



## Utilization of Kalapsha Kaolin to Prepare High Purity Alumina

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**K**ALABSHA kaolin was calcined at 700°C then treated with hydrochloric acid to produce aluminum chloride hexahydrate. The hexahydrate was obtained in crystalline form through injection of hydrogen chloride gas in saturated solution and purified on several steps to obtain alumina of high purity. Acid leaching conditions, namely, acid to kaolin stoichiometric ratio(S), reaction time (*t*) and reaction temperature (*T*) were optimized using surface response methodology. A maximum alumina recovery of 83.2% was predicted on using 1.4 stoichiometric acid to solid ratio, a reaction temperature of 104°C and a reaction time of 3 hours. This result was then assessed experimentally. The hexahydrate crystals obtained were subsequently purified in a three stage process to increase their purity to 99.961%. Calcination of these crystals for 4 hours at 1100°C produced highly crystalline alumina with purity 99.9%.

**Keywords:** Alumina, Kaolin, Leaching, HCl, Statistical Study, Crystallization, Calcination.

### Introduction

For a long time, alumina has been widely used in diverse fields such as refractory material [1, 2], a source of aluminum [3], as abrasive material [4, 5], in the ceramic industry [6] and in the glass industry [7]. Alumina also found applications in bone prostheses [8] and as catalyst in some industrial reactions [9, 10].

In the past few decades, high purity alumina has emerged as an excellent electrical insulator [11], as an insulating substrate for the deposition of printed circuits [12], in lithium batteries [13] and an essential component in the manufacture of light-emitting diode (LED) lenses and light appliances in its transparent form [13].

Traditionally, the most widely used method for the preparation of commercial alumina has been the Bayer process. In that process, bauxite (hydrated alumina ore) is treated with NaOH to produce soluble aluminate. This solution, when hydrolyzed, produces aluminum hydroxide which can then be calcined to alumina [3]. In Egypt, this

is hardly a feasible method, owing to the rarity of bauxite ores. Consequently, research has been directed towards the production of alumina from one of the most available local ores, namely kaolin.

Acid leaching of calcined kaolin has been studied by a number of authors using different acids. In an early work, Ford [15] investigated the kinetics of leaching of calcined Natal kaolin (South Africa) in sulfuric acid. He deduced activation energy of 67.4 kJ.mol<sup>-1</sup> for the process and assessed the possibility of describing the reaction by a shrinking core model. A different value for activation energy was obtained by Godswill [16] on studying leaching of Ukpok and Udi kaolin samples (Nigeria) by sulfuric acid (17.76 kJ.mol<sup>-1</sup> and 20.39 kJ.mol<sup>-1</sup> respectively) suggesting the pronounced effect of the kaolin origin on activation energy of the leaching reaction. This author also determined the activation energy of dissolution in nitric acid as 20.11 and 22.71 kJ.mol<sup>-1</sup> for both clay types respectively. A similar figure was obtained recently by Lima et al [17] on investigating the kinetics of nitric acid leaching

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of a Brazilian type of kaolin. They also found out that the process is controlled by reaction at interface between solid and liquid phases. On the other hand, leaching with phosphoric acid was researched by Hernández et al [18] working on a Mexican type of kaolin (Hidalgo).

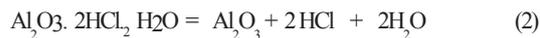
Their purpose was bleaching of kaolin for use in ceramic and paper industries. They obtained an iron removal of 98% on using 3M acid after 2 hours at room temperature. Besides, some other workers tried leaching experiments using organic acids which were less successful in accomplishing a high yield of aluminum salt product through proper removal of iron impurities [19, 20].

Leaching of calcined kaolin by hydrochloric acid was researched by Godswill [16] who suggested an Erofeev type relation to interpret the dissolution kinetics of his samples. He reported activation energy of about  $19.6 \text{ kJ}\cdot\text{mol}^{-1}$  for the reaction. On the other hand, Dong et al [21] used mechanical activation by ball milling to study its effect on the leaching process by HCl (20%). They deduced that while coarse kaolin particles yielded activation energy of  $43 \text{ kJ}\cdot\text{mol}^{-1}$  for dissolution, the corresponding figure for fine particles was  $24 \text{ kJ}\cdot\text{mol}^{-1}$ .

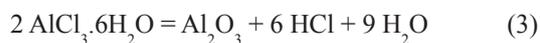
Several workers have researched leaching of local Aswan clays using hydrochloric acid: Early attempts were performed by Bakr et al [22, 23] who stated that up to 80% recovery was possible depending on the particle size of clay and acid concentration. Further work carried out by Ismail et al [24] and Baioumi et al [25] associated with chemical characterization of deposits was not relevant as for alumina recovery. Also, the work of El-Sherbiny et al [26] was only concerned with enhancing the physical properties of kaolin for use in paper coating.

The purification of hexahydrate crystals has been studied by Mahi et al [27] as part of a research aiming at alumina recovery. It was found that the solubility of aluminum chloride decreased sharply with increasing HCl concentration in the aqueous phase. They also recommended introducing HCl gas for better purification.

The thermal decomposition of aluminum chloride hexahydrate crystals was carried out by Hartman et al [28] who based their conclusions on thermal analyses and XRD data. They concluded that the decomposition of the hexahydrate proceeds through the following set of reactions:



They concluded that the reaction reached 95% alumina recovery below  $300^\circ\text{C}$  and was described by an Avrami – Erofeev type of nucleation and grain growth mechanism. They also obtained an activation energy of  $135.9 \text{ kJ}\cdot\text{mol}^{-1}$  for the global reaction:



This mechanism was also recently confirmed by Zhang et al [29] who obtained a conversion of about 99% and an average activation energy of  $59.67 \text{ kJ}\cdot\text{mol}^{-1}$ .

The aim of this work is to obtain high purity alumina by, dissolution of calcined Kalapsha kaolin (Aswan) using hydrochloric acid then purification of aluminum chloride hydrate through multi stage crystallization. The multistage crystallization step includes dissolving precipitated aluminum hydrate crystals in 25% HCl followed by crystallization. This step is then repeated two more times and finally, the calcination of the hydrate crystals to produce alumina with high purity.

## Experiment

### Materials

The main raw material used in this study is kaolin ore derived from Kalabsha region, Aswan, Egypt. The kaolin was used after calcination in an electrical furnace at  $700^\circ\text{C}$  for two hours. HCl commercial grade (32%) was purchased from Gomhorya Company and stated to be of at least 99.5% purity by the manufacturer. This was used in the leaching and crystallization processes. Distilled and deionized water were used in preparation of dissolution and crystallization samples respectively.

### Apparatuses

- X-ray fluorescence (XRF), Pananalytical XRF (Model Advanced Axios, Netherland) was used to determine elemental composition of Kaolin and alumina produced after calcination.

- Thermo gravimetric analyzer (TGA), (STA-504, USA) was used to follow up for the dissociation of kaolin in air at a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$  to decide about the proper temperature of calcination; also TGA and DTA (STA-504, USA) were used to study the thermal decomposition reactions of aluminum chloride hexahydrate. The thermal dissociation reactions were carried out non-isothermally up to  $1100^\circ\text{C}$  at different heating rates ( $10, 20$  and  $30^\circ\text{C}\cdot\text{min}^{-1}$ ) in a continuous

flowing of argon gas ( $40 \text{ ml} \cdot \text{min}^{-1}$ ).

- X-ray diffraction (XRD) was performed using mono-achromatized Copper  $K\alpha$  radiation at 40 mA and 40 kV. A Philips diffract-meter type (PW 1730) was employed with a scanning speed of  $20^\circ/\text{min}$  B (Ni- filtered Cu  $K\alpha$  radiation), the diffraction pattern is used to perceive the specimen's crystalline phases

- Inductively coupled plasma (ICP) was used for the analysis of aluminum chloride hexahydrate crystals

-An electrical Tube furnace was used for the calcination of aluminum chloride hexa hydrate crystals. This consisted of a horizontal tube furnace (length = 900 mm, inner diameter = 70 mm) in which a fused alumina tube (length = 120 mm, diameter = 55 mm) was fitted.

#### Sample preparation

##### Dissolution of kaolin in HCl

Leaching of kaolin was carried out using hydrochloric acid (32%) with a solid to liquid ratio of 1:5 at different stoichiometries. The reaction mixture consisted of 50 g of calcined kaolin and 250 mL of diluted HCl (At different concentrations according to reaction conditions). Diluted HCl (250 ml) was put in a 1000 ml beaker (sample beaker) which was heated on a water oil bath according to the reaction temperature. The kaolin sample was added to the acid only when the required temperature was reached. The mechanical stirrer was run at a fixed speed of 260 rpm. At the end of the reaction, the reaction mixture was filtered then washed with hot distilled water. The filtrate and wash were collected in separate bottles and the solid residue dried and its weight recorded. Volumes of wash and filtrate were recorded and the filtrate density calculated. Volumetric analysis was carried out for the filtrate and wash to calculate the dissolution percentage of  $\text{Fe}_2\text{O}_3$  [30]. The  $\text{TiO}_2$  content was determined using a spectrophotometric method [31], while gravimetric analysis was applied to calculate the percentage recovery of  $\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{Fe}_2\text{O}_3$ . The percentage recovery of alumina was subsequently determined.

##### Statistical Model for the Leaching Process

The variables investigated in acid leaching were: the temperature of reaction ( $T^\circ\text{C}$ ), the stoichiometric acid to solid ratio ( $S$ ) and reaction time ( $t$  h). The Box - Behnken statistical design in 33 factorial design as a tool for simulation and op-

timization of the dissolution process [32]. This was carried out using Statistical Design-Expert 9.0.3, Stat-Ease, Inc., MN, USA, software\*. The percent alumina recovery ( $Y$ ) was subsequently related to the three variables by a second order equation in the form:

$$Y = \beta_0 + \beta_1 T + \beta_2 S + \beta_3 t + \beta_{12} T \cdot S + \beta_{23} S \cdot t + \beta_{31} t \cdot T + \beta_{11} T^2 + \beta_{22} S^2 + \beta_{33} t^2 \quad (4)$$

The chosen values of the three parameters

TABLE 1. Selected reaction parameters.

Variable	Min.	Center	Max.
$T$	90	97	104
$S$	1	1.2	1.4
$t$	1	2	3

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are shown in Table 1. These were selected following a set of preliminary trials.

##### Crystallization of Aluminum Chloride Hexahydrate

The objective of this step was to obtain high purity crystals of aluminum chloride hexahydrate to be converted in a calcination step into high purity alumina. Aluminum chloride hexahydrate solution obtained from the previous leaching stage was concentrated through evaporation to obtain a saturated solution. Selective crystallization of aluminum chloride was achieved by injection of HCl (g) through a saturated aluminum chloride solution [33]. As the concentration of acid in solution increases, the solubility of aluminum chloride decreases and the formation of crystals starts. The process was stopped before reaching the azeotropic point at 20% by weight HCl to avoid a decrease in acid concentration in aluminum chloride solution due to the evolution of water vapor which leads to the dissolution of formed crystals.

Multi stage crystallization was further carried out to improve the purity of obtained crystals. 25% HCl solution was used in dissolving the obtained  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  crystals in a first stage to be recrystallized in second stage and subsequently used in dissolving the crystals from that second stage to be recrystallized in a third stage. At the end of each crystallization run, the crystals formed were separated from the slurry by vacuum filtration, washed with 70 ml of concentrated HCl (ANALAR), then washed with 30 ml deionized water to be finally dried overnight at  $80^\circ\text{C}$  and saved in desiccator. The hydrochloric acid and deionized water used in this process were analyzed using ICP (Inductive Coupled Plasma). The acid

contained no more than 76 ppm impurities while the impurities in water did not exceed 12 ppb.

#### Calcination of Purified Crystals

The purified crystals obtained from the previous step were calcined in alumina boats in a tube furnace. In these tests, about 30 g sample was placed in a fused alumina boat and placed in the middle of the hot zone of the furnace. The sample was heated at a controlled rate of  $10\text{K}\cdot\text{min}^{-1}$  up to the pre-determined temperature (600, 900 and  $1100^{\circ}\text{C}$ ) in a flow of inert gas (argon) till reaching the required temperature and kept constant at this temperature for 4 hours. The resulting powder was characterized each time by XRD for phase composition.

## Results and Discussion

#### Characterization of kaolin

The chemical analysis of kaolin sample is displayed in Table 2

On the other hand, XRD was performed on the sample and revealed the presence of lines of kaolinite, quartz and rutile ( $\text{TiO}_2$ ) which is

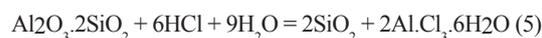
compatible with XRF findings.

Thermal analysis of kaolin powder was carried out for TGA assessment to decide about the proper temperature of calcination. The result is shown in Fig.1 and indicates a loss of moisture of slightly less than 4% ending at about  $200^{\circ}\text{C}$  followed by a drop in weight of 11.6% ending at a temperature slightly above  $600^{\circ}\text{C}$ . The loss in weight obtained is fairly compatible with the LOI of the dry sample (Table 2).

Consequently, the kaolin samples were calcined to  $700^{\circ}\text{C}$  for two hours to ensure full conversion to active metakaolin. This was confirmed by the XRD of the fired sample which showed no lines of kaolinite.

#### Statistical model

The leaching reaction of metakaolin by hydrochloric acid produces aluminum chloride hexahydrate [16]:



Using the values of the three investigated parameters in Table 1, a set of 17 experiments

TABLE 2. Chemical analysis of kaolin sample.

Oxide	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	CaO	$\text{SO}_3$	$\text{ZrO}_2$	$\text{Cr}_2\text{O}_3$	Minor	LOI	Total
%Wt	32.91	48.93	4.22	1.19	0.505	0.29	0.46	0.14	0.32	10.9	99.865

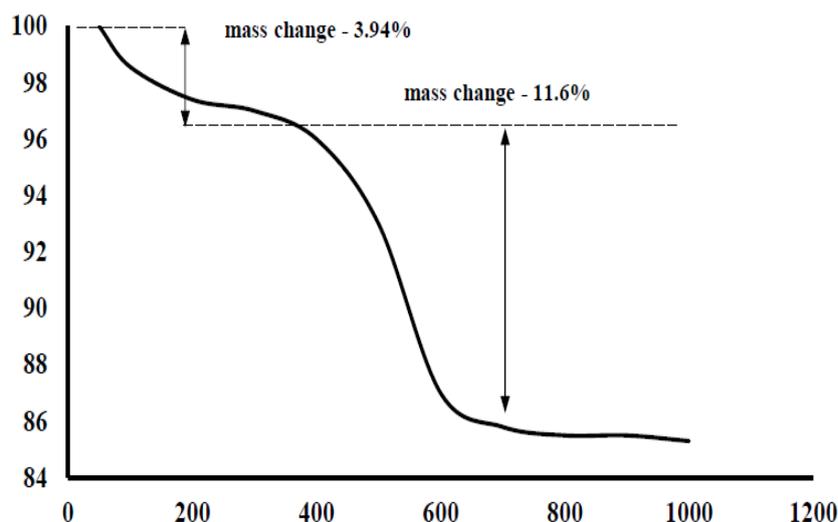


Fig. 1. TGA of kaolin sample ( $10^{\circ}\text{C}\cdot\text{min}^{-1}$ ).

TABLE 3. Results of alumina recovery.

Run #	S	T °C	t h	Alumina Recovery, Y %
1	1.4	97	3	76.1
2	1	90	2	56
3	1.4	97	1	72.89
4	1.2	104	3	74
5	1.4	90	2	66.96
6	1	104	2	61.99
7	1.2	104	1	64.3
8	1.2	97	2	65.53
9	1.2	90	3	58.2
10	1.2	97	2	65.25
11	1.4	104	2	77.8
12	1.2	97	2	64.9
13	1.2	97	2	63
14	1	97	1	58.3
15	1	97	3	62.1
16	1.2	90	1	58
17	1.2	97	2	65.8

were carried out and the alumina yield calculated. The results are illustrated in Table 3.

Following these runs, the aforementioned software was used to deduce a second order expression. This took the form:

$$\text{Alumina recovery (Y\%)} = -82.798 - 183.354S + 4.78T - 30.69t + 0.866S \cdot T - 0.738S \cdot t + 0.339 T \cdot t + 56.425S^2 - 0.03T^2 + 0.1945t^2 \quad (6)$$

#### Interaction between the different parameters

##### a. Effect of stoichiometric ratio and reaction temperature on alumina recovery

The effect of the simultaneous variation in stoichiometric ratio and reaction temperature on alumina recovery at different levels of reaction time (1, 2 and 3 hours) is illustrated in Fig. 2. In general, the percent alumina recovery increased with increasing stoichiometric ratio from 1.0 to 1.4 (60-70% at time = 1h). Also, increasing the reaction temperature from 90 to 104°C showed significant effect on alumina recovery. Figure 2 (C) also indicates that at higher time of reaction = 3h, recovery increased to 80%. Actually, contour lines even suggest that reaction at 104°C for 3 hours at stoichiometric ratio = 1.4 would raise conversion over 80%.

##### b. Effect of stoichiometric ratio and reaction time on percent alumina recovery (%)

The simultaneous effect of varying stoichiometric ratio and reaction time on the percent alumina recovery at different levels of reaction temperatures (90, 97 and 104°C) is shown in the set of Fig. 3. These results reveal that, at low reaction temperature (90°C), there is no increase in alumina recovery with increasing reaction time (h) at all stoichiometric ratios as shown in Fig. 3 A. However, at high reaction temperature (104°C),

the alumina recovery increased from 75% to 80% with increasing time as shown in Fig 3 C. On the other, hand, at low times of reaction increasing the stoichiometry from 1.1 to 1.4 increased the conversion in the range (56% -66%) Fig. (3 A). This means that the variation in alumina recovery is more sensitive to stoichiometric ratio variation than time especially at low reaction temperatures.

##### c. Effect of reaction temperature and reaction time on percent alumina recovery

The combined effect of varying calcination temperature and reaction time on percent alumina recovery at different stoichiometric ratios (1.0, 1.2, 1.4) is revealed in Fig. (4) (A, B and C). These results indicate that the studied parameters highly interact as it can be seen that alumina recovery increases slightly with increasing time at low stoichiometric ratio (Fig. 4 A). On the other hand, at the higher stoichiometric ratio of 1.4 (Fig. 4 C), alumina recovery increased from 75% to 80% with increasing reaction time.

All experimental results were then plotted on the 3-D cube graph as shown in Fig. 5. This cube shows that the highest alumina recovery 83.22% can be obtained at highest stoichiometric ratio (1.4), highest reaction temperature (104°C) and highest reaction time (3 h).

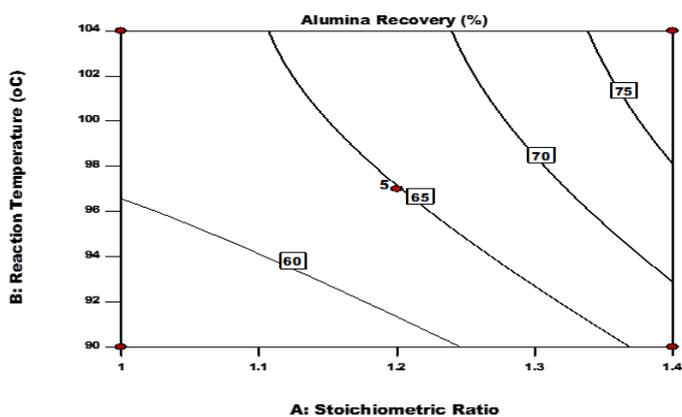


Fig. 2 A. Effect of stoichiometric ratio and reaction temperature on alumina recovery at reaction time = 1 h.

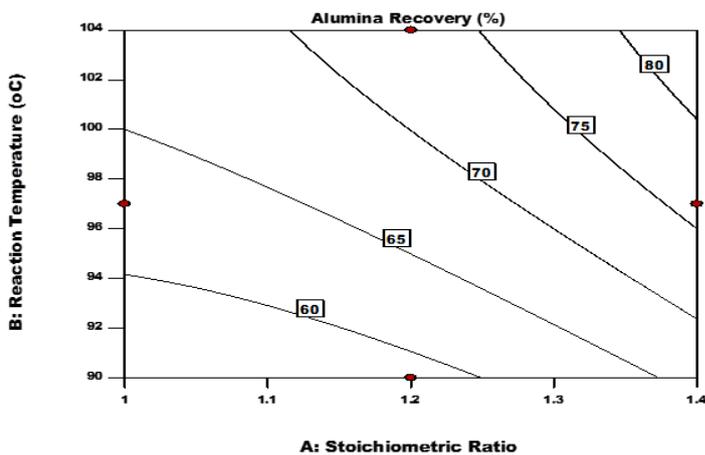


Fig. 2 B. Effect of stoichiometric ratio and reaction temperature on alumina recovery at reaction time = 2 h.

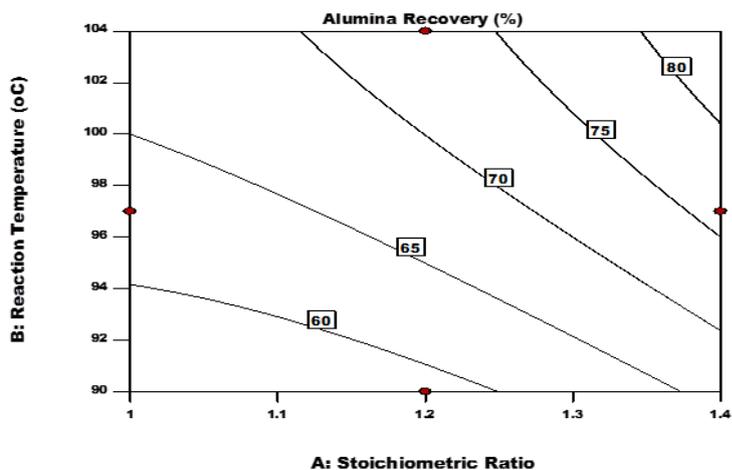


Fig. 2 C. Effect of stoichiometric ratio and reaction temperature on alumina recovery at reaction time = 3 h.

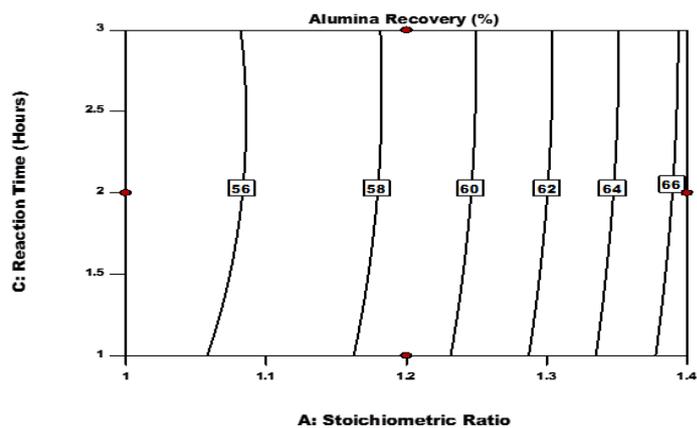


Fig. 3 A. Effect of stoichiometric ratio and time on alumina recovery at reaction at temperature = 90°C.

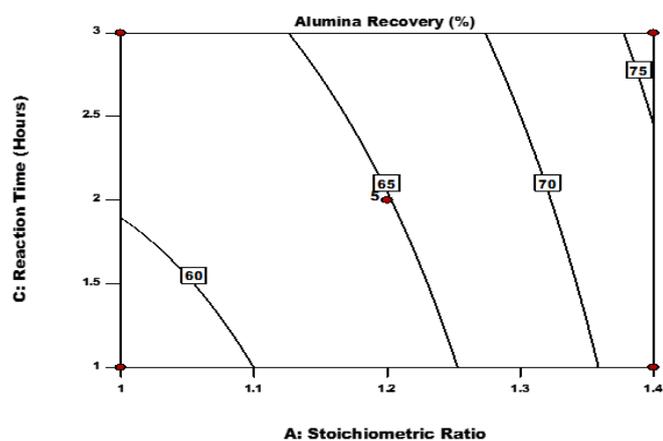


Fig. 3 B. Effect of stoichiometric ratio and time on alumina recovery at reaction temperature = 97°C.

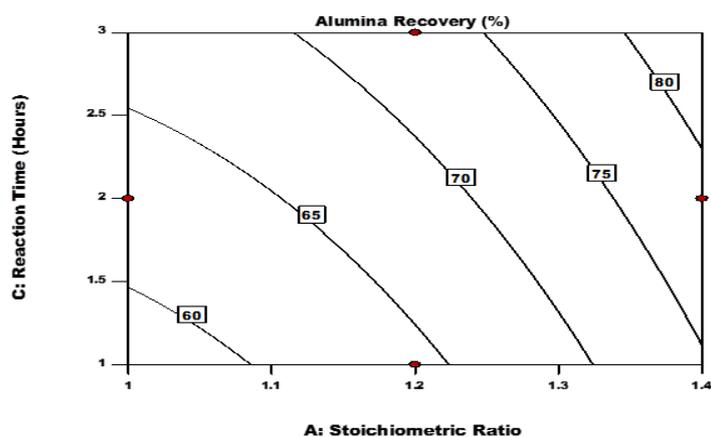


Fig. 3 C. Effect of stoichiometric ratio and time on alumina recovery at reaction temperature = 104°C.

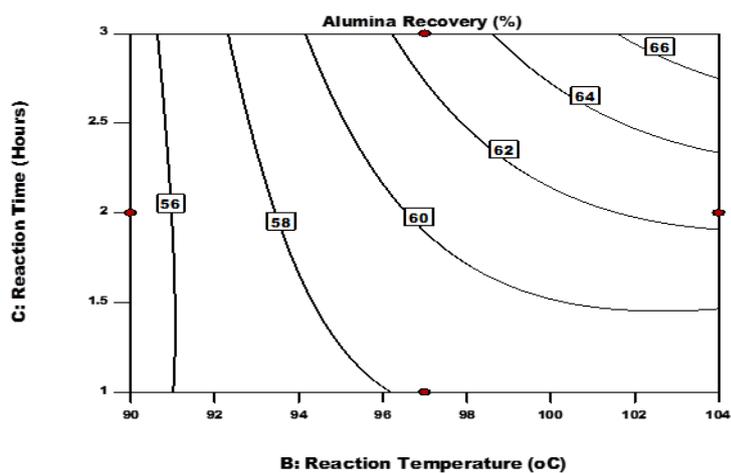


Fig. 4 A. Effects of reaction temperature and reaction time on alumina recovery (Stoichiometric Ratio = 1).

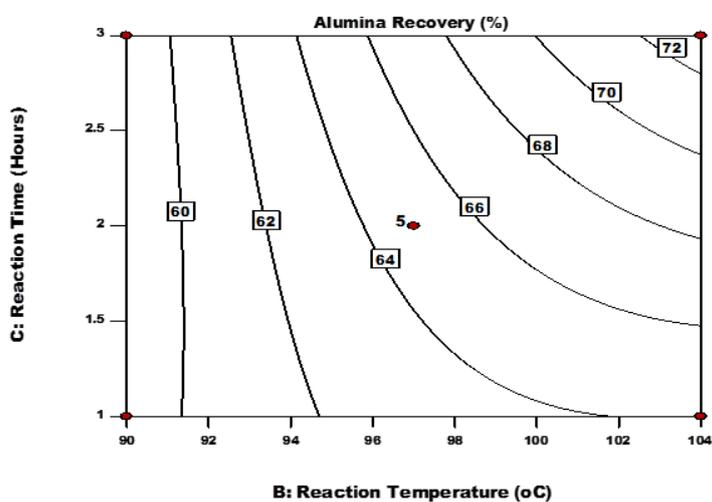


Fig. 4 B. Effects of Reaction Temperature and Reaction Time on Alumina Recovery (Stoichiometric Ratio = 1.2).

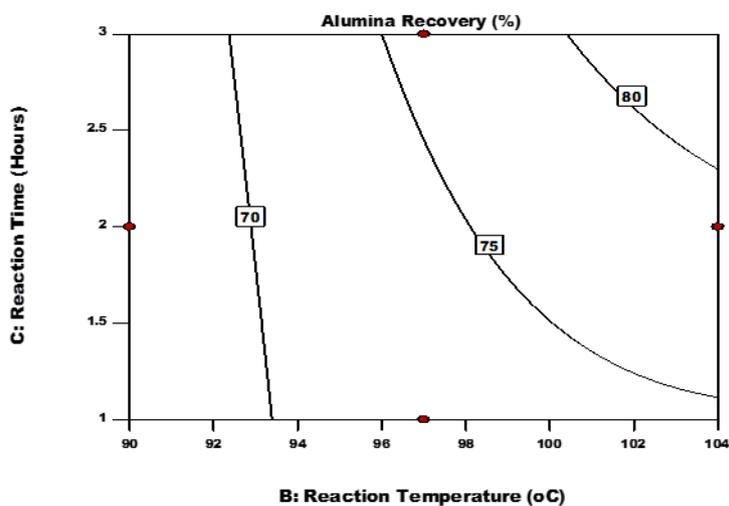


Fig. 4 C. Effects of reaction temperature and reaction time on alumina recovery (Stoichiometric ratio = 1.4)

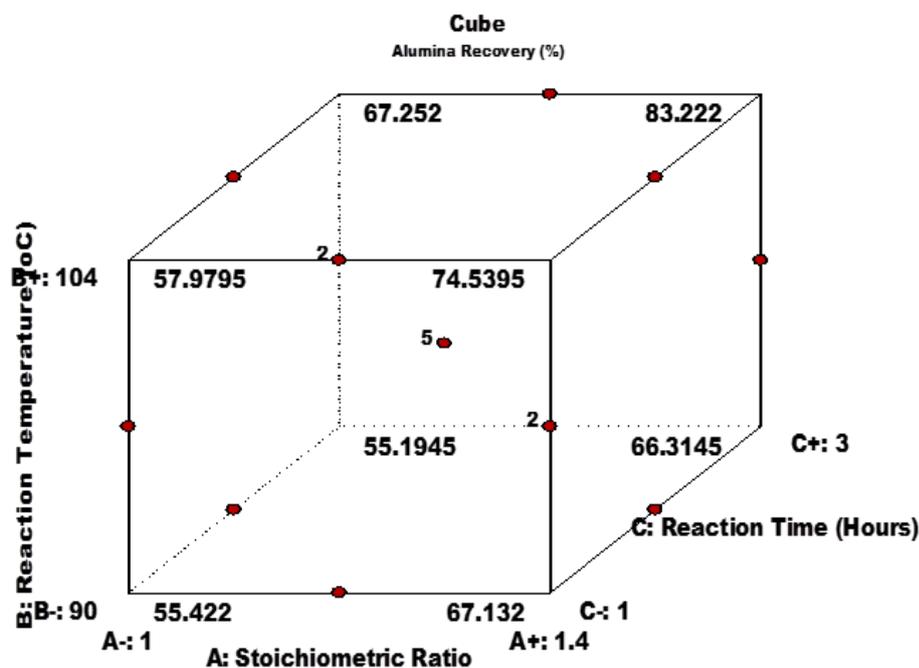


Fig. 5. 3-D. Plot for the results of alumina recovery (%) from kaolin leaching.

To assess the validity of these findings, 9 runs were performed at the aforementioned conditions. They produced a mean percentage of alumina recovery = 81.33% with a standard deviation = 1.09%. This proves the validity of the suggested model as the percent error did not exceed 2.3%.

#### Multistage crystallization

As pointed out earlier, crystallization was carried out on three stages. The following Table 4 shows the analyses of the crystals obtained from each stage (Using ICP analysis). As can be inferred from that table, the purity of the crystals slightly increases on passing from one stage to the next. This is mainly due to decrease in iron and magnesium ions by acid leaching. At the end of the third stage, the purity of the crystals reached 99.961%.

A micrograph of scanning electron microscope (SEM) Model Quanta 250 FEG is shown in Fig. 6. The figure indicates well crystalline phase with clear boundary.

The shape of crystals shown in figure agree with the findings of Ketelaar et al [34] who classified these crystals as monoclinic with equal  $a$  and  $b$  lattice constants (0.591 nm) and a much bigger  $c$  value (1.572 nm).

#### Kinetics of Thermal Decomposition of Aluminum Chloride hexa hydrate

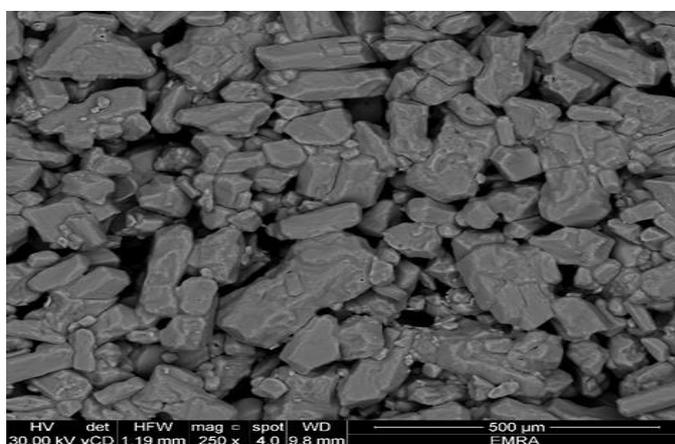
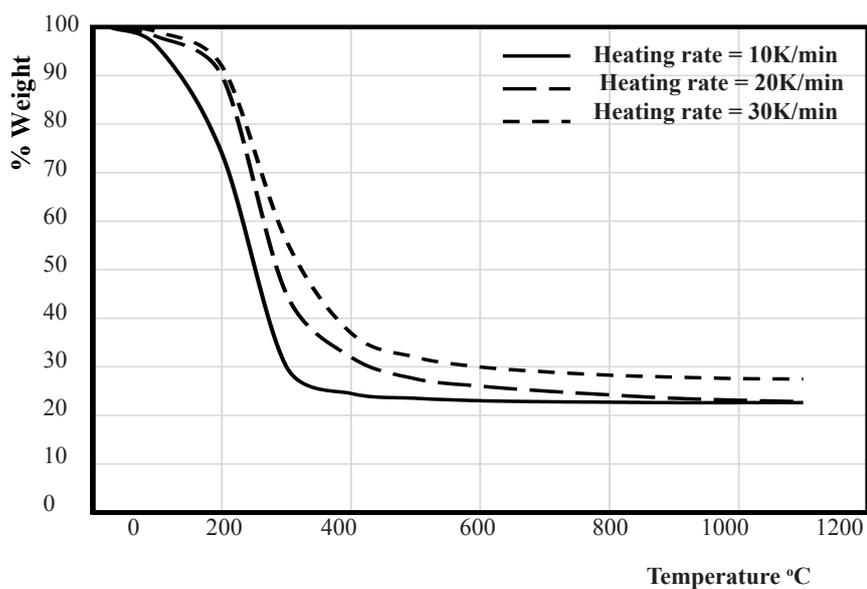
The kinetics of decomposition of the hydrates to alumina was carried out using the Flynn – Wall – Ozawa method of equal conversions [35]. To that aim, a plot of loss in weight was carried out against temperature at three different heating rates  $\beta = 10, 20$  and  $30^{\circ}\text{C}\cdot\text{min}^{-1}$  using TG data (Fig. 7), ( $\beta$  is the heating rate of  $^{\circ}\text{C}\cdot\text{min}^{-1}$ ), this is predetermined by programming the TGA apparatus prior to starting the run).

Form that plot, the conversion to alumina could be deduced since the stoichiometric percent weight loss = 78.88%, as calculated from equation (3).

As can be seen form that figure, the conversion to alumina proceeds at temperatures that increase with the applied heating rate, which is a commonly observed phenomenon [36, 37]. The stoichiometric weight loss following reaction (3) is about 78.88%, which is slightly higher than the values obtained in Fig. 7. For example, at the lowest heating rate ( $10^{\circ}\text{C}\cdot\text{min}^{-1}$ ), the maximum recovery is 77.9%.

**TABLE 4.** ICP Analysis for crystals obtained from Different Stage.

Element	Stage 1 (ppm)	Stage 2 (ppm)	Stage 3 (ppm)
Fe	0.05	0.02	0.02
Zn	-	-	-
Mg	0.21	0.17	0.02
Ca	0.08	N.D.	0.15
K	0.02	0.03	0.03
Na	0.16	0.24	0.17
Si	-	-	-
Ti	-	-	-
Total impurities	0.52	0.46	0.39
%AlCl <sub>3</sub> .6H <sub>2</sub> O	99.948	99.954	99.961

**Fig. 6.** SEM of a purified crystal of aluminum chloride hexahydrate.**Fig. 7.** TG results for loss in weight in reaction (3) at different heating rates.

The fractional conversion  $\alpha$  is then obtained from the weight  $W$  from the expression:

$$\alpha = \frac{100-W}{78.88} \quad (7)$$

According to the Flynn – Wall – Ozawa method, equal conversions were chosen at the three rates and the corresponding temperatures ( $T$  K) determined. Then a plot of  $\log \beta$  against ( $1/T$ ) is performed to obtain a series of more or less parallel straight lines at the chosen values of conversion. The slope=  $(0.4567E/R)$ , from which the activation energy could be deduced (Fig. 8).

The average slope was determined and possesses a numerical value of about 2748 K. This corresponds to an average activation energy  $E = 60.3 \text{ kJ.mol}^{-1}$ , a value comparable to that obtained by Zhang et al [19] ( $59.67 \text{ kJ.mol}^{-1}$ ).

#### Calcination of hexahydrate crystals

The crystals obtained were calcined to different temperatures varying from 600 to 1100°C. The reason of that choice stems from the fact that in their work, Hartman et al [19] reported that although the conversion to alumina exceeded 99% at 270°C, the undecomposed species  $\text{Al}_2\text{O}_3 \cdot 2\text{HCl} \cdot 2\text{H}_2\text{O}$  remained as a porous mass that hindered more decomposition. In order to obtain a recovery close to 100%, it was thought necessary to increase both calcination temperature and time. Actually, three trials were performed in which calcination was carried out at 600, 900 and 1100°C and kept constant at these temperatures for 4 hours in continuous flowing of argon gas to purge out the formed hydrogen chloride gas. XRD of the calcination products showed poor crystallinity at 600°C (Fig. 9). This improved on heating at 900°C and ultimately produced extremely sharp peaks on calcination at 1100°C for 4 hours (Fig. 10). The purity of the alumina powder obtained was determined to be 99.

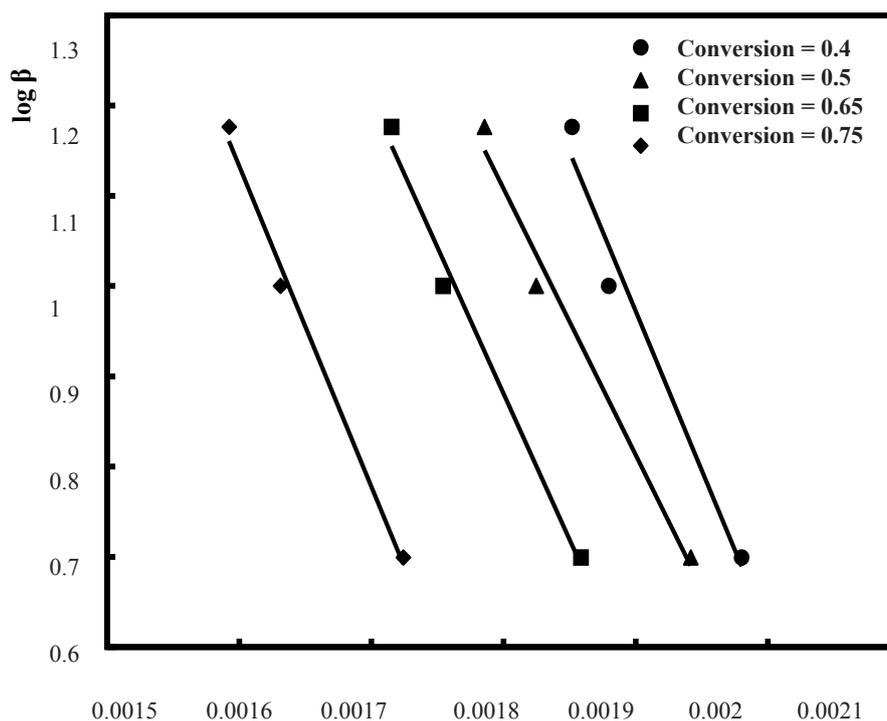


Fig. 8. Flynn – Wall – Ozawa plot for aluminum chloride hydrate calcination.

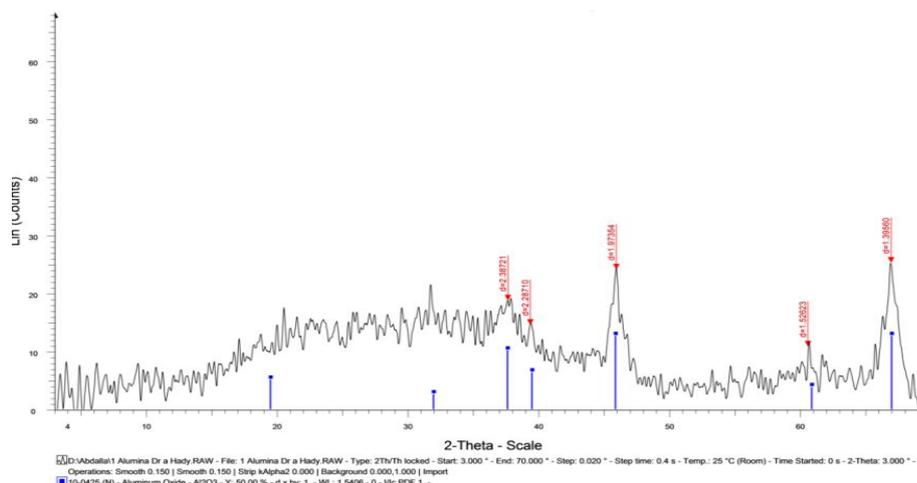


Fig. 9. XRD of obtained alumina on firing at 600°C for 4 hours.

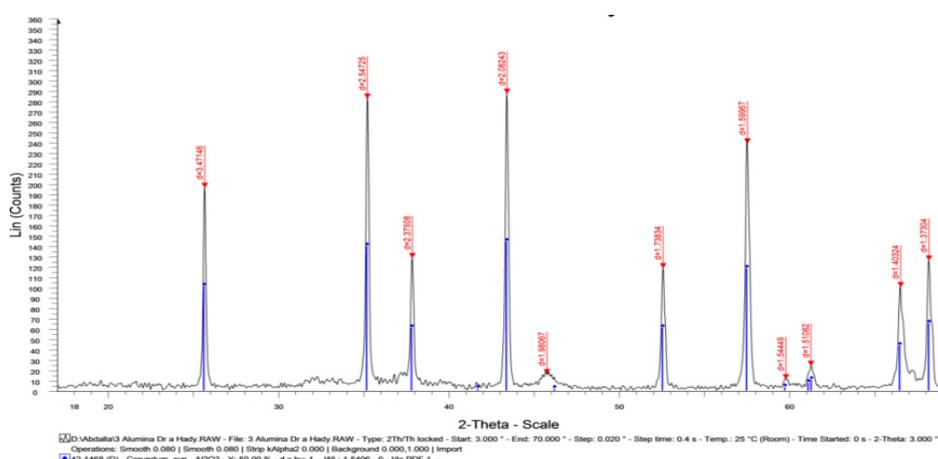


Fig. 10. XRD obtained on firing the hexahydrate at 600°C for 4 hours.

## Conclusion

Form the analysis of the data obtained in this work, the following conclusions could be drawn:

1. A maximum alumina recovery of 83.2% was predicted by the statistical model on using 1.4 stoichiometric acid to solid ratio, a reaction temperature of 104°C and a reaction time of 3 hours. The predicted result was assessed by carrying out nine runs at the optimum conditions. The mean percentage of alumina recovery obtained was 81.33% which proves the validity of the suggested model.
2. The purity of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  crystals was found to slightly increase following passing from one purification stage to the next. The final product from the third stage was analyzed by ICP and found to be of 99.961% purity.

3. The kinetics of decomposition of aluminum chloride hydrate was studied using the Flynn – Wall – Ozawa method and the average activation energy of the overall reaction found to be 60.3  $\text{kJ}\cdot\text{mol}^{-1}$ .
4. The crystals obtained were calcined at temperatures of 600, 900 and 1100°C for 4 hours. XRD showed that their crystallinity increased with increased calcination temperature. The alumina purity of the samples fired at 1100°C was determined as 99.9%.

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## References

1. Smith J.D and Fahrenholtz W.G., Refractory Oxides. In: Shackelford J.F., Doremus R.H. (ed.) *Ceramic and Glass Materials*, Springer, Boston, MA, 87 – 110 (2008).
2. Sarkar R., *Refractory Technology: Fundamentals and Applications*. CRC Press, Taylor & Francis, p. 5/102 – 6/120 (2016).
3. Lumley R., *Fundamentals of Aluminum Metallurgy*. 1<sup>st</sup> ed, Woodhead Pub. Part 1(2010).
4. Parikh P.B., Alumina Ceramics: Engineering Applications and Domestic market Potential. *Ceram. Soc*, **54** (5), 179 – 184 (1995).
5. Kim D-W., Cho M-W., Seo T-I and Shin Y-J., Abrasive Particle Behavior in MR Polishing for MEMS Applications. *Sensors*, **8** (1), 222 – 235 (2008).
6. El Khesheh A.A., Effect of Alumina Addition on Properties of Glass/Ceramic Composite. *Brit. Ceram.Trans*, **102** (5), 205 – 209 (2003).
7. Pires R.A., Abrahams E., Nunes T.G and Hawkes G.E., The role of alumina in aluminoborosilicate. *J. Mater. Chem*, (22), 124 – 129(2009).
8. Hulbert S.F., *The Use of Alumina and Zirconia in Surgical Implants” An Introduction to Bioceramics*. Ed. L. Hench, 27 – 47 (2013).
9. Paranjpe K.Y., Alpha, Beta and Gamma Alumina as Catalyst. *Pharma Innov, J*. **6** (11), 236 – 238 (2017).
10. El Fadly A.M., Badawy A.M., Yehia F.Z., Mohamed Y.A., Betiha M.A and Rabie A.M., Selective Nano Alumina Supported Vanadium Oxide Catalysts for Oxidative Dehydrogenation of Ethylbenzene to Styrene Using CO<sub>2</sub> as Soft Oxidant. *Egypt J. Chem*. (22), 373 – 380 (2013).
11. Mehta N.S., Sahu P.K., Tripathi P., Pyare R and Majhi M.R., Influence of Alumina and Silica Addition on the Physico-mechanical and Dielectric Behavior of Ceramic Porcelain Insulator at High Sintering Temperature. *Bull. Spanish Ceram. Glass Soc*, **57** (4), 151 – 159 (2018).
12. Beepy S.P., Printing Thick Films Mechanical Microsystems (MEMS). In: *Materials Science and Applications in Sensors, Electronics and Photonics*. Woodhead Ed, Section 10.3 (2012).
13. U.S. Department of Energy ARPA-E RANGE., Alumina Provides Ultra-Thin Solution in Battery Development” *Ceramic Industry* (2017).
14. Ramisetty M., Sastri S., Kashalikar U., Goldman L.M and Nag N., Transparent Polycrystalline
15. Cubic Spinel Protect and Defend. *Amer. Ceram.. Soc. Bull*, **92** (2), 20 – 25 (2013).
16. Ford K.J.R., Leaching of Fine and Pelletised Natal Kaolin Using Sulfuric Acid. *Hydrometallurgy*, **29** (1 – 3), 109 – 130 (1992).
17. Godswill M.O., Kinetics of Alumina Leaching of Calcined Clay Using Acids (Chloric, nitric and Sulfuric acids)” *Ph.D. Thesis* Submitted to Chalmers University of Technology, Göteborg, Sweden (2009).
18. Lima P.E., Angélica R.S and Neves R.F., Dissolution kinetics of Amazonian metakaolin in nitric acid. *Cerâmica*, **64** (369), 86-90 (2018).
19. Hernández R.A.H., Garcia F.L., Cruz F.L.H and Jacuinde A.B., Kaolin Bleaching by Leaching Using Phosphoric Acid solutions. *J. Mex. Chem. Soc*, **59**(3), 198 – 202 (2015).
20. Cameselle C., Núñez M.J and Lema J.M., Leaching of Kaolin Iron-Oxides with Organic Acids. *J. Chem. Tech. Biotech*, **70** (4), 349 – 354 (1997).
21. Hernández R.A.H., Garcia F.L., Cruz F.L.H and Luevanos A.M., Iron Removal from a Kaolinitic Clay by Leaching to Obtain High Whiteness Index. *IOP Conf. Series Mater. Sci. Eng*. **45** (1), 2002 – 2007 (2013).
22. Dong T.A., Su L., Li C and Wei W., Effect of Mechanical Activation on Acid -Leaching of Kaolin Residue. *Appl. Clay Sci*, **48** (3), 296 – 299 (2010).
23. Bakr M.Y and El Abd M.A., Extraction of Alumina from Egyptian Clays and Kaolins: Hydrochloric Acid Process for the Recovery of Alumina. *Sprechsaal Jahrg*, **100**(23), 412-418 (1967).
24. Bakr M.Y and El Abd M.A., Extraction of Alumina from Egyptian Kaolins and Clays. *Ind. J. Tech*. (7), 405– 409 (1969).
25. Ismail I.S., Abdel Rahman M.K and Hassan M.S., Influence of Vibration Grinding and Calcination on the Physico-Chemical Properties of Egyptian Kaolinite. *Mineral Petrol*, **67**(1-2), 45 – 57 (1999).

26. Baioumi H.M and Gilg H.A., Pisolitic Flint Kaolin from Kalabsha, Egypt: A laterite-Derived Facies. *Sedim. Geol.*, **236**(1), 141 – 152 (2011).
27. El-Sherbiny S., Morsy F.A., Badr M and Mohamed H.F., Enhancing Egyptian kaolinite via Calcination and Dealumination for application in paper coating. *J. Coat. Tech. Res.*, **12**(4), 9672 – 9675 (2015).
28. Mahi P., Livingston W.R., Rogers D.A., Chapman R.J and Bailey N.T, The Purification and Crystallisation of Chloride and Chloride/Fluoride Leach Liquors by HCl Gas Precipitation. *Hydrometallurgy*, **26** (1), 75 – 91 (1991).
29. Hartman M., Trnka O and Šolcová O., Thermal Decomposition of Aluminum Chloride Hexahydrate. *Ind.Eng. Chem. Res.*, **44** (17), 6591 – 6597 (2005).
30. Zhang N., Yang Y., Wang Z., Shi Z., Gao B., Hu X., Tao W., Liu F and Yu J. “Study on the Thermal Decomposition of Aluminum Chloride hexahydrate. *Can. Metal. Quarte.*, **57**(2), 235-243 (2017).
31. Harvey D., *Modern Analytical Chemistry*, 1<sup>st</sup> ed., McGraw-Hill, New York, (2000).
32. ASTM E 2371 – 13., Standard Test Method for Analysis of Titanium and Titanium Alloys by Direct
33. Current Plasma and Inductively Coupled Plasma Atomic Emission Spectrometry, (2013). [32] Lazić Z.R., Design of Experiments in Chemical Engineering. Wiley – VCH Ed, (2004).
34. <https://www.911metallurgist.com/producing-aluminum-chloride-hexahydrate-kaolinitic-clay/>
35. Ketelaar J.A.A., MacGillavry C.H and Renes P.A., The Crystal Structure of Aluminum Chloride. *Rec. Trav Chim. Pays-Bas*, **68**(8), 501 – 512(1947).
36. Ventakesh M., Ravi P and Tewari S.P., Isoconversional Kinetic Analysis of Decomposition of Nitroimidazoles: Friedman method vs Flynn–Wall–Ozawa Method. *J. Phys. Chem.*, **110** (40), 10162 –10169 (2013).
37. Jimenez P and Fereres S., Effect of Heating Rates and Composition on the Thermal Decomposition of Nitrate Based Molten Salts. *Energy. Proc* (69), 654 – 662 (2015).
38. Rafat F., Effect of Different Heating rate on the Thermal Decomposition of urea. *Arch. Appl. Sci. Res.*, **6**(5), 75 – 78 (2014).

### استخدام كاولين كلابشة لتحضير الومنيوم عالي النقاوة

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تم حرق عينات من كاولين كلابشة عند 700°م و إذابة الناتج في حمض هيدروكلوريك للحصول على كلوريد الألومنيوم المائي. تم بللورة كلوريد الألومنيوم المائي بواسطة التبخير للمحلول للوصول الى محلول مشبع ثم الحقن بغاز كلوريد الهيدروجين للحصول على بللورات نقية. تم رفع نقاوة البللورات التي تم الحصول عليها من خلال اعادة البللورة عدة مراحل تمهيدا لكسنتها للحصول على ألومينا عالية النقاوة. تم الحصول على أمثل الظروف للتفاعل بين الحمض و الكاولين المكلسن باستخدام طريقة إحصائية (Surface Response Methodology) التي تنبئت بالحصول على نسبة استخراج للألومينا = 83.2% عند نسبة حمض للكاولين = 1.4 النسبة النظرية و درجة حرارة = 104°م و زمن للتفاعل = 3 ساعات و قد تم التحقق من هذه النتيجة عمليا. ثم تم تنقية البللورات التي تم الحصول عليها من خلال ثلاث مراحل حيث تم الحصول على درجة نقاء = 99.961% و عند كلسنة هذه البللورات لمدة أربع ساعات عند 1100°م تم الحصول على ألومينا عالية التبلر بدرجة نقاء = 99.9%.