

## ALUMINA RECOVERY FROM IRAQI KAOLINITIC CLAY BY HYDROCHLORIC ACID ROUTE

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### ABSTRACT

The extraction and recovery of alumina ( $Al_2O_3$ ) from white kaolinite clay in hydrochloric acid solution was investigated on laboratory scale. The extraction rate was found to increase with calcination temperature (up to a certain limit), calcination time and acid concentration. Under optimum conditions of 720°C calcination temperature for 45 min with 28% HCl, by weight and 45 min leaching time at 100°C, alumina extraction was about 99 %. The recovery of alumina by gas (Hydrogen Chloride) precipitation technique has proven satisfactory and it was of about 93%, with purity of about 99.98%  $Al_2O_3$ . This purity of the produced alumina was found in accordance with that of commercial grade, which is in the range of (99 – 99.5)%  $Al_2O_3$ .

### استرجاع الالومينا من أطيان الكاؤولين العراقية بطريقة حامض الهيدروكلوريك

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#### المستخلص

تناول هذا البحث الذي اجري على نطاق مختبري لاستخلاص واسترجاع الالومينا ( $Al_2O_3$ ) من أطيان الكاؤولين العراقية الأبيض باستعمال محلول حامض الهيدروكلوريك ولقد تبين ان نسبة الاستخلاص تزداد بازدياد زمن ودرجة حرارة الكلسنة ( لحد معين ) وكذلك تركيز حامض الهيدروكلوريك . تحت الظروف المثلى التي تم التوصل إليها من درجة حرارة الكلسنة 720 °م ، بزمن الكلسنة 45 دقيقة و تركيز حامض 28 % HCl وزناً وبزمن تفاعل 45 دقيقة بدرجة 100 °م أمكن استخلاص الالومينا بنسبة تصل الى حوالي 99%. ولقد بينت عملية استرجاع الالومينا بتقنية الترسيب بغاز كلوريد الهيدروجين كفاءتها وكانت نسبة الاسترجاع بحدود 93% وبنقاوة تصل إلى حوالي 99.98 %  $Al_2O_3$  وهي مطابقة لمواصفات الالومينا التجارية والتي هي بمدى (99 – 99.5) %.

### INTRODUCTION

More than 90% of the world's commercial production of alumina is obtained by hydrochemical sodium hydroxide extraction of bauxite using the conventional Bayer Process. In this process it is uneconomical to treat bauxite containing more than 7% reactive silica, due to excessive alumina and soda losses (Connor, 1988). Such quality of bauxite deposits are fairly rare and most of those available being controlled by world's largest aluminum manufacturing concerns. Intensive research and engineering effort has been carried out in many countries on the alumina extraction from a variety of naturally occurring non-bauxitic materials such as laterites, clay, aluminous shales, nepheline, alunite and fly ash. A range of

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acid and alkali hydrometallurgical processes have been proposed as routes for extraction of alumina. Acid rather than alkali processes are preferred for treating aluminum silicates and especially for processing of kaolinitic material.

Kaolinite is a two layer silicate mineral that typifies the kaolin group, it may be represented by  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  (Grim, 1968). The structure is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer. The structural units are held together in the basal plane by hydrogen bonding between oxygen ions of the tetrahedral sheet and hydroxyl ions of the octahedral sheet.

Thermal treatment of clay in the temperature range (500 – 900)C° is necessary to render alumina soluble (Phillips and Wills, 1982 and Gajam and Raghavan, 1985). The process is generally thought to increase clay reactivity by affecting dehydratation transformation of the kaolinite to amorphous metakaolinite ( $\text{Al}_2\text{SiO}_7$ ), which is known to be more reactive and render alumina easily extracted by acid or alkali (Connor, 1988; Phillips and Wills, 1982).

Various mineral acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_3$  and  $\text{HNO}_3$ ) for alumina extraction have been investigated (Peters et al., 1962 and 1963; Hulbert and Huff 1970; Bengston 1979; Gajam and Raghavan, 1985 and Hammodi and Abdulla, 1987). Among these, hydrochloric acid has several advantages over other acids, particularly for processing pure kaolinitic clay (Connor, 1988). These include the ease of filtration of digestion liquors, ease of iron removal, ease of recovery of the acid, but corrosion can be a problem.

Nevertheless, optimum acid leaching conditions for extracting alumina from non-bauxitic materials depends on the mineralogical and chemical analysis of the materials. The objective of the work presented here is to investigate the hydrochloric acid treatment of Iraqi white kaolin from Duwaikhla Mine, to propose an understanding of the mode of the extraction process and the recovery of alumina as an alternative to the sulfuric acid route, which was carried out by Al-Saadi and Al-Azzawi (1982) on this local material.

## **MATERIALS AND METHODS**

The raw kaolinitic clay sample that used in this work assaying 33.3 %  $\text{Al}_2\text{O}_3$ , 50.5 %  $\text{SiO}_2$  and 0.98 %  $\text{TiO}_2$ . The X-ray diffraction data indicate that it is composed mainly of kaolinite and quartz (Fig. 1 a). The X-ray patterns were obtained with Phillips PW 1890 X-ray diffractometer, Ni filtered  $\text{CuK}\alpha$  radiation (all the analysis was carried out in the laboratories of the State Company of Geological Survey and Mining). Calcination of the clay samples was carried out in a laboratory rotary electrical furnace for a predetermined temperature and time.

Leach tests have been conducted in a glass vessel using acid concentrations of ( 22, 24, and 28%  $\text{HCl}$  by mass ) for reaction times of 15, 30 and 45 min at reaction temperature of  $100\text{C}^\circ \pm 5^\circ$  (heating was effected by a hot plate). At the

end of each test the slurry was filtered and the filtrate chemically analyzed for  $\text{Al}_2\text{O}_3$ . The filtrate containing aluminum salt was then injected by HCl gas to precipitate the aluminum salt ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ). The salt was separated, dried and ignited at  $1000^\circ\text{C}$  to form alumina ( $\text{Al}_2\text{O}_3$ ). The alumina was weight and analyzed for  $\text{Al}_2\text{O}_3$ .

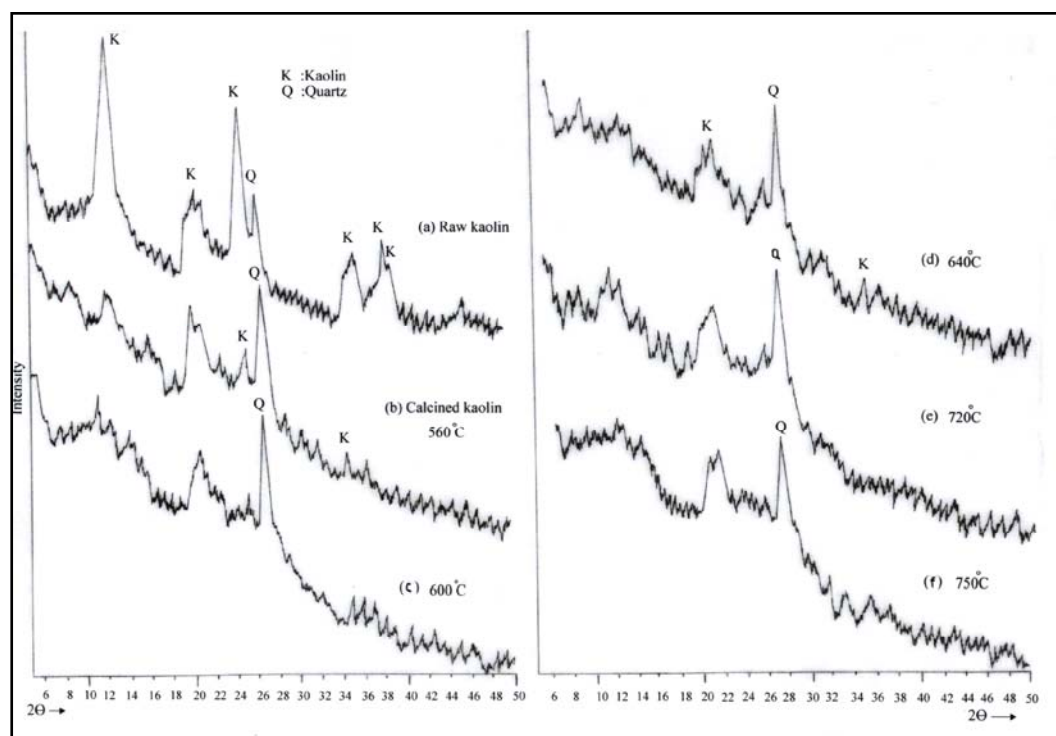


Fig. (1): (a, b, c, d, e, and f) X-Ray diffraction pattern for raw kaolin (a) and that calcined (b-f) at (560, 600, 640, 720, and 750  $^\circ\text{C}$ ) for 45 min

## RESULTS AND DISCUSSION

### Calcination of kaoline

The X-ray diffraction patterns of raw clay sample and those calcined at different temperatures (560–750) $^\circ\text{C}$  are shown in (Fig.1 a – f). These patterns indicate that the kaolinite of the raw clay tested is of a well crystalline order (as it can be seen at  $2\theta$  value of  $35^\circ - 40^\circ$ ) and as a consequence of the calcination a marked change in the crystallinity occurred. Figure (1e) shows that the clay crystallinity was highly reduced and it becomes amorphous at  $720^\circ\text{C}$ . This amorphous phase is commonly referred to as met kaolin (Gajam and Raghavan, 1985). Further calcination at  $750^\circ\text{C}$  resulted in a minor recrystalline phase formation of aluminum silicate as can be seen clearly in (Fig .1f).

**Leach tests**

The first series of leach tests, to extract alumina was carried out on clay samples that had been calcined at 560C° and 600C° for periods of 30 min and 45 min each. The effect of leaching time and acid (HCl) concentration on alumina extraction are shown in Fig. (2 a and b) and Fig. (3 a and b). Generally, these figures indicate that the percentage of alumina extraction increases as both leaching time and acid concentration increases. The highest value achieved was at 45 min leach time with 28% HCl concentration. Direct comparison of the data at 30 min and 45 min calcination time reveals that for the 560C° calcination temperature (Fig.2 a and b), alumina extraction was slightly enhanced as the time increases from 30 to 45 min. The extraction percentage was found about 93% and 94 %, respectively. For the 600C° calcination temperature (Fig.3 a and b), the results were nearly the same with alumina extraction of 94%.

The second series of experiments was carried out to optimize the calcination temperature. In this aspect, three different calcination temperatures 64C°, 720C° and 750C° were chosen. The samples which were calcined at these temperatures for periods of 30 min and 45 min, were reacted with 28% HCl for 45 min at 100C°. The results of alumina extraction of these tests with that obtained from the first test series, are presented in Fig. (4). From this figure it can be clearly seen that for both calcination times (30 and 45 ) min, the alumina extraction increases with increasing calcination temperature up to 720C° and then marginally decreases with increasing temperature to 750C°. Perhaps this can be attributed to the crystallographic changes that occur in the clay structure during the heat treatment (Fig.1 a and f), which indicate that the kaolinite became completely amorphous phase at 720C°, which is more reactive and easily leached by acid (Phillips and Wills, 1982). It can be claimed from these results that, if the clay is calcined at 720C° for 45 min, almost 99% of the alumina can be extracted. Therefore, these conditions can be considered as optimum for the extraction process that carried out in this work.

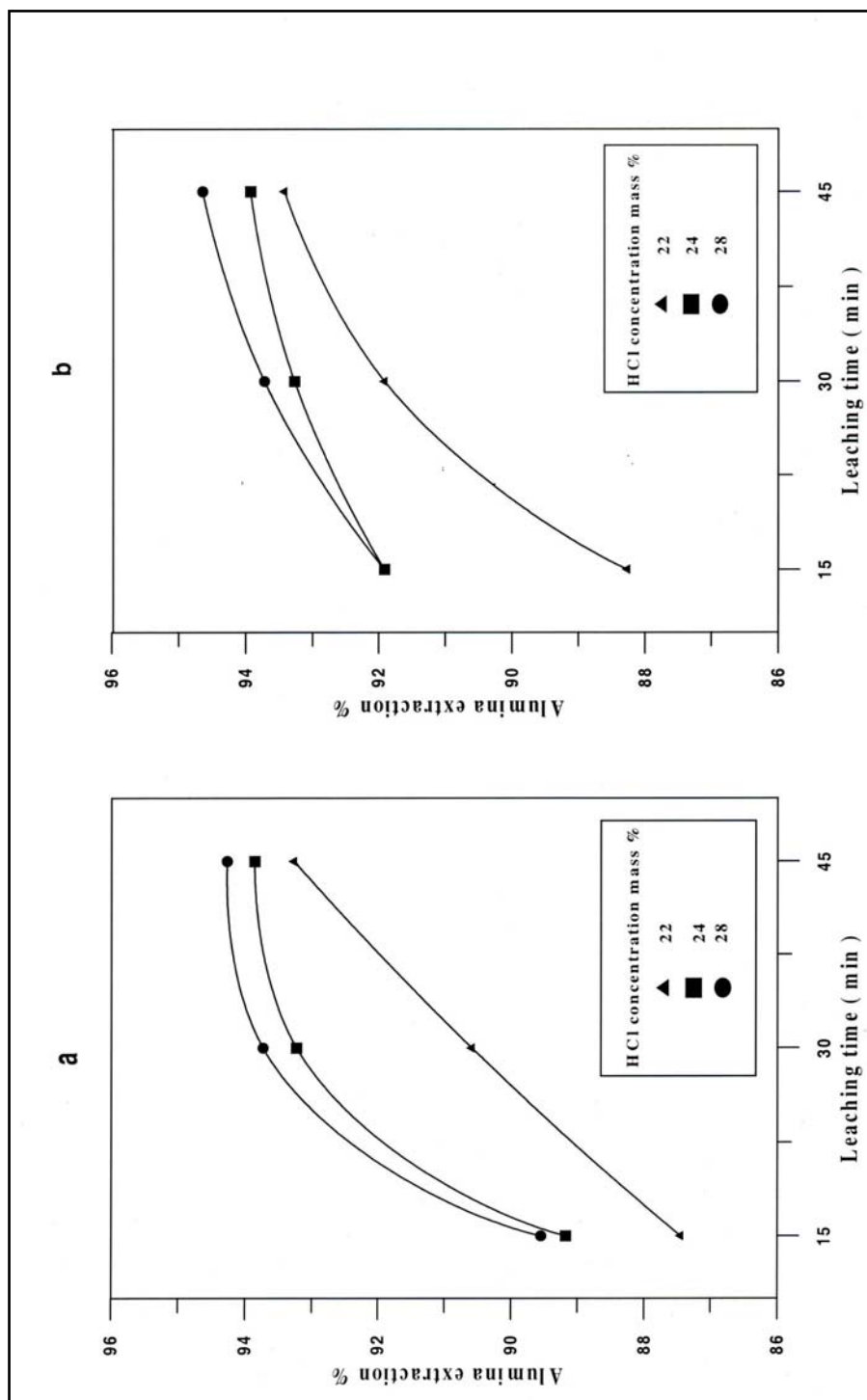


Fig. (2): Effect of leaching time with different HCl concentrations (mass %) on alumina extraction from clay sample calcined at 560 C° for 30 min (a) and 45 min (b)

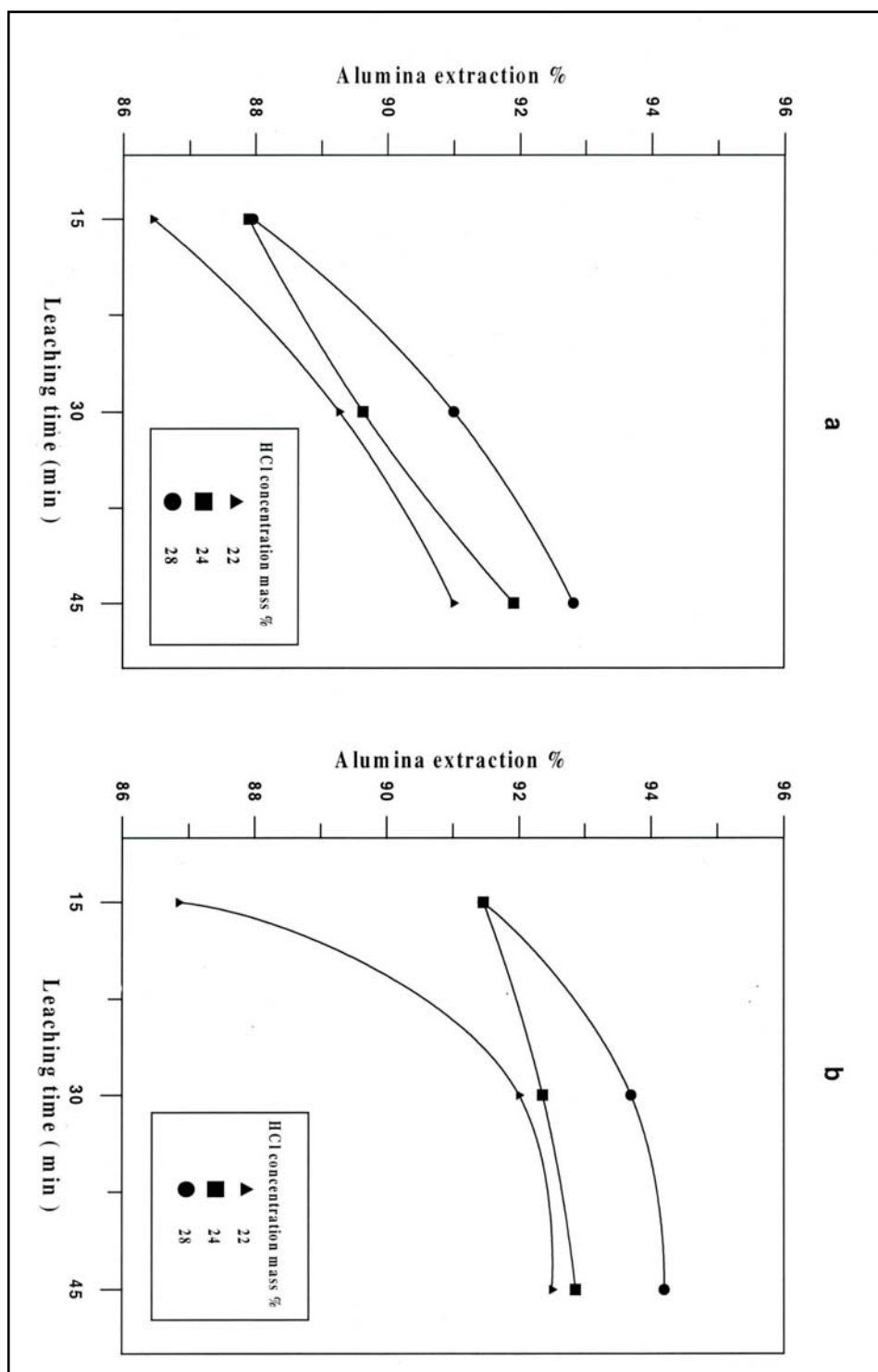


Fig. (3): Effect of leaching time with different HCl concentrations (mass %) on alumina extraction from clay sample calcined at 600°C for 30 min (a) and 45 min (b)

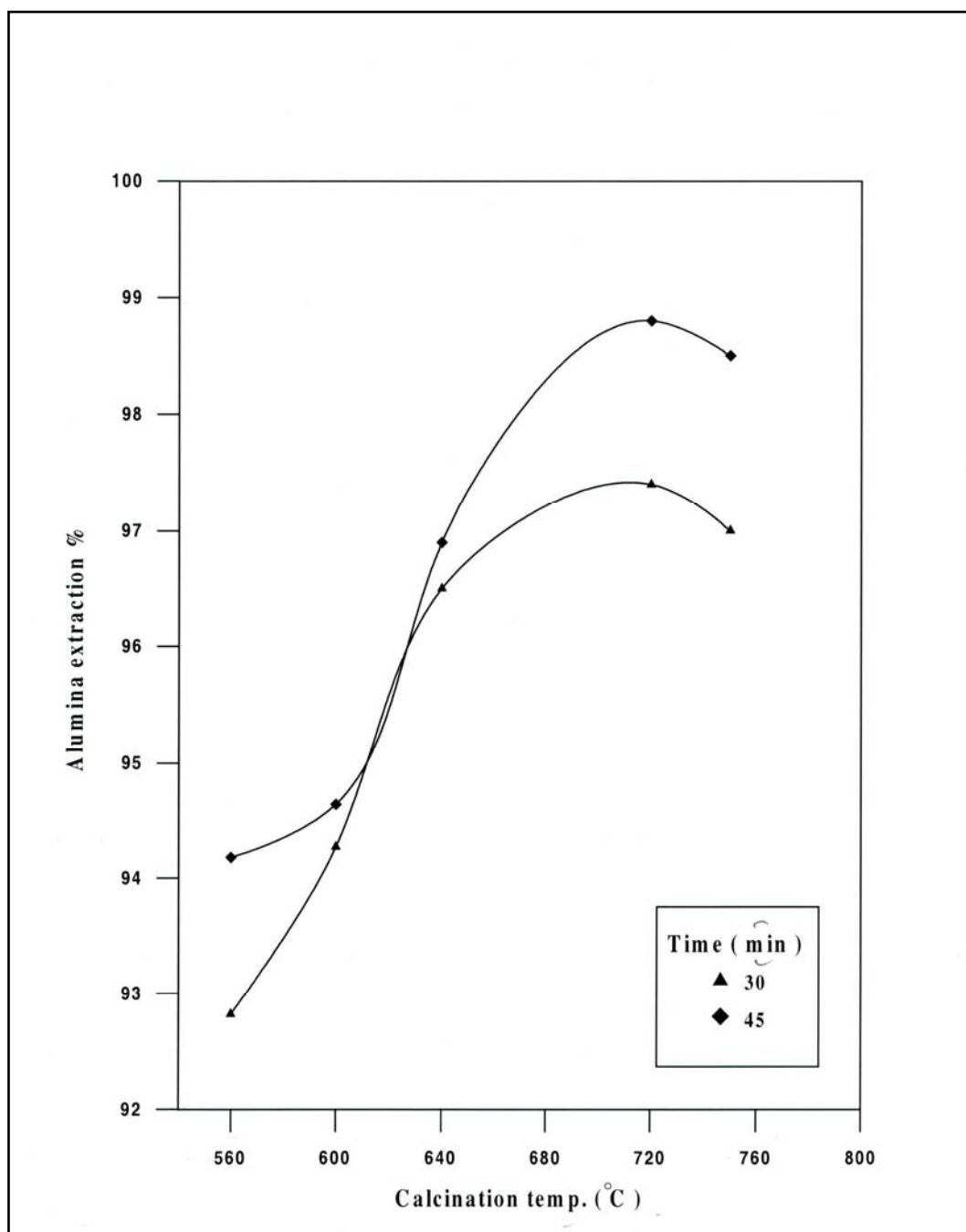


Fig. (4): Alumina extraction from clay samples calcined at different temperatures for 30 and 45 min (28 % HCl and leaching time 45 min)

**Alumina recovery**

The main principle of alumina ( $\text{Al}_2\text{O}_3$ ) recovery by gas injection crystallization precipitation is simple in a way, that the crystallization of aluminum trichloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) is based on its decreasing solubility with increasing HCl concentration (Lowry and Cavin, 1949 and Peters et al., 1962). This method of separation is very selective for  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  precipitation and hence all the impurities (especially that of iron) will remain in solution and removed by filtration and washing of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  crystals.

HCl gas was injected into the leach solution (composed mainly of  $\text{AlCl}_3$  and  $\text{FeCl}_3$ ) at a certain flow rate for different length of time 10, 20 and 30 min, to assess the effect of gas injection duration on aluminum chloride salt precipitation and hence alumina recovery. The results of alumina recovery with respect to the gas injection time are shown in Fig. (5). It can be seen clearly from this figure that the recovery of alumina increases as the gas injection time increases, up to a certain limit 20 min and it remains unchanged with further increase in time to 25 min. Thus, it can be concluded that within the range of experimental conditions employed, the highest value of alumina recovery was of about 93% at 20 min injection time of the hydrogen chloride gas into the aluminum chloride solution. The chemical analysis of the produced alumina showed that it is of a high grade (99.9 %  $\text{Al}_2\text{O}_3$ ) as compared with that of commercial one, which is in the range of (99 – 99.5 %)  $\text{Al}_2\text{O}_3$  (Douglas, 1974).

However, from the work of Al-Sa'adi and Al-Azzawi (1982) which was conducted on the same kaolin (Duwaikhla white kaolin) using sulfuric acid ( $\text{H}_2\text{SO}_4$ ), it was found that the produced alumina (by evaporation and crystallization of the aluminum sulfate solution and heat treatment at  $1200^\circ\text{C}$ ) have a low purity. The  $\text{Al}_2\text{O}_3$  percentage does not exceed 87%, and subsequent treatment is necessary to arrive at the required grade level. The alumina recovery was also low, which is about 84%. Table (1) shows the chemical analysis of the alumina produced in this study and that obtained by Al-Sa'adi and Al-Azzawi (1982), as compared with the commercial grade (Douglas, 1974). It is clearly apparent from this table that the alumina produced from this study (by HCl) is of a very high purity as compared with that produced from the previous study using  $\text{H}_2\text{SO}_4$  (Al-Sa'ady and Al-Azzawi, 1982) and in accordance with that of commercial grade.



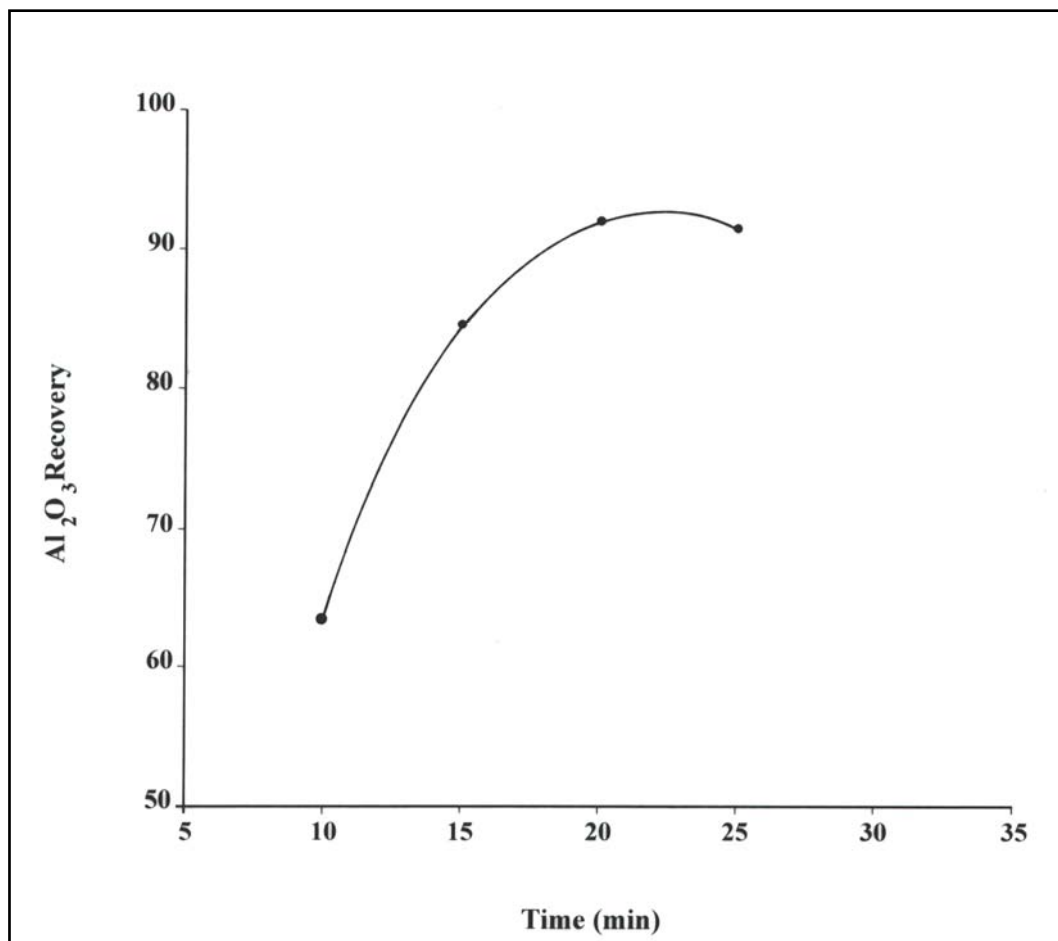


Fig. (5): Effect of gas injection time on alumina recovery (gas flow rate =  $0.0025 \text{ m}^3/\text{min}$ )

Table 1: Chemical analysis of the alumina produced from Iraqi white kaolin and that of commercial grade

Type of alumina	wt %				
	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Zn
Produced in this study (HCl – route)	99.98	0.007	Nil	Nil	Nil
Produced in previous study (H <sub>2</sub> SO <sub>4</sub> – route)	87.1	3.03	2.6	0.01	N.D
Produced commercially	99 – 99.5	0.005 – 0.03	0.005 – 0.01	0.005	0.03 – 0.01

## CONCLUSIONS

From the experimental conditions employed in this study, it can be concluded that:

- The crystallinity of Duwaikhla white kaolin is consecutively reduced as the kaolin calcined at temperature range (560–750)C° and it becomes highly amorphous at 720C°.
- Calcination temperature and calcination time, besides hydrochloric acid concentration and leaching time have a pronounced effect on the alumina extraction.
- Calcination of raw kaolin at a temperature of about 720C° render almost 99% of its alumina soluble in hot (100C° ± 5°) 28% HCl (by mass) within 45 min reaction time.
- High grade alumina can be prepared satisfactorily by using HCl gas injection precipitation method.
- Alumina recovery of about 93% with purity of 99.98% can be achieved at 20 min HCl gas injection.

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