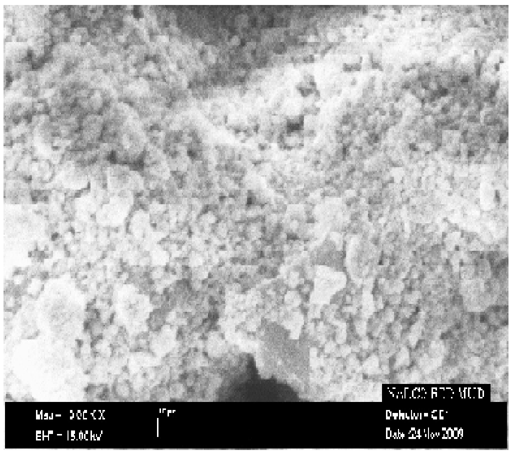

Fig. 9. SEM of Red Mud

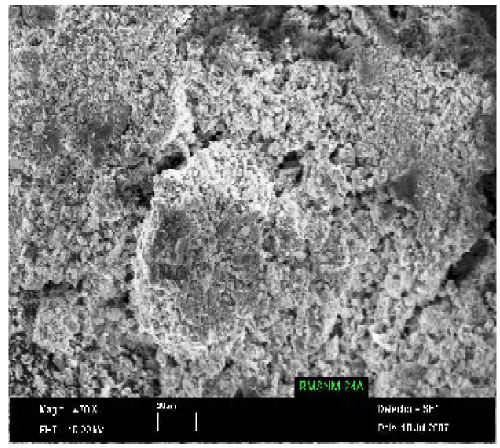

Fig.10. SEM of Sintered Red Mud at 1100°C

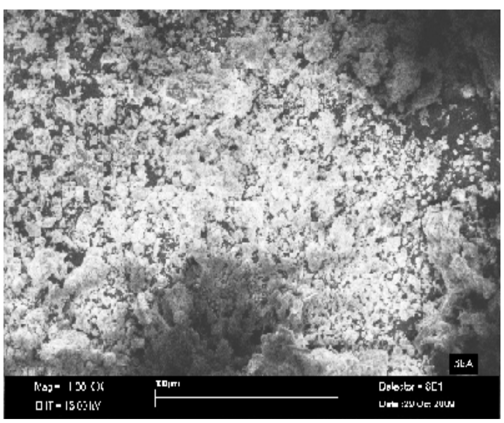

Fig. 11. SEM of sintered red mud with lime grit and sodium carbonate at 1100°C before leaching (1500X)

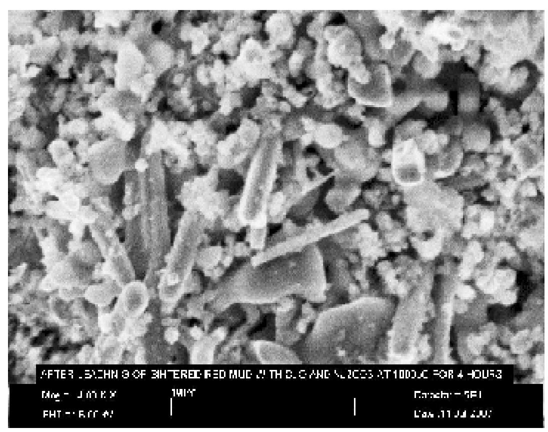

Fig. 12. Formation of $Ca_2Fe_2O_5$, $CaSiO_3$, CaV_2O_5 & $CaMnO_3$ in leaching of sintered red mud with lime grit and sodium carbonate at 1100°C (5000X)

During leaching of the sintered product with sodium hydroxide solution the sodium aluminate is soluble in sodium hydroxide and leaving the stable non-reactive red mud having $Ca_2Fe_2O_5$, (d-value=2.10 Å, 2.67 Å, 2.70 Å), CaV_2O_6 (d value =2.67 Å, 2.70 Å), $CaSiO_3$ (d value =2.21 Å, 2.70 Å) and $CaMnO_3$ (d value =2.67 Å) phases. The peak of sodium aluminate diminishing after leaching and leaving the stable calcium compounds which were confirmed by XRD (Fig. 4). The SEM photograph (Fig. 12) shows the formation of rod like structures of $Ca_2Fe_2O_5$. The formation of above phases enhances alumina extraction and impurities immobilization as shown in (Fig. 6 to Fig. 8). Table 3 shows the formation of different phases of sintered products.

Table 3. Major phases present in XRD scans of 1100 °C sinter products

Experiment	Synthetic new lime Na_2CO_3 sinter		Synthetic existing lime Na_2CO_3 sinter	
Target Phase	Na_2CaSiO_4 $+NaAlO_2$	Na_2CaSiO_4 $+NaAlO_2+NaFeO_2$	Ca_2SiO_4 $+NaAlO_2$	Ca_2SiO_4+ $+NaAlO_2+NaFeO_2$
Phase Present in XRD	Na_2CaSiO_4 $+NaAlO_2$	Na_2CaSiO_4 $+Na_2AlFeO_4$	Ca_2SiO_4 +NaAlO2	Ca_2SiO_4+ $Na_2AlFeO_4+Ca_2Fe_2O_5$

4 CONCLUSION

Studies showed that it was possible to extract alumina from the red mud with very high alumina extraction efficiency followed by formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts. The optimum conditions of the process were 20% CaO and 25% Na_2CO_3 addition of the red mud weight, 1100 °C sintering temperature, 4 hr of sintering time and 1 hour of the leaching time at 105 °C with 80 gpl caustic. Under these optimum conditions, the highest extraction efficiency of alumina was obtained as 97.64% and shows the formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts. The alumina extraction efficiency reached with sintering at 1100 °C was higher than that at 900 °C. But 1100 °C was chosen as an optimum sintering temperature. This temperature can be accepted as more economical, suitable and agreeable method for extracting maximum alumina as well as formation of CaV_2O_6, $CaSiO_3$ and $CaMnO_3$ salts from red mud by lime soda ash sinter process and applicable to alumina refinery.

The formation of CaV_2O_6 (d value=2.67 Å, 2.70 Å), $CaSiO_3$ (d value=2.21 Å, 2.70 Å) and $CaMnO_3$ (d value =2.67 Å) salts during sintering at 1100 °C followed by leaching with 80 gpl caustic at 105 °C for 1 hr which were remain in leached residue. These signify maximum alumina extraction from red mud followed by impurities immobilization.

The treated red mud is environment friendly and can be suitable for making of cement and refractory bricks due to low soda content.

Studies is going on for removal of Fluoride and Arsenic from the drinking water using the residue after extraction of alumina as the mud contains oxide of calcium ferrite in hydrous form.

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