

EXTRACTION OF ALUMINA FROM IRAQI COLORED KAOLIN BY LIME-SINTER PROCESS

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ABSTRACT

In this work lime -sinter method was investigated to recover alumina from Iraqi colored kaolinitic claystone. The claystone was intimately mixed with limestone and the mixture was sintered. The annealed sintered material dusts to a fine powder which required no grinding. This material was leached with sodium carbonate solution, and an alumina extract (sodium aluminate solution) was obtained. By bubbling carbon dioxide gas into this extract solution, gibbsite $[Al(OH)_3]$ precipitated and on calcinations at $1350\text{ }^\circ\text{C}$, alumina in the form of alpha ($\alpha - Al_2O_3$) of high purity (98%) can be obtained. In the course of this investigation, the effect of sintering temperature and time, concentration of sodium carbonate solution, leaching time and sintered powder to sodium carbonate solution ratio were studied. About 85% of the alumina in the claystone was extracted at the optimum conditions. The alumina obtained in this method assaying 98% Al_2O_3 , 1.45% SiO_2 , 0.04% Fe_2O_3 , and 0.13% CaO and, 0.15% Na_2O .

استخلاص الألومينا من أطيان الكاؤولين العراقية الملونة بطريقة التلييد مع النوره

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المستخلص

في هذا العمل جرى البحث لاستخدام عملية التلييد مع النوره لاستخلاص الألومينا من أطيان الكاؤولين العراقية الملونة، بمزج الكاؤولين مع حجر الكلس بشكل جيد و تلييده في فرن كهربائي وعند تبريد المادة الملبدة تنفتت ذاتياً الى مسحوق ناعم دون الحاجة للجوء لعملية الطحن. ويتم معاملة هذا المسحوق مع محلول من كاربونات الصوديوم لإذابة واستخلاص الألومينا بلهرار غاز ثاني أوكسيد الكاربون خلال محلول الاستخلاص الناتج من الإذابة يترسب هيدروكسيد الألومنيوم $[Al(OH)_3]$ والذي بعد حرقه عند درجة حرارة $1350\text{ }^\circ\text{C}$ يتحول الى الومينا من نوع الفا ($\alpha - Al_2O_3$) في هذا البحث تم دراسة تأثير كل من العوامل (درجة حرارة، زمن التلييد، تركيز محلول كاربونات الصوديوم، زمن الإذابة ونسبة مسحوق المادة الملبدة الى محلول كاربونات الصوديوم) على نسبة استخلاص الألومينا. وعند الظروف المثلى أمكن استخلاص حوالي 85% من الألومينا الموجودة في الكاؤولين. المواصفات الكيميائية للألومينا المستحصلة بهذه الطريقة هي:

Al_2O_3 98%, SiO_2 1.45%, Fe_2O_3 0.04%, CaO 0.13% and Na_2O 0.15%

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INTRODUCTION

Bauxite deposits are considered the main source for alumina production by Bayer process that uses a caustic hot pressure leach of the ore. The process, however, is tightly bound to high-grade bauxite particularly with respect to silica (SiO_2) content, which should be of less than 7% (O'Connor, 1988). Currently, only few of this quality bauxite being utilized, and most of which being controlled by world's largest aluminum producing concerns. As a result, interest has been focused on a local alternative source of alumina raw materials other than bauxite such as nephelin, kaolin, fly ash, etc. for alumina production. Obviously, this change in the pattern of source material and their geographic location of supply would augment the industrial strength of the producing countries.

However, our domestic clays of the kaolin type are a potentially immense source of alumina that warrants research into methods for alumina production. To date, many processes for extracting alumina from clays have been investigated (O'Connor, 1988; Smith, 2008, and Bai *et al.*, 2010). Generally two processes were classified for extracting alumina from clays; **1**) an acid process that uses sulfuric acid, hydrochloric acid, or nitric acid to selectively dissolve the alumina, usually after the clay has been roasted (James *et al.*, 1982; Al-Ajeel *et al.*, 1993; Claude *et al.*, 2005; Zahrani and Abdul Majeed, 2009, and Ajemba and Onukwuli, 2012), and **2**) an alkali process that uses water or a dilute alkali to selectively dissolve the alumina from a sintered mixture of lime and clay or lime, soda and clay (Flint *et al.*, 1947; Kapolyi *et al.*, 1980; Grzymek *et al.*, 1989; DeCarlo *et al.*, 1991, and Bai *et al.*, 2010).

Occurrences of kaolin clays in Iraq are vast, particularly that of Al-Hussayniat colored kaolinitic claystone (averaging about 8% Fe_2O_3) located in the Western Desert. Therefore, research is needed on this clay as a possible source of alumina. The method adopted for this investigation is the lime sinter process.

In brief, the lime sinter process consists of the following sequential steps: **1**) Mixing ground siliceous alumina bearing ore (such as clay) with ground calcium carbonate in proportions to give after sintering at a suitable temperature (of a round 1350 C) a mixture corresponding to the composition of dicalcium silicate ($2\text{CaO}.\text{SiO}_2$), and calcium aluminate compounds (mainly as $12\text{CaO}.7\text{Al}_2\text{O}_3$), and ($\text{CaO}.\text{Al}_2\text{O}_3$) **(2)** Leaching of the calcium aluminate compound by dilute sodium carbonate solution in such a manner as to dissolve alumina (in the form of sodium aluminate) and leave nearly all undissolved silica, lime, and any other materials present in the sintered material, **(3)** Treating the sodium aluminate solution with carbon dioxide to precipitate alumina trihydrate (gibbsite) and regenerate the sodium carbonate solution, which can be recycled, and **(4)** Calcining the gibbsite at 1350 °C to produce alumina (Al_2O_3) of alpha (α) phase (Grzymek *et al.*, 1989).

MATERIALS AND METHODS

▪ Materials

The raw materials used were Al-Hussayniat red kaolin claystone from Al-Hussayniat region and limestone from Wadi Ghadaf. The chemical composition of the tested samples is given in Table (1). Both deposits are located in the Western Desert of Iraq.

Table 1: Chemical composition of raw materials used in this work

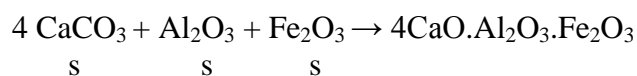
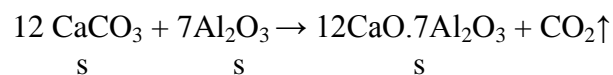
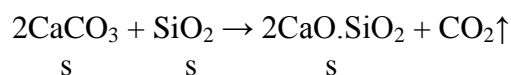
Materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	L.O.I
	(%)								
Kaolin	41.04	33.1	7.8	2.1	0.38	0.41	0.3	0.09	13
Limestone	0.84	0.15	0.06	0.006	54.6	0.14	n.a.	n.a.	42.28

Other materials used include, soda ash (sodium carbonate) and CO₂ gas.

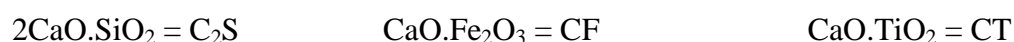
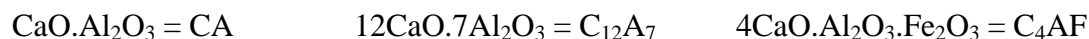
n.a.: not analyzed.

▪ Preparation of Sinter Charge

Based on the chemical composition shown in Table (1), mixture (sinter feed) of ground (pass 75 micron) kaolin and limestone was prepared that, after burning, the composition of the resulting material would contain Al₂O₃ as CaO.Al₂O₃, 12CaO.7Al₂O₃ and 4CaO.Al₂O₃.Fe₂O₃, SiO₂ as 2CaO.SiO₂, TiO₂ as CaO.TiO₂ and Fe₂O₃ as CaO.Fe₂O₃ (Kapolyi *et al.*, 1980; Wenzel and Vamos, 1980 and Grzymek *et al.*, 1989). This means that for each mole of SiO₂ present in the kaolin there must be 2 mol of CaO (CaCO₃) added and approximately 1.7 mol of CaO for each mole of Al₂O₃ and so on for other compounds. The equations below describe the primary reactions involved.



For simplicity, the compounds will be abbreviated as below:



The kaolin and limestone mixture, whose chemical composition is given in Table (2), was heated in electrical muffle furnace under various temperature (1250, 1300 and 1350 °C) and time (30, 45 and 60 min). Once the time of heating (sintering) elapsed, the furnace was allowed to cool down for annealing of the sintered material to achieve self-disintegration (or powdering). The process of self-powdering was followed by shifting the material on 325 mesh (45 micron sieve opening) ASTM sieve. This would determine the degree of the sinter mass described and in turn alluded for the sintering efficiency. Portion of the self-disintegrated sintered material was then drawn out for chemical and mineralogical analysis.

Table 2: Chemical composition of raw materials mix in (wt %)

SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	MgO	L.O.I
(%)						
14.06	2.8	9.4	0.7	37.5	0.27	33.14

▪ Extraction of Alumina

Alumina extraction from the finally powdered (self-disintegrated) sinter was done with solution containing sodium carbonate, using mechanical stirring sufficiently high (about 600 rpm) to prevent settling. Fifty-gram sample was used in each extraction or leaching experiment that were carried out at 70 °C; the choice of this temperature was based on previous work (Wenczel and Vamos, 1982; Grzymek *et al.*, 1989 and Al-Ajeel *et al.*, 1993). On completion of the reaction time, the insoluble material was filtered, washed, dried and analyzed for Al₂O₃ to determine its extraction percentage. In the course of alumina leaching experiments different concentrations of sodium carbonate solution (50, 60, 70 and 80 g/l), reaction time (15, 30 and 60 min), and solid: liquid ratios (1:3, 1:4 and 1:5) were tested.

The alumina present in the extract solution (mainly in the form of sodium aluminate) obtained from the best conditions studied above was subsequently precipitated as gibbsite [Al(OH)₃] by carbonization (CO₂ gas was bubbled through the solution at a certain rate and time). Carbonization was carried out at solution temperature of 80 °C. The gibbsite was filtered from the solution, washed, dried and then calcined at 1350 °C for (1 hr.) to gain α – alumina (α – Al₂O₃) compound. The produced alumina was mineralogically (XRD) and chemically analyzed to determine its phase type and purity.

RESULTS AND DISCUSSION

▪ Sintering

The objective of this step in the process is to convert the mixed materials (limestone and clay) mainly into (C₂S) and (C₁₂A₇) compounds. Thus alumina can be extracted from the last compound by leaching with dilute sodium carbonate solution. The dicalcium silicate (C₂S), however, plays extremely important role. First, its development is complete enough to tie up nearly all of the silica present in a form not soluble in the leached liquor. Second, it undergoes a crystallographic transformation on cooling with an increase in volume which results in reduction of the sintered mass to a powder, making the soluble alumina compounds easily dissolved by the leach solution without grinding (Kapolyi *et al.*, 1980 and DeCarlo *et al.*, 1991). This phenomenon is commonly called self-disintegration or powdering. In sintering process, tri calcium silicate (C₃S), however, should not form even in small quantities as it is one of the inhibitors of the self-disintegration of the sinter mass (Kapolyi *et al.*, 1973). In the first series or course of the sintering experiments, samples of the mixture (Al-Hussayniat claystone and limestone) were heated at (1250, 1300, and 1350 °C) for 60 min holding time. The powdering or self-disintegration efficiency of the sintered mass was followed up by screening on 325 mesh (45 micron) ASTM sieve. The results are presented in Figure (1).

It can be seen clearly from the data of Figure (1) that, the powdering of the sintered mass is significantly enhanced as the temperature rises to 1350 °C. The weight percentage of the material pass 325 mesh was of 98%. Reducing the sintering time to 30 and 45 min showed a mediocre powdering efficiency. The results obtained indicate that the material that passed through 325 meshes does not exceed 82 wt%. This denotes that a sintering operation at 1350 °C for 60 min would result in almost complete transformation of the silica (SiO₂) in the kaolin to dicalcium silicate (C₂S) which is reflected by the high powdering efficiency (98% of the sintered mass that passed the 325 mesh). The property of self-disintegration of the C₂S, however, is attributed to the crystalline transformation from (β) to (γ) modification that takes place during the course of annealing (cooling) of the sinter mass. Such transformation is accompanied by molar volume increase of about 10%, and the stress created by this volume increase causes the sinter mass to disintegrate into fine powder (Flint *et al.*, 1947; Kapolyi

et al., 1973 and Kapolyi et al., 1980). This phenomena of the C₂S is very advantageous for the extraction of alumina by the lime sinter process, as the grinding of the sintered material, one of the most power consuming operation (Wills, 2006), can be eliminated.

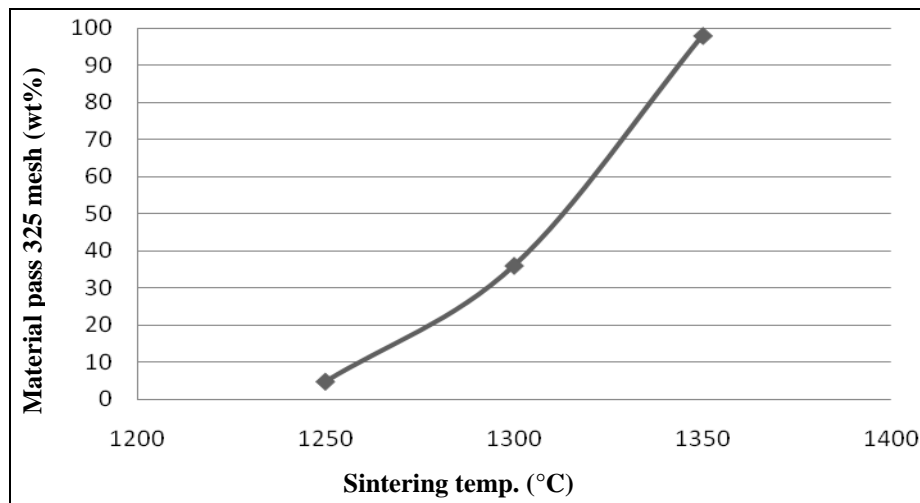


Fig.1: Effect of sintering temperature on the powdering of the produced sintered material

However, the XRD pattern, as well as the chemical composition of the calcium-bearing compounds C₂S, C₁₂A₇, etc. of the produced sinter material formed at the conditions (1350 °C and 60 min sintering time) is shown in Fig. (2) and Table (3).

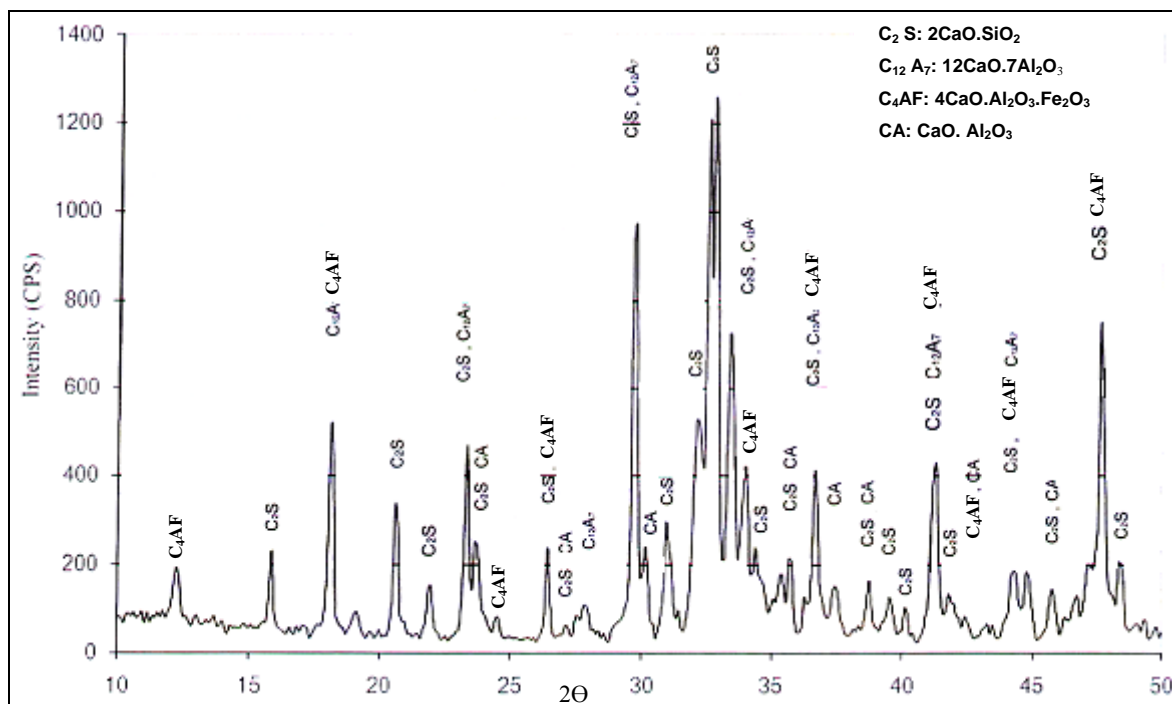


Fig.2: XRD pattern of the self-disintegrated material produced from Al-Hussayniat kaolin with Wadi Ghadaf limestone

Table 3: Chemical composition of the self-disintegrated material produced at (60 min sintering time and 1350 °C)

SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
(%)								
20	4.8	14.23	1.58	57.5	0.53	0.30	0.08	< 0.02

It is obvious from the pattern of the XRD (Fig.2), that the calcium compounds phases formed conform highly were to the calculated amounts of the raw materials (claystone and limestone) fed to the furnace. It can be seen that, the C₂S and C₁₂A₇, which have their impact on the phenomena of powdering of the sintered mass and leachability or dissolution of alumina respectively, were the major phases (compounds) formed. Further the XRD analysis could not show any formation of neither tricalcium silicate (C₃S), which inhibit the disintegration phenomena, or dicalcium alumino silicate (C₂AS) compound which badly influence the recovery of alumina (Wenzel and Vamos, 1982 and Kapolyi *et al.*, 1980).

▪ Alumina extraction

In this course of investigation the action of sodium carbonate solution concentration (50, 60, 70, and 80 g/l) on alumina extraction was studied using solid to liquid (S/L) ratio of 1:4 and 15 min contact time, at a temperature of about 70 °C. The results are presented in fig (3) in term of sodium carbonate solution concentration versus alumina extraction percentages. It can be noted from these data, that the alumina extraction was significantly increased as the solution concentration increased to 70 g/l, and a slight increase in alumina extraction occurred beyond. At the end, it can be claimed that a leaching solution of 70 g/l concentration would be favorable to achieve 82% alumina extraction.

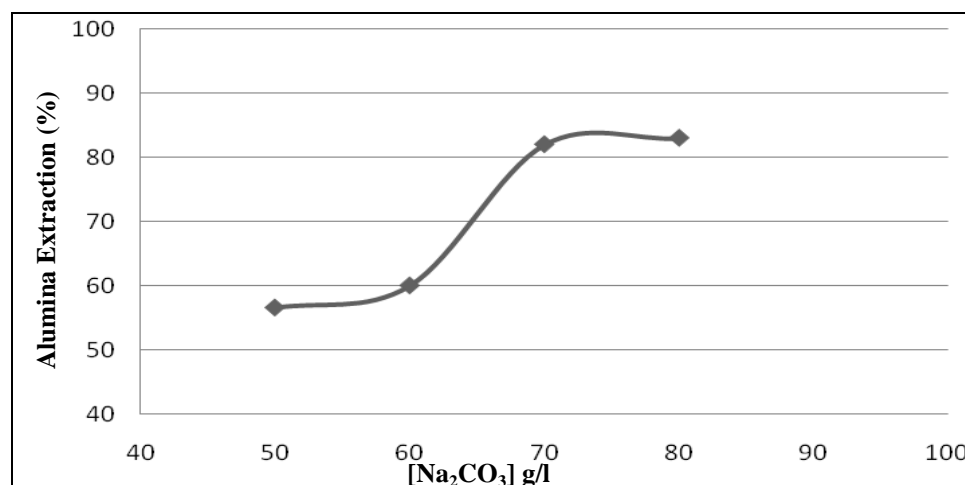


Fig.3: Effect of sodium carbonate concentration on alumina extraction

Next, the effect of increasing or decreasing the (S/L) ratio on alumina extraction was studied. The experiments were conducted at 70 °C, 70 g/l sodium carbonate solution concentration and, 15 min leaching time, whereas the (S/L) ratio was varied up to 1/4 wt/vol (20%) solid and 1/5 wt/vol (about 16.7%) solid. It can be noted from Fig. (4) that, alumina extraction was significantly dropped as the value of S/L ratio becomes to 1/3 wt/vol (25% solid), while it was increased by 3% at a (S/L) ratio of wt/vol 1/5. Accordingly, it can be inferred that, within the prevailing conditions of this set of tests, alumina extraction is directly proportional to the solid to liquid ratio of the reactant. The results (including that of 1/4 S/L ratio) are demonstrated in Fig (4).

Furthermore, the effect of leaching time on alumina extraction was subsequently tested. The tests were carried out at the same conditions mentioned above, and a leaching time of 30 min and 60 min were employed. The results obtained (Table 4) indicate that, the alumina extraction at 30 min reaction time remains at the same level of 85% obtained at 15 min, while at 60 min a slight increase (1%) in alumina extraction is detected. Obviously a contact time of 15 min between the sinter powder and leaching solution would be preferable for the extraction process. However, the reaction involved in the extraction process is shown below:

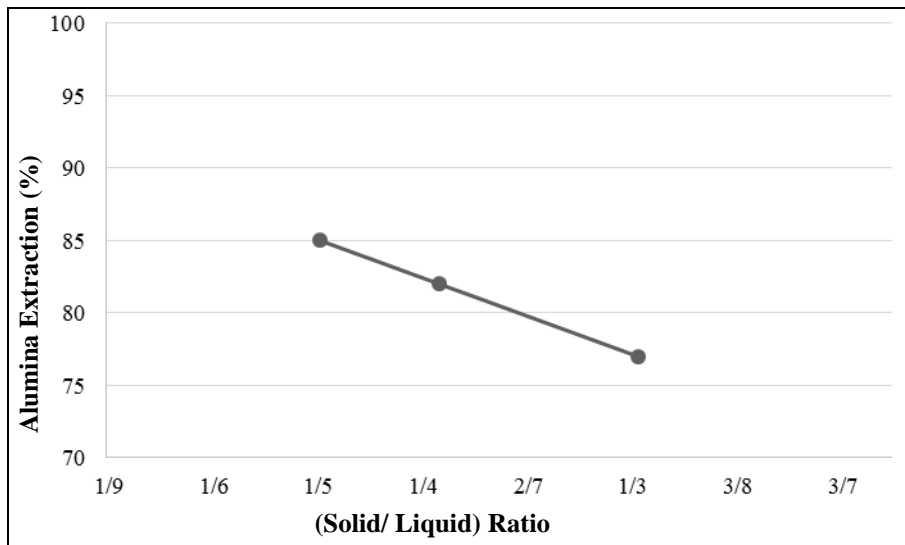
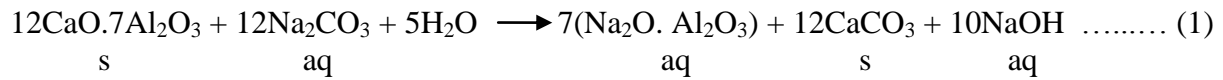


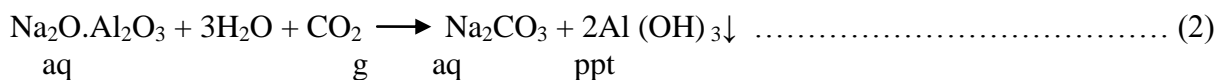
Fig.4: Effect of (solid/ liquid) ratio on alumina extraction

Table 4: Results of Alumina extraction at different reaction time using 1:5 S/L ratio, 70 g/l sodium carbonate solution, and temperature about 70 °C

Reaction Time (min)	15	30	60
Alumina Extraction (%)	85	85	86

▪ **Alumina recovery**

The alumina content in the sodium aluminate solution (Na₂O.Al₂O₃) was precipitated as gibbsite [Al (OH)₃] by bubbling carbon dioxide gas into the solution which was then converted to alumina (Al₂O₃) by calcination at 1350 °C. 99% of the alumina in the solution was recovered in this process. The chemical reactions involved are as below.



The XRD analysis result Fig. (5) reveals that, the precipitated aluminum hydroxide has been completely converted to alpha alumina ($\alpha - \text{Al}_2\text{O}_3$) on heating at 1350 °C for 60 min. The chemical analysis results show (Table 4) that the produced alumina is of a high purity, and this would have a wide field of applications, particularly in refractory industry.

However, the silica content of the produced alumina can be reduced to less than 0.3% by desilication (not included in this work) of the sodium aluminate solution using solution of lime (Flint *et al.*, 1947; Gryzmek *et al.*, 1989 and Bai *et al.*, 2010); consequently a very high purity alumina can be produced.

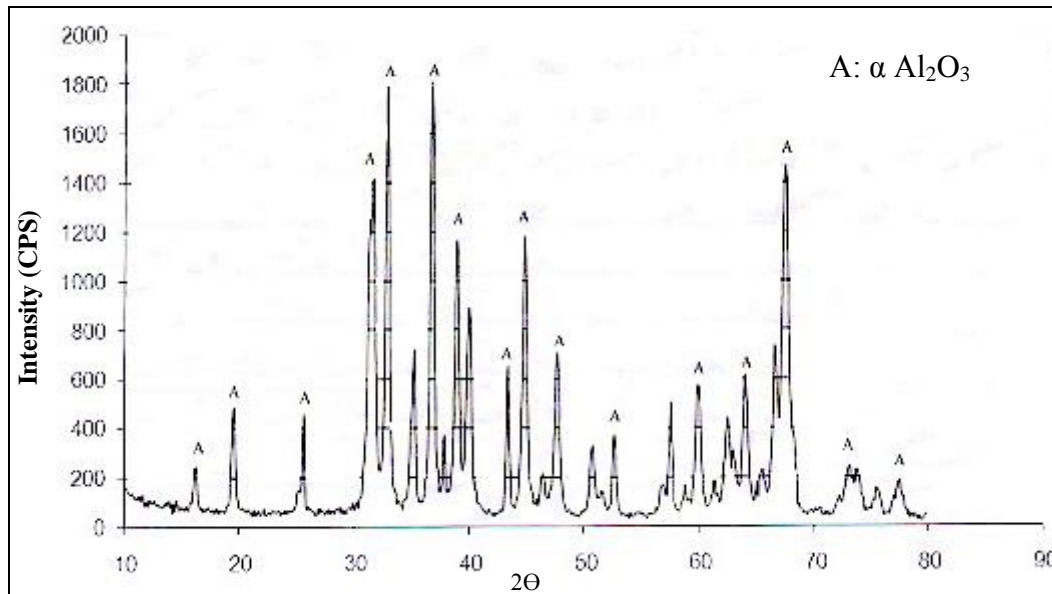


Fig.5: XRD Pattern of alumina produced from Al-Hussayniat kaolin

Table 5: Chemical composition of the alumina obtained in this work

SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	Na ₂ O
(%)					
1.45	0.04	98.05	< 0.02	0.13	0.15

CONCLUSIONS

According to the tests results of this investigation the following conclusions can be highlighted.

- The colored kaolin claystone of Al-Hussayniat deposit can be a potential source to produce high purity alumina by lime – sinter process.
- Conversion of silica content of the raw materials mix (claystone and limestone) into a dicalcium silicate after firing is of great importance for self-powdering of the sintered material.
- Achieving self-disintegration or powdering of the sintered material can eliminate grinding of the produced sinter.
- The favorable operating condition for the sintering of limestone and Al-Hussayniat claystone to produce efficient self-powdering are, firing the materials at 1350 °C for 1 hr.

- The optimum conditions for extracting (85%) alumina from the sintered powder by sodium carbonate solution are:
 - 70 g/l sodium carbonate solution concentration
 - 15 min extraction time
 - 1:5 solid to liquid ratio
 - 70 °C extraction temperature
- The alumina recovery after carbonation and calcinations at 1350 °C is about 85%.

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