

## ALUMINA EXTRACTION FROM LOW-GRADE DIASPORIC BAUXITE BY PYRO-HYDRO METALLURGICAL PROCESS

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### ÖZET

Isparta – Yalvaç yöresinden temin edilen diasporitik boksit numuneleri kırılmış ve 100 µm elek altı olacak şekilde öğütülmüştür. Numunelerin öncelikle kimyasal analizi ve tane boyut dağılımı tespit edilmiştir. Statik ve dinamik termal analizi ve XRD çalışmaları ile karakterizasyonu yapıldıktan sonra CaO ve Na<sub>2</sub>CO<sub>3</sub> ilave edilmiş boksit numuneleri 900 °C'de kalsine edilmiştir. 20, 40, 60 ve 80 dakikalık kalsinasyon ve 15, 30, 45 ve 60 dakikalık liç süreleri ile 25, 50, 75 ve 100 °C lik liç sıcaklıklarında alümina ekstraksiyon çalışmaları yapılmıştır. En yüksek alümina liç verimi (% 85,04) 60 dakika kalsinasyon ve 50 °C sıcaklıkta yapılan 15 dakikalık liç işlemiyle elde edilmiştir. Elde edilen sonuçlardan, bu tip demirli diasporitik boksit cevherlerinin düşük sıcaklık ve alkali konsantrasyonunda çözündürülebilmesi için gereken optimum koşullar belirlenmiştir.

**Anahtar Kelimeler:** Fakir diasporitik boksit cevheri, CaO ilavesi, Soda ilavesi, Kalsinasyon, Liç, Alumina

## FAKİR DIASPORİTİK BOKSİTLERDEN PİRO-HİDRO METALURJİK PROSESLE ALÜMİNA EKSTRAKSİYONU

### ABSTRACT

Diasporic bauxite samples obtained from Isparta-Yalvaç region were crashed and sieved with a 100 µm sieve. After determining the composition by chemical analysis, grain size distribution of the samples were determined. Then the characterization of the sample was recorded by static and dynamic thermal analysis and XRD studies. Bauxite samples added CaO and Na<sub>2</sub>CO<sub>3</sub> were calcined at 900 °C. Alumina extraction studies were performed for 20, 40, 60, 80 minutes of calcination time and 15, 30, 45, 60 minutes of leach time and 25, 50, 75, 100 °C of leach temperature. It was found that the maximum leach yield (85.04 %) was obtained at 60 minutes of calcination time and 15 minutes of leach time and 50 °C of leach temperature. These results demonstrated that the optimum conditions for dissolving to this type of iron-rich low grade diasporic bauxite minerals at low-temperature and alkaline concentration were determined.

**Keywords:** Low grade diasporic bauxite, CaO additive, Soda additive, Calcination, Leaching, Alumina extraction.

## 1. INTRODUCTION

Today, bauxite is regarded as the most commonly used and economic raw material with known technological conditions for the aluminum production. Bauxite is a name of a group of aluminum-rich minerals which were formed by outer factors to different rocks [1]. Bauxite minerals are classified into two groups as lateritic and carstic according to their geological formation. Lateritic bauxites, which are also named as silicate bauxites, are formed by changes of silicate rocks with tropical conditions and have high level of gibbsite. The bauxite reserves of Turkey are also in carstic bauxite group [2]. World bauxite reserve has been estimated to be 55-75 billion tons. 33 % of it is in South America, 27 % in Africa, 17 % in Asia, 13 % in Australia and 10 % in other countries [3].

Turkey's total bauxite reserves have been estimated to be 421.9 million tons. There are still some regions that have never been searched. These bauxite reserves can be classified into different groups according to reserve contents and technological properties [2]. There are 45 million tones of diasporic, 45.8 million tones of boehmitic and 331.1 million tones of diasporic-boehmitic bauxite reserves in Turkey. Only 36.5 million tones of boehmitic bauxite reserves have been used for the alumina production hitherto. However, most part of 376.1 million tones of diasporic bauxites has not been investigated until now. The bauxite reserve of Isparta region has also been estimated as 115 million tons [4]. This reserve constitutes approximately 29 % of the total bauxite reserves of Turkey and has not been investigated for any purpose.

Being diasporic kind is the most disadvantage of this bauxite for the industrial process, for it is low grade for the alumina production. Diasporites are known to need higher digestion temperatures and much more alkaline concentrations in the solution compared to boehmite and gibbsite. These parameters cause some difficulties or problems in the following steps of the process. Therefore, decreasing the digestion temperature of bauxite and alkaline concentration of the solvent is very important for the favor of the process. This is especially important in the countries of Mediterranean zone where diasporic bauxites are found in huge amounts.

Diasporite with a chemical formula of  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  has been formed with light metamorphism of boehmite. Diasporite can take different colors such as earth color; gray, yellow, white etc., and can be transparent or semi-transparent. The hardness of orthorhombic crystals of diasporite in the form of prisma or thin layers is 6,5-7,0 mohs and its density is 3,3-3,5  $\text{g/cm}^3$ . Diasporite is generally found with corundum and emery-stone along with dolomite and in granular clay stones or in crystallized schists. Diasporic bauxites which are not used in alumina production due to their mineralogical

properties and used as abrasive can also be used in the refractor brick production [5]. The bauxites used in this study are iron-rich diasporic bauxites (Isparta region) which are low-grade bauxites and contain %30-40  $\text{Al}_2\text{O}_3$  and %17-25  $\text{SiO}_2$ . And therefore; bauxites of this region have not been used in alumina and aluminum production [2].

Alumina, which has large inner surface due to its porous structure, is very pure and amorphous material. The density of alumina varies between 3.8-4.0  $\text{g.cm}^{-3}$ . Its hardness (9 Mohs) is little less than that of diamond. If transparent or colored with metal oxides, they are regarded as precious stones. Alumina has high melting and boiling point [6]. Among the engineering ceramics, today, alumina has the highest, 85 %, usage rate. Due to its high stability and melting temperature and low electrical and thermal conductivity, alumina is used as refractor. It can be used for cutting edges, in thermal engines and as parts and/or components of power-stations, which are vulnerable and exposed to corrosion, on corrosive and composite materials [7]. Due to its high purity and resistance to the corrosion, it can also be used in thread shuttles and spray nozzles. Dense alumina is used for spark-plug production. Alumina is densely used on ceramic cutter sets, hard metal coating, refractory wearing material and light armor [8, 9]. In addition, high purity alumina is used for production of some chemicals, especially for aluminum compounds [10].

If mass ratio of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  is greater than 10, it is regarded as high-grade bauxite, and can be processed directly by the Bayer process. For the low-grade bauxite, if mass ratio of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  is below 8, a sintering process or combination of Sintering and Bayer process can be used. The sintering process is extremely energy-intensive and environmentally unfriendly, incurring a high alumina production cost [11]. The essential of the Bayer process is dissolution of alumina-rich minerals into hot caustic solution, separation of the insoluble phases, followed by gibbsite precipitation and calcination of the gibbsite to alumina ( $\text{Al}_2\text{O}_3$ ). In the sintering process the raw material is heated, together with another chemical (usually an alkali) to induce a solid-state reaction. An alkaline leach is then performed to separate the aluminous material from the insolubles [12]. High digestion temperatures also increase the reactivity of impurities such as silica which is the most detrimental impurity both by its quantity and impact. Dissolved silica precipitates as "desilication product" which primarily consists of Bayer sodalite and Bayer cancrinite are of the chemical compound as sodium aluminum silicate hydrate. The precipitation of silica not only consumes useful caustic and alumina but also leads to the slow release of soda from red mud residues in storage areas [13].

The main purpose of this study is to investigate and find the favorable ways for the production of alumina from low-grade diasporic bauxite using the low calcination temperature, because of its low production cost. Billion

tones of diasporic bauxites in the world are waiting to be used for the alumina production. This study shows that the alumina production from low-grade diasporic bauxites is possible by using a simpler and more economic process with lower temperature and alkaline concentration.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Mineral samples collected from Isparta-Yalvaç region were crashed and ground as wet in mill with iron marbles. Separated from aqueous phase, ground bauxite was completely dried and sieved with different sieves to determine the grain size distribution.

### 2.2. Chemical Analysis

The chemical analysis of bauxite sample was done by common analytical methods. For this purpose, 1 g bauxite sample was dissolved using with sodium hydroxide by heating at 550 °C in a platinum crucible. Then, the mixture was solved in hydrochloric acid solution to determine the components of bauxite sample quantitatively. In addition, some amount of bauxite sample was heated in a platinum crucible up to 1100 °C for an half an hour. During this process, total heat loss due to dehydration or decomposition was determined.

### 2.3. Calcination Studies

Calcination or thermal analysis studies were performed by two methods, static and dynamic. Static method is based on thermal decomposition reaction at a constant temperature. Dynamic method, however, is based on weight change measurements at increasing temperatures.

An electrical oven with  $\pm 10$  °C sensitivity was used for the study of the static method. The sample in platinum crucible was kept at constant temperatures (100, 200,...1100 °C) for 30 minutes. It was cooled down in desiccators and weighed. Eventually, the % weight loss due to dehydration or decomposition was calculated. For the study of dynamic method, a thermal analysis instrument was used, which could simultaneously draw thermogravimetric analysis (TG), and derivatographic analysis (DTG) curves as a function of temperature change.

The study was carried out by heating at 10 °C /min. heating rate starting from room temperature, with 0.2 mV sensitivity in atmospheric conditions, and the changes in the sample due to heating were observed.

### 2.4. X-Ray Diffraction Studies

X-ray diffraction study was used for qualitative analysis of the sample. X-ray diffraction pattern was obtained by Shimadzu XRD-6000 model x-ray diffractometer equipment with  $\text{CuK}_{\alpha}$  x-ray tube ( $\lambda=1.5405 \text{ \AA}$ ).

### 2.5. Alumina Extraction Studies

The outcomes of another study about diasporites from Mugla, a different region in Turkey showed that the solubility of the bauxite minerals can be enhanced by pre-calcination at 900 °C [14]. Therefore, this temperature was taken as reference for the initial part of the extraction process. The same study also showed that the contribution of an alkaline for high alumina leach yield and low amount of  $\text{SiO}_2$  passing to the solution was necessary. The amount of alkaline for the purpose was estimated to be  $X_{\text{CaO}} = X_{\text{Na}_2\text{CO}_3} = 0.5$  mole fractions of total alkaline. For this reason, in alumina extraction studies, before the calcination process, 1.0226 gram CaO and 1.9356 gram  $\text{Na}_2\text{CO}_3$  were added to 3.0 gram bauxite mineral, and the mixture was homogenized as much as possible.

Prepared samples of bauxite-alkaline were calcinated at 900 °C for 20, 40, 60, and 80 minutes. After calcination, the samples were cooled down in desiccators and then were leached. A stainless steel reactor connected with a cooler and a heater with a magnetic stirrer was used for leach process. NaOH was used as a leach solution and constant stirring was performed in all experiments. The solution concentration used in leach process was 1.5 M  $\text{Na}_2\text{O}$  and solid/liquid ratio was 1/30 and the temperatures for the leach process were 25, 50, 75, and 100 °C. In the studies aiming to find out the effect of the leach time for  $\text{Al}_2\text{O}_3$  extraction yield, alkaline added calcined bauxite samples were leached at 25, 50, 75, and 100 °C temperatures for 15, 30, 45 and 60 minutes. After the leach process, the samples were filtered and the percentage of dissolved  $\text{Al}_2\text{O}_3$  was determined.

## 3. RESULTS AND DISCUSSION

### 3.1. Particle size and chemical analysis of bauxite sample

After being ground to smaller than 100  $\mu\text{m}$ , the grain size distribution of the sample was determined by sieving it, with different size sieves, and the percentages in all grains were shown as a histogram in Figure 1.

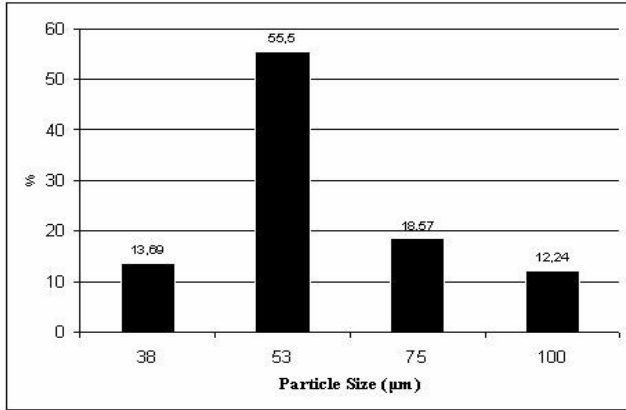


Figure 1. The particle size distribution of bauxite sample

The components of the bauxite sample were determined by chemical analysis and were given in Table 1.

Table 1. The chemical analysis of the bauxite

Compound	%
Al <sub>2</sub> O <sub>3</sub>	27,43
Fe <sub>2</sub> O <sub>3</sub>	28,57
SiO <sub>2</sub>	20,86
TiO <sub>2</sub>	2,45
CaO	4,11
CO <sub>2</sub>	3,23
LOI	15,00
Other	1,58
Total	100

### 3.2. Calcination Studies

The calcination results obtained by static method are shown in Figure 2.

As it can be seen from the Figure 2, while only 3 % weight loss was observed up to 400 °C, it was 7.5 % at 500 °C and reached to 9 % at 600 °C. Rapid weight loss was observed at 400-600 °C temperature range. 40 % of the total weight loss happened at this temperature range because of the chemical water removal in diasporite and kaolin. However, the water removal continued up to 750 °C. After this temperature carbonates were decomposed. The weight loss between 600-1100 °C was 5 % and, the 33.33% of the total weight loss was observed at this temperature range.

The results of calcination studies by dynamic method are given as TG and DTG curves in Figure 3.

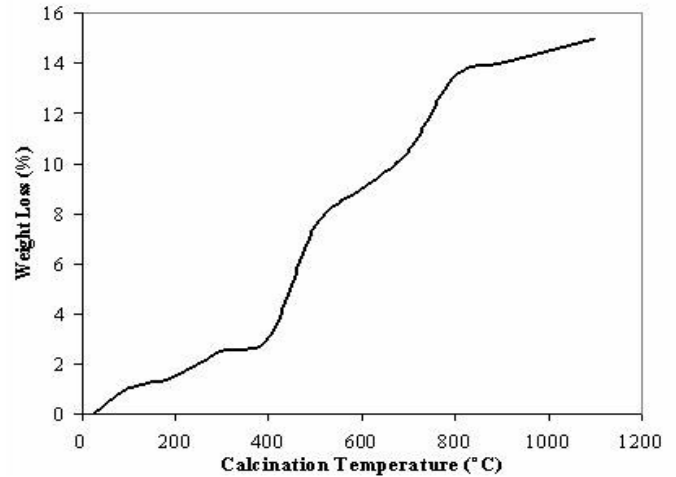


Figure 2. The relationship between calcination temperature and weight loss (%) of sample

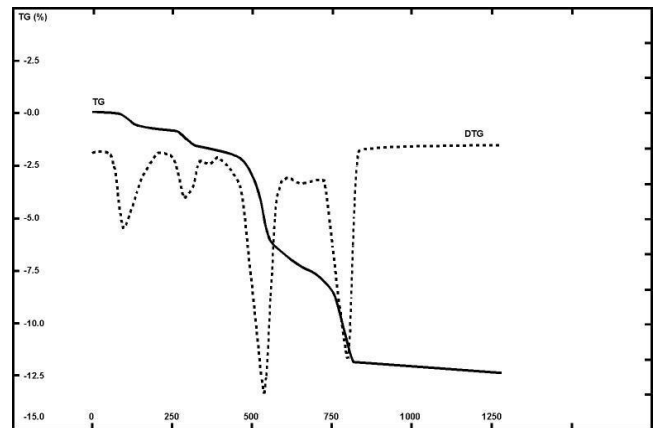


Figure 3. TG-DTG curves of the bauxite sample

As it can be seen from DTG curve in Fig. 3, the first weight loss starting around 73 °C and continuing up to 200 °C, was due to physical and adsorbed surface water. After this temperature two-step weight loss was observed. This two-step weight loss was because of dehydration of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) in the sample. The largest part of the weight loss of the sample can be seen as the big peak on DTG curve between 382-604 °C. The weight loss due to the removal of crystal water of diasporite was calculated to be 4.84 % from TG curve. After this point, the weight loss seen as a small peak on DTG curve was calculated to be 0.83 % from TG curve. This weight loss was due to dehydration of kaolin. The rapid weight loss after this temperature was due to the calcite which was detected by X-ray diffraction.

### 3.3. X-Ray Diffraction Studies

The results of X-ray diffraction of the bauxite sample are shown in Figure 4.

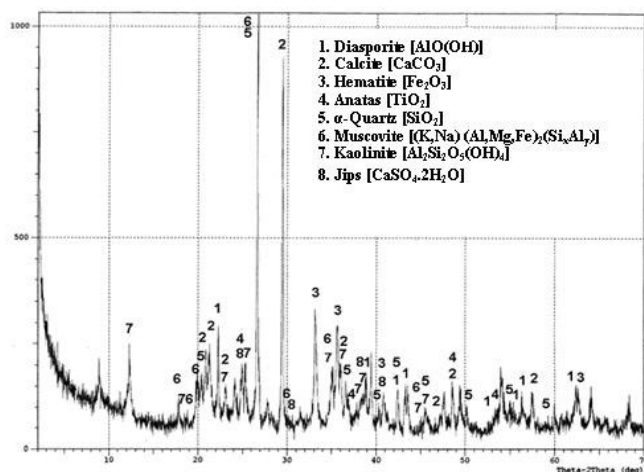


Figure 4. The X-ray diffraction curve of the bauxite sample

Possible phases represented by different peaks on XRD pattern were identified by comparing with the ASTM cards and shown on Fig.4. The evaluation of this phase revealed that  $Al_2O_3$  in bauxite samples was diasporic. In addition, some part of the  $Al_2O_3$  was found to be in kaolin ( $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ ) structure and large part of the silica was also found to be connected to that structure whereas some part was to be found in muscovite  $[(K,Na)(Al,Mg,Fe)_2(Si_xAl_y)O_2(OH)_2]$  and quartz ( $SiO_2$ ) structure.

The bauxite's iron component were found to be in the form of hematite ( $Fe_2O_3$ ) and titanium oxide as anatas. Calcium component was mainly found to be in calcite ( $CaCO_3$ ), but also in gypsum ( $CaSO_4 \cdot 2H_2O$ ) structure.

### 3.4. Alumina Extraction Studies

The products obtained after calcinations at 900 °C for 20, 40, 60, and 80 minutes were leached at 25 °C for 15, 30, 45, and 60 minutes. Percentages of  $Al_2O_3$  extraction yields are given in Figure 5.

As can be seen from Fig.5 in the leach process at room temperature, the more calcination and leach time increases, the more %  $Al_2O_3$  extraction yield increases. Depending on the leach time, this increase happens in different steps. When, only 20 and 40 minute calcinations were performed, the yields obtained in the same time were similar. However, percent alumina yields obtained after 80 minute calcinations were observed to be less than that of 60 minute calcinations. This fact was due to the formation of sodium aluminum silicates as calcinations time increases, which bonded

alumina in the solid phase and were insoluble in liquid phase. Considering leach process performed at room temperature, it is noticeable that even in 15 minute calcination time, more than 60 % alumina yield was obtained. This result shows the formation of alkali aluminates in solid phase ( $Na_2O \cdot Al_2O_3$  ve  $3CaO \cdot Al_2O_3$ ) which can easily dissolve in alkali solution.

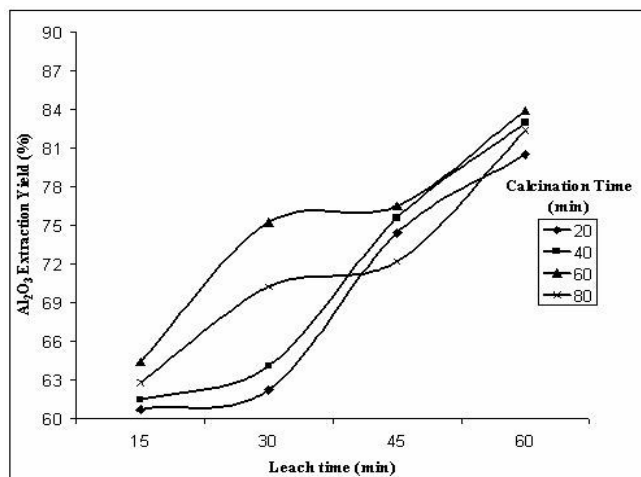


Figure 5. Effect of calcinations and leach time on alumina extraction yield at 25 °C

%  $Al_2O_3$  extraction yields of the products calcined at the same conditions, obtained after the leach process performed at 50 °C for 15, 30, 45 and 60 minutes are shown in Fig.6.

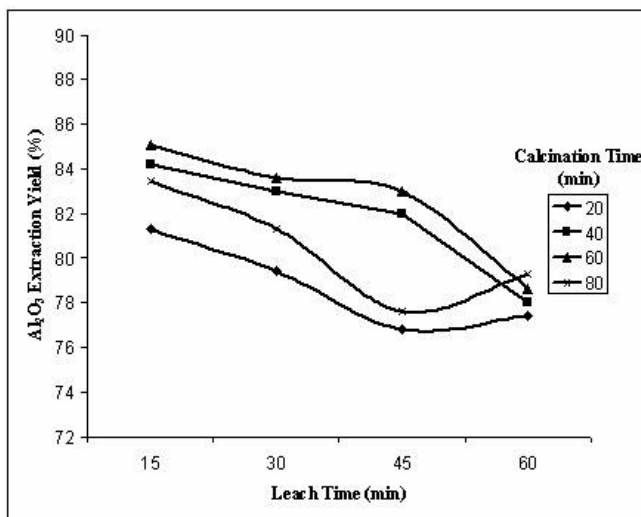


Figure 6. Effect of calcinations and leach time on alumina extraction yield at 50 °C

As can be seen from Fig.6, compared to the room temperature leach process, alumina extraction yields were much higher in the studies performed at 50 °C. It is well

known that the temperature improves the dissolution and the speed of solid-liquid phase reactions. As a result, it is natural to have high yields. Here, in contrast to the previous one, as leach time increased, the % alumina yield decreased. On the other hand, as calcination time increased, the % yield increased as seen previously.

However, 80 minutes calcination time affected alumina extraction yield in a negative way. This was obviously due to sodium aluminum silicate which formed in solid phase but did not dissolve in aqueous solution. It was also the case at 75 and 100 °C. Considering there was high amount of silica (20.86 %) in the sample, even if a large part of it were dissolved, it would still be impossible to reach that high yields. Because 2 mole-g silica can carry at least 1 mole-g alumina to the red mud as a solid form. The reason for the high alumina yields higher than 76 % was the formation of calcium silicates in the solid phase with added CaO during calcination, therefore, silica's solubility in alkali solution is decreased [14].

Figure 7 shows the percentages of Al<sub>2</sub>O<sub>3</sub> extraction yields obtained from the leach process performed at 75 °C and in different leach times.

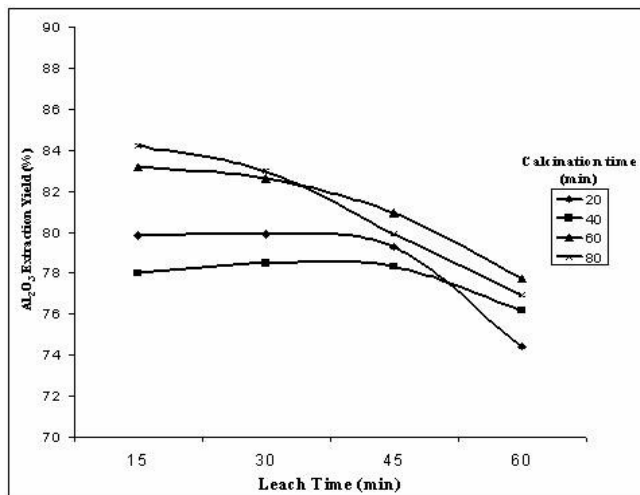


Figure 7. Effect of calcinations and leach time on alumina extraction yield at 75 °C

As can be seen from Fig.7, calcination time increased the alumina extraction yield. However, for products calcined for 60 and 80 minutes, the more the leach time increases, leach yield decreased. This can be explained by the fact that, as temperature increased, some silica which passed to the solution as sodium silicate could easily form sodium alumina silicate solid precipitates which was not possible at lower temperatures.

In Figure 8, the percentage of Al<sub>2</sub>O<sub>3</sub> extraction yields obtained from the leach process performed at 100 °C for the same leach times above are shown.

Similar results were obtained from 100 °C process compared to 50 and 75 °C processes. While increased calcination time usually increased the yield, it was decreased by increased leach time. High amount of silica in the mineral forms sodium aluminum silicate precipitates at high temperatures by time.

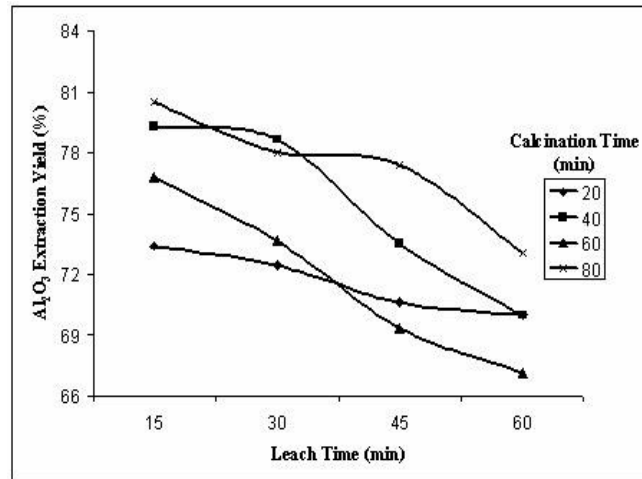


Figure 8. Effect of calcinations and leach time on alumina extraction yield at 100 °C

#### 4. CONCLUSIONS

Approximately 70 % of all grains in the bauxite sample used in this study, grinding -100 μm, was found to be smaller than 53 μm. The alumina content of the mineral was found to be 27.43 % by chemical analysis. X-ray diffraction studies showed that this alumina was bound to diasporite. Similarly, it was found that there was 28.57 % hematite (Fe<sub>2</sub>O<sub>3</sub>) and 20.86 % silica (SiO<sub>2</sub>) in the form of quartz, kaolin and muscovite in the mineral. Besides, there were CaO in the form of calcite and titanium oxide in the form of anatase. Between 12-15 % mass loss due to dehydration and decomposition was calculated both by static and dynamic calcination studies.

The maximum extraction yield on aluminum extraction studies performed with equal mol fraction alkali contribution was obtained at 50 °C leach process. At higher temperatures the amount of SiO<sub>2</sub> transferred to the solution increased. During the process, silica in the liquid phase binding alumina to itself as sodium alumina silicate passed to the solid phase leading to decrease in alumina extraction. While long calcination time increased Al<sub>2</sub>O<sub>3</sub> extraction at the initial phase of leach process, increasing the leach time decreased the extraction yield. Similar situation was valid for higher temperatures. This fact showed that, sodium

aluminum silicate forms much easily at high leach temperatures in liquid phase.

Reaching such high alumina yields even at room temperature solution process, shows the formation of alkaline aluminate structure during calcination process which is easily soluble in alkaline liquid solvent. This study executes the availability of obtaining high alumina extraction yields from low grade bauxite minerals with high amount of silica, which are not readily used for alumina production.

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