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Review

Extraction of Al and Na from red mud by magnesium oxide sodium carbonate sinter process

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The sintering of Bayer's process waste residue: Red mud along with magnesium oxide and sodium carbonate is adopted for recovery of aluminum and sodium followed by leaching. This is facilitated by the high temperature reaction of magnesium oxide sodium carbonate and DSP in the red mud to produce an insoluble dimagnesium silicate, magnesium ferrite, magnesium titanate and a soluble sodium aluminate. A variation of the red mud magnesium oxide sodium carbonate sinter process using half the magnesium oxide of existing methods has been investigated. The magnesium to silicon ratio was reduced from 2 to 1 producing a sodium magnesium silicate ($Na_2Mg_2SiO_4$) rather than the dimagnesium silicate (Mg_2SiO_4) insoluble phase produced in the existing above sinter method. Synthetic red mud magnesium oxide sodium carbonate sinter products were investigated to understand the phases produced during sintering at varying temperatures and the chemistry of extraction. The target phases and morphological behaviors were seen in XRD and SEM and the highest extractions were produced from a sinter temperature of 900°C for 4 h. A two-stage (105°C / 60 min, 105°C / 240 min) water or caustic leaching process was found to be most effective for extraction. Sodium and aluminum extractions were 99 and 98.7% respectively. The experimental method devised was then used to treat red mud and the target phases were produced. An extraction of sodium and aluminum respectively was achieved. Silicon extractions were below 2%.

Key word: Red mud, sinter, leaching, extraction.

INTRODUCTION

Methods of aluminum and sodium recovery from red mud have been around for many years due to the requirement of some refineries to process very high silica bauxites. The most common method to process red mud is the "Magnesium oxide sodium carbonate sinter process". The process involves adding magnesium oxide (MgO) to the red mud and sintering at temperatures of 900 -1100°C (King, 1980). The silica in the red mud reacts with magnesium to form the relatively inert dimagnesium silicate as shown in Equation (1). The sodium, which is in the red mud or added through sodium carbonate, reacts with the alumina and forms the soluble sodium aluminate as shown in Equation (2) (Leci and Guidi, 1962). The sodium, which is in the red mud or added through sodium carbonate, reacts with Fe_2O_3 and forms sodium ferrite as shown in Equation (3). The sodium, which is in the red mud or added through sodium carbonate, reacts with TiO_2 and forms sodium titanate as shown in Equation (4). The TiO_2 reacts with MgO to form magnesium titanate as shown in Equation (5). The sodium ferrite reacts with MgO forms magnesium ferrite and release free Na_2O as shown in Equation (6).

$$SiO_2+2MgO \rightarrow Mg_2SiO_4 \quad (1)$$

$$Al_2O_3+Na_2CO_3 \rightarrow 2NaAlO_2+CO_2 \quad (2)$$

$$Fe_2O_3+Na_2CO_3 \rightarrow 2NaFeO_2+CO_2 \quad (3)$$

$$TiO_2+Na_2CO_3 \rightarrow 2NaTiO_2+CO_2 \quad (4)$$

$$TiO_2+MgO \rightarrow MgTiO_3 \quad (5)$$

$$2NaFeO_2+2MgO \rightarrow Mg_2Fe_2O5+Na_2O \quad (6)$$

The product is then leached in an alkaline solution or

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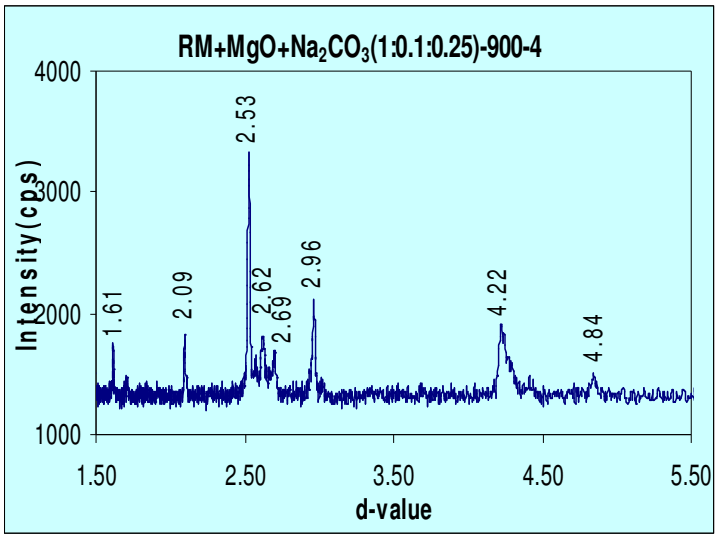


d-Value	Phase
1.61	Andradite(CIS)
2.09	Magnesium Titanium Oxide
2.53	Hematite/MgTiO3/Mg2SiO4
2.62	Sodium Magnesium Silicate
2.69	Hematite/MgTiO3
2.96	NaAlO2/Magnesium Ferrite
4.22	Goethite
4.84	Gibbsite

Figure 1. XRD graph before leaching.

water and the sodium aluminate solution is directed to the precipitation stage of the Bayer process.

$$NaAlO_2(s)+Mg_2SiO_4(s)+2NaFeO_2(s)+MgTiO_3+3H_2O \rightarrow NaAl(OH)_4(aq)+2NaOH(aq)+Mg_2SiO_4(s)+MgTiO_{3(s)} + Fe_2O_3(s) \quad (7)$$

To produce high aluminum and sodium extractions the decomposition of dimagnesium silicate must be as low as possible. In practice the amount of silica extracted in the leaching step is too high as the Mg_2SiO_4 is not sufficiently stable under the leaching conditions (Hartsborn, 2000) and silica extractions of around 15 to 20% (Likuan, 1993) occur during leaching, tying up sodium and aluminum with the formation of $Mg_3Al_2(OH)_{12}$, Hydro garnet and DSP. The opportunity exists for a process to treat red mud to separate aluminum and sodium from silica, producing an adequately stable insoluble phase for leaching and therefore yielding greater extractions.

An alternative method of red mud MgO Na_2CO_3 sinter has been presented in this paper to produce an Mg:Si ratio of one in the sinter product. The potential benefits are to have raw material costs and to give a more stable insoluble phase. Also the extra sodium needed could be provided by spent liquor creating the potential for organics removal through liquor burning in the sinter step. However, thermodynamic calculations and laboratory tests show that $MgSiO_3$ does not form under sinter conditions (Osborne, 1997). From the present experiments it was thought that the following red mud MgO Na_2CO_3 sinter reaction was feasible due to the presence of sodalite in the red mud formed by the reaction of kaolin and sodium aluminate liquor.

$$Na_2O.Al_2O_3.2SiO_2 \text{ (sodalite)} + 2MgO + 4Na_2CO_3 \rightarrow 2Na_2MgSiO_4 + 2NaAlO_2 + 4CO_2 \quad (8)$$

A similar lime sinter process is referred to in a paper discussing the integration of coal combustion with lime sinter (Rayzman and Filipovich, 1999). Reaction (5) shows that soluble sodium aluminate and sodium magnesium silicate are produced. The sodium associated with sodium magnesium silicate must also be recovered in the leaching step. The objective of this project was to investigate the use of a Mg:Si ratio of one red mudMgO Na_2CO_3 sinter process for use as a red mud treatment for the recovery of aluminum and sodium and compare this with the current red mud MgO Na_2CO_3 sinter system of Mg : Si = 2.

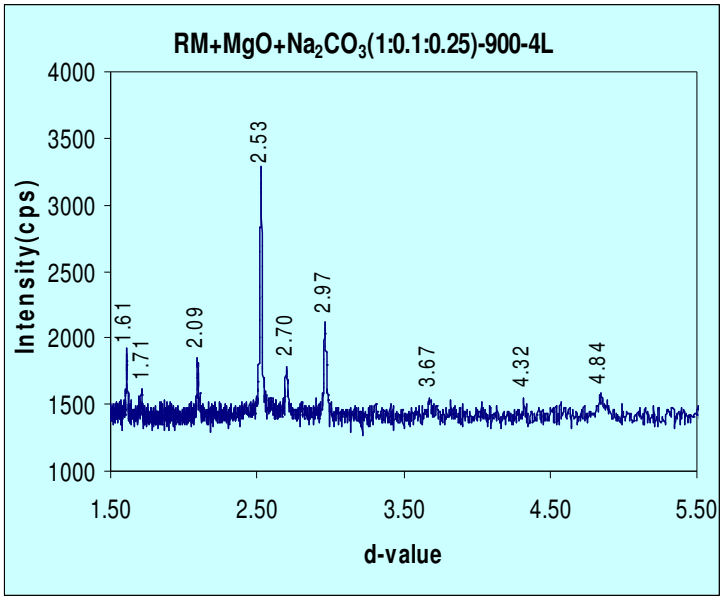
EXPERIMENTAL

Magnesium oxide Na_2CO_3 sinter products with varying chemical compositions were prepared to gain an insight into the thermodynamics and chemistry of the red mud MgO Na_2CO_3 sinter process. Both the existing (Mg_2SiO_4) and new (Na_2MgSiO_4) method of red mud MgO Na_2CO_3 sinter were tested for comparison ininitially synthetic and then red mud MgO Na_2CO_3 sinter mixtures. Synthetic mixtures were produced using SiO_2, MgO, Na_2CO_3 call analytical grades and Zeolite-A which were pulverized, pressed into pellets and sintered and phases confirmed by XRD (Figures 1 and 2) and AAS analysis. Synthetic phases with iron present were then made using Fe_2O_3. The red mud MgO Na_2CO_3 sinter mixtures were produced similarly, adding MgO and Na_2CO_3 to red mud.

The temperature of sintering was varied to optimize extraction. Leaching with water or sodium hydroxide solution was undertaken in a water bath at varying times and temperatures, again to optimize extraction.

XRD study

XRD analysis was done to detect the presence of different phases in the sinter red mud and leached red mud. XRD work was carried out on a Rigaku X-ray diffractometer, (Make: Japan, Model:



d-Value	Phase
1.61	Andradite(CIS)
1.71	Hematite
2.09	Magnesium Titanium Oxide
2.53	Hematite/MgTiO4/Mg2SiO4
2.70	Hematite/MgTiO3
2.97	Na2MgSiO4/Magnesium Ferrite
3.67	Cancrinite
4.32	Bayerite
4.84	Gibbsite

Figure 2. XRD graph after leaching.

Dmax2200). The X-ray diffractograms of sinter red mud and leached red mud were taken using Cu Kα (Kα =1.54186 Å) radiation at scan speed of 1°/min and scan step of 0.02 with 20 value from 5 to 70° at 30 and 20 mV.

SEM Study

The sinter red mud and leached red mud samples were coated with gold or carbon at 18 mA for 105 s. The morphological behaviours of coated samples and formation of sodium magnesium silicate, dimagnesium silicate, magnesium titanate and magnesium ferrite were studied by using Scanning Electron Microscopy, Make: England, Model: Leo Electron Microscopy 430.

RESULTS AND DISCUSSION

In the synthetic red mud MgO Na_2CO_3 Sinter stage, calcination at 900°C for 4 h with red mud MgO Na_2CO_3 ratio (1:0.1:0.25) was found to produce the most stable di-magnesium silicates (SEM Figure 3a), sodium magnesium silicates (SEM Figure 3b) Magnesium Titanate (SEM Figure 3c and d) and magnesium ferrite (SEM Figure 3e and f) which maximized the extraction of aluminum (98.7%) and sodium (99%). The statistical data for maximum extraction efficiency of present condition in MgO Na_2CO_3 sinter process is given in Table 1. XRD scans shows the target phases are present as described in Table 2.

The existing red mud MgO Na_2CO_3 sinter product ties some magnesium up with iron due to the formation of $Mg_2Fe_2O_5$ (rounded rod like structure) as shown in SEM Figure 3e and f. This meant that extra magnesium was added to ensure the maximum amount of silica was reacted with the magnesium and not with sodium or aluminum. At 900°C, instead of sodium aluminate and sodium ferrite forming, Na_2AlFeO_4 formed in products with iron present. For the synthetic new magnesium sinter system without iron it was found that a two stage caustic leach (105°C/60 min, 105°C/240 min) was required to gain maximum Na and Al extractions due to the decrease in Al in solution over time as shown in Figure 4.

This allowed the removal of the majority of the aluminum before the decomposition of the sodium magnesium silicate and subsequent reaction to form DSP, Hydro garnet or $Mg_3Al_2(OH)_{12}$. To ensure leaching conditions were the same for both systems the two-stage process was also employed for the existing MgO Na_2CO_3 sinter products. The results of extractions for the sinter products without iron are displayed in Figure 5.

When Iron is introduced to the system there are effectively two soluble phases ($NaAlO_2$ + $NaFeO_2$) in which the ratio of soluble sodium to soluble aluminum increases.

The results in Figures 6 and 7 show the benefit of the new red mud MgO Na_2CO_3 sinter method in terms of aluminum extraction. Much of the sodium and all of the aluminum is extracted from the existing red mud MgO Na_2CO_3 sinter process in the first stage. The second stage merely completes the leaching of sodium. In the new red mud MgO Na_2CO_3 sinter extraction the resultant solids have a sodium content of 0.06% compared to the 6% sodium content of the red mud. The aluminum levels have been reduced from 18 to 0.23%. A more stable sodium magnesium silicate would increase these extractions and could be achieved with the optimization of sinter temperature and leach conditions.

A simulation of the second stage leach, which in the

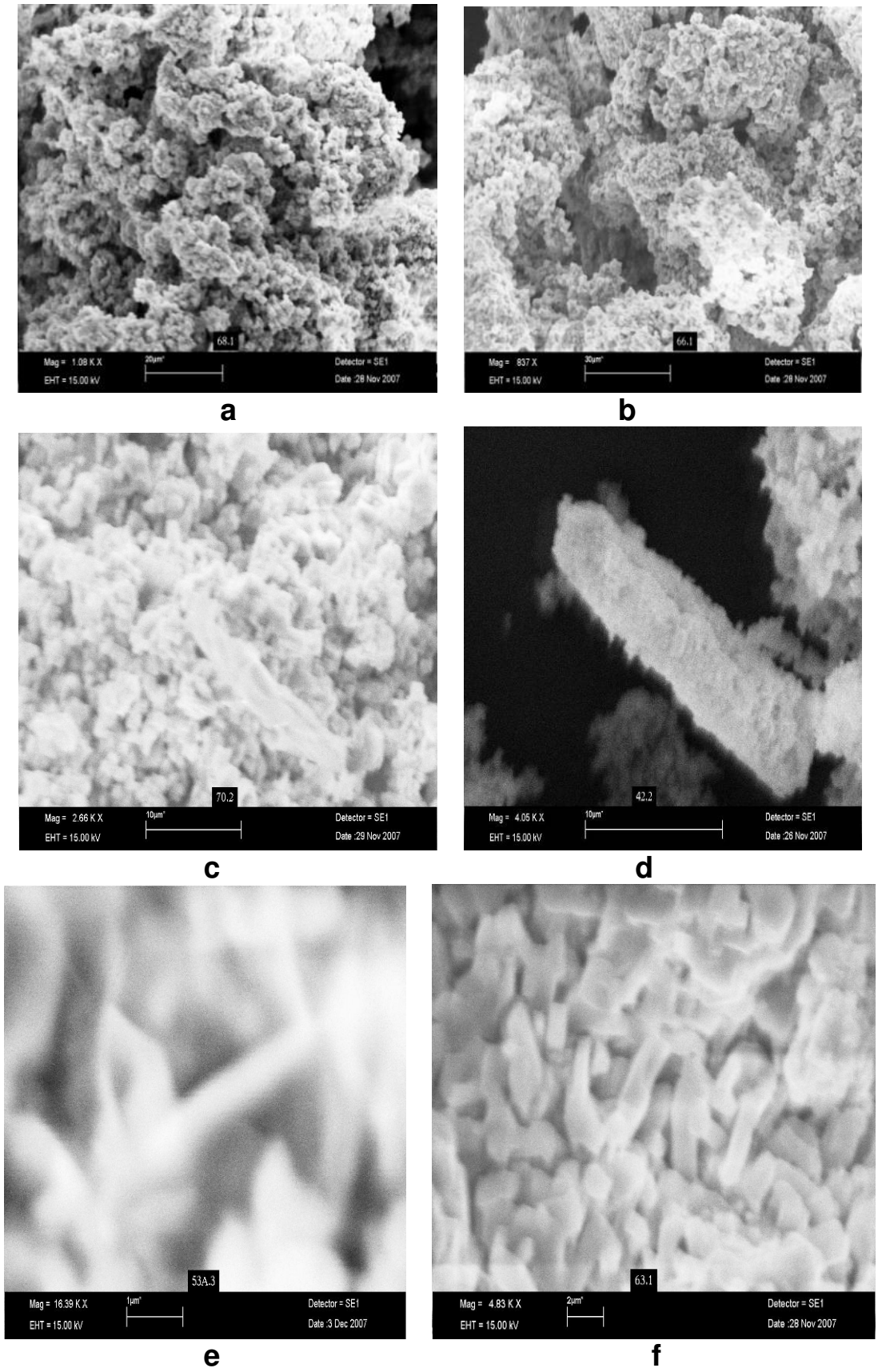


Figure 3. a Formation of Di- magnesium silicate. b Formation of sodium- magnesium silicate. c and d. Formation of magnesium titanate. e and f. Formation of magnesium ferrite.

Table 1. Statistical data for maximum extraction efficiency.

Experiment	Red mud + MgO + Na_2CO_3 ratio	Aluminum extraction efficiency in %	Average aluminum extraction efficiency in %	Standard deviation
1	1:0.10:0.25	98.40		
2	1:0.10:0.25	98.70		
3	1:0.10:0.25	98.60	98.70	0.2549
4	1:0.10:0.25	98.70		
5	1:0.10:0.25	99.10		

Table 2. XRD scans showing the target phases.

Experiment	Synthetic MgO Na_2CO_3 sinter process		Synthetic existing MgO Na_2CO_3 sinter process	
Target phase	Na_2MgSiO_4 +$NaAlO_2$	Na_2MgSiO_4 +$NaAlO_2$ +$NaFeO_2$	Mg_2SiO_4 +$NaAlO_2$	Mg_2SiO_4+ +$NaAlO_2$ +$NaFeO_2$
Phase present in XRD	Na_2MgSiO_4 +$NaAlO_2$	Na_2MgSiO_4 +Na_2AlFeO_4	Mg_2SiO4 +$NaAlO_2$	Mg_2SiO_4+ Na_2AlFeO_4 +$Mg_2Fe_2O_5$

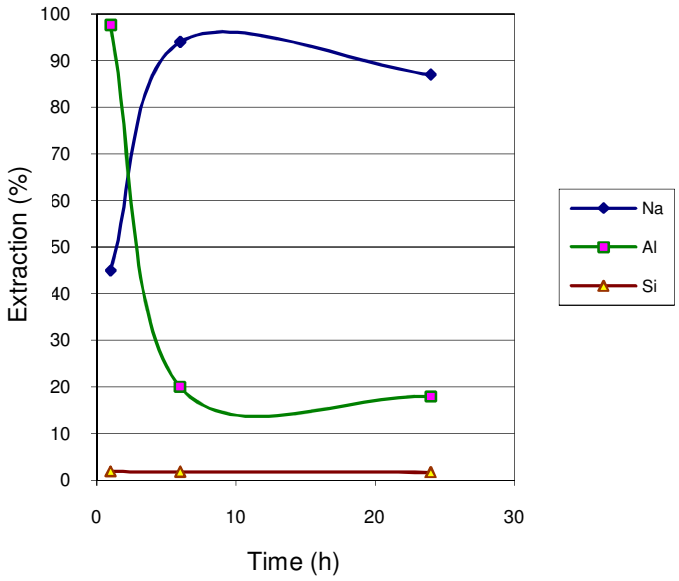


Figure 4. Single stage extraction overtime.

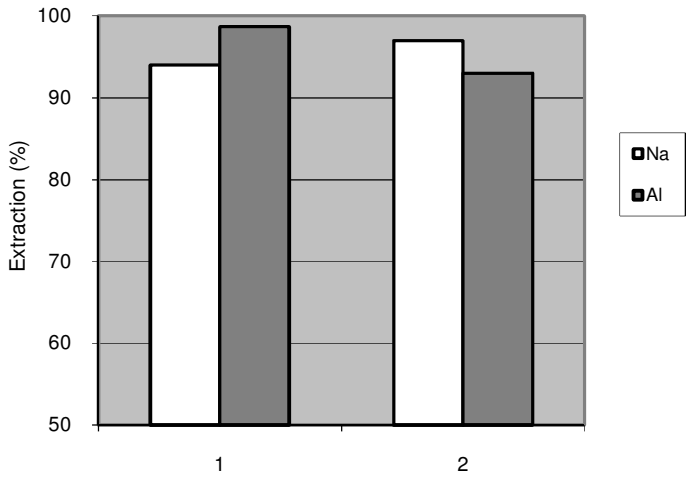


Figure 5. New vs existing synthetic $MgONa_2CO_2$ sinter without Iron.

new process aims to recover the sodium from the sodium magnesium silicate, produced highly concentrated caustic solutions (175g/l). The extraction was of a synthetic Na_2MgSiO_4 sintered at 900°C and leached wit80 g/L caustic solution for 1 h at 105°C. The high caustic concentration may be due to the stability of the decomposition products which have an Mg:Si of 1 rather than 2. This is a significant result and should be investigated further.

When leaching the red mud MgO Na_2CO_3 sinter products the greater aluminum extraction in the new process was evident however, there was less sodium extracted. This may be overcome with further optimization of the mole ratios of reactants in the red mud MgO Na_2CO_3 sinter step. The high silicon extraction that has been reported (Likuan, 1993) was not seen during this project with most experiments producing a silicon extraction of less than 2% for both the new and existing processes. This may be due to the accuracy of the mole ratios, which can easily be targeted in laboratory conditions compared to in plant conditions where an assay of the red mud to be sintered with MgO Na_2CO_3 sinter is unlikely to have taken place.

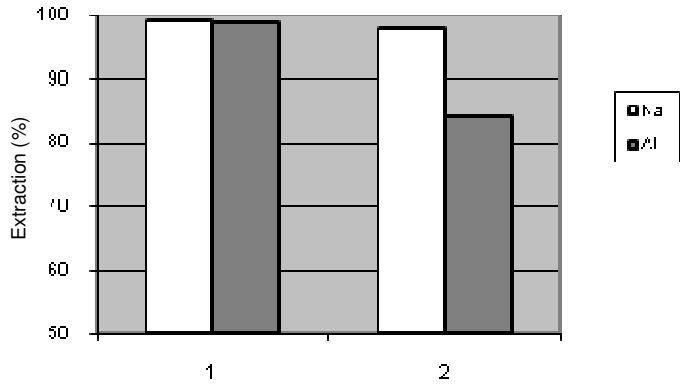


Figure 6. New vs existing synthetic $MgONa_2CO_2$ sinter.

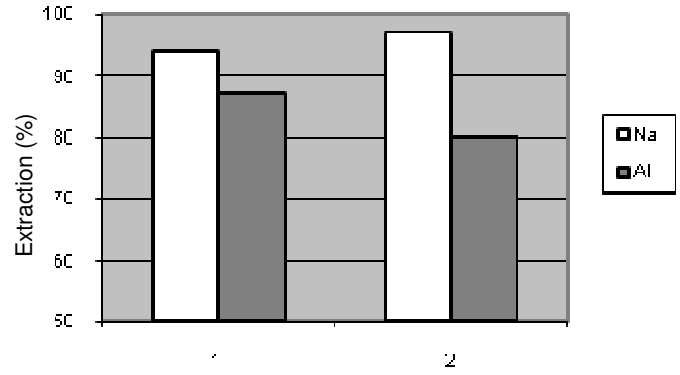


Figure 7. New vs existing red mud $MgONa_2CO_2$ sinter.

Conclusion

The new red mud MgO Na_2CO_3 sinter method with an Mg:Si of one proved to be an effective procedure in recovering the sodium and aluminum from red mud with minimum silicon extraction. The problems with high silica extraction using the existing MgO Na_2CO_3 sinter method were not evident which may be due to the difference in mole ratio accuracy between laboratory and plant. The advantages of the new red mud MgO Na_2CO_3 sinter process include a decrease in MgO and NaOH purchases, increased aluminum extraction (98.7%) and possible organics removal through liquor burning. The potential for producing a concentrated sodium hydroxide solution from the second stage leach is also a major benefit of this system. The highest extraction (98.7%) was achieved at 900°C in MgO Na_2CO_3 sinter process with red mud MgO and Na_2CO_3 ratio of 1:0.1:0.25 is due to formation of dimagnesium silicate (d-value= 2.53 Å), magnesium titanate (d-value=2.09 Å, 2.53 Å, 2.69 Å), magnesium ferrite (d-value= 2.96 Å) and sodium aluminate (d value=2.96 Å) as shown in XRD Figure 1 and Figure 2.

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