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Studying the Efficiency of Lime-Soda Sinter Process to Extract Alumina from Colored Kaolinite Ores Using Factorial Technique of Design of Experiments

Abstract- *As the increasing demand for alumina in recent years with the result diminishing reserve of bauxite, the need to secure a domestic raw material base is driving research in new technologies to process low grade ores into alumina, with the intention that these technologies will lead to a significant reduction of bauxite and alumina transportation costs, allow the extraction of more valuable components from the ore and reduce environmental impact. Clays are types of the low-grade aluminum ores, they're also well abundant which make them a potential substitutes for Bauxite. In this work, lime soda sinter process was adopted for extracting alumina from kaolinitic claystone from Al-Ga'ara formation (Duekhla) quarry in western Iraq. The operation efficiency of sintering was studied in which the whole process has been done with three stages: the sintering process for the raw materials, leaching and carbonizing processes to precipitate and separate the alumina from the leach pregnant solution . Factorial technique of Design of Experiments (DOE) module in Minitab was used as a principal methodology to examine the sintering efficiency over alumina extraction. The results obtained showed that the optimum parameters for the sintering operation were CaO/SiO2 molar ratio of 2.2, Na_2O/Al_2O_3 molar ratio of 1.2, sintering temperature at 1213 °C for 90 min. The sintered materials were leached with sodium carbonate solution, and sodium aluminate solution was obtained. By bubbling carbon dioxide gas into this extract solution aluminum hydroxide [$Al(OH)_3$] has been precipitated and on calcination at 1200 °C for 2 hrs, alpha alumina (α-Al_2O_3) was obtained with purity of 98.5 %.*

Keywords- *Lime-soda, Kaolin, Extract Alumina, DOE, Factorial Technique*

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1. Introduction

Because of the growing demand for alumina and aluminum, the production characteristic becomes linked to the source of the raw material [1]. Alumina for the production of aluminum is obtained from aluminum ores. The most important natural resource is known as Bauxite, where it is chiefly in the form of gibbsite ($Al_2O_3.3H_2O$) with relatively low silicon content. Bauxite is used for the aluminum production by Bayer process, which has been discovered since1888 by Carl Josef Bayer [2]. Other aluminum resources contain high amount of silica compared with bauxite, and other impurities such as iron, titanium. These resources include clays; kaolin, shales and other aluminum silicates as kainite and anorthosite [3]. Kaolinite is very important group of clay minerals usually white mineral dioctahedral phyllosilicates (sheet silicates). The general formula for it is $Al_4[Si_4O_{10}]$ $(OH)_8$ [4]. Among these kaolinite clays are numerous raw materials distributed on larger scale in Iraq. Kaolinitic clay stone in Iraq is mainly found in the Western Desert, the upper parts of the Ga`ara Formation. Al-Ga`ara is characterized by kaolinitic claystone deposits of various types including white and colored varieties. They are also known in the lower parts of the Hussainiyat Formation along Wadi Hussainiyat and in the Amij Formation at Wadi Amij [5, 6]. The kaolinites are highly ferruginous and of lower grade as shown in Table 1. Flint-clays are known as karst-fill deposits association with bauxite and bauxitic clay in very restricted localities in the Western Desert [7]. Kaolinite is the third most important mineral resources in Iraq after phosphate and limestone [8]. The total reserves of kaolinitic clay stone deposits in Iraq are estimated at about 1200 MT [5].

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Table 1: The chemical analyses of kaolinitic clay stone deposits.

Wt. %	Ga'ara Formation		Hussainiyat Formation		Amij Formation
	White	Colored	north	south	
SiO_2	48.1	51.1	50.7	45.0	48.0
TiO_2	1.1	1.5	1.4	1.9	1.5
Al_2O_3	35.7	28.7	28.7	31.0	29.0
Fe_2O_3	0.9	7.0	5.5	5.5	6.1
L.O. I	12.7	10.3	9.6	12.3	11.0
Σ Wt.%	98.5	98.6	95.9	95.7	95.6

2. Production of Alumina

Production of alumina can be divided generally into two main types depending on the raw materials used [9, 10]:

I. Primary production

Which include all the industrial processes for the naturally occurring aluminum ores, (bauxite and non-bauxite ores).

II. Secondary production

Which include all the industrial processes for the scrap.

3. Production of Alumina from Non-bauxite

It is well known that the poor-quality bauxite or material having low alumina and high silica content are not suitable for the production of alumina in accordance with Bayer process, tow processes are classified for the extraction alumina from clays which are acid process and alkaline process [11].

4. Alkaline Process for Extraction of Alumina from Clay

This method used water or a dilute alkaline solution (usually Na_2CO_3) to selectively dissolve the alumina with a series steps leaching after the ore has been mixed with lime and/or sodium carbonate, pelletized and sintered at high temperature [12].

5. Fundamentals of Alkaline Process

In accordance with the objective of this research, the lime, or lime soda-sinter process will take the prime consideration. Figure 1, shows the whole process flowchart in which the essential process steps are [12,13]:

1. Preparation and mixing of raw materials (grinding of clay and limestone and mixing with certain proportions).
2. Sintering the mix materials at high temperature.
3. Leaching of the alumina content in the sinter with dilute sodium carbonate solution.
4. Purification of the solution (or desilication).
5. Recovery of alumina trihydrate ($Al_2O_3.3H_2O$) from the solution by carbonizing.
6. Calcination of alumina trihydrate into alpha alumina (α-Al_2O_3).

6. Materials and Experimental Work

I. Materials

The raw material samples used in this work were supplied by Iraqi Geological Survey. The kaolin sample was brought from Duekhla quarry, while limestone brought from Wadi Ghadaf, both areas are located in Al-Anbar region in the West of Iraq. The chemical composition of the raw materials shown in Table 2, indicated the presence of high Al_2O_3 and SiO_2 in kaolin. Analytical grade of sodium carbonate (Na_2CO_3), with purity of 99 % from AppliChem, Germany, were used in sintering and leaching processes.

II. Experimental Procedure

The kaolinite clay and limestone samples were crushed by a laboratory jaw crushed to pass 1 mm , then ground by laboratory ball mill to a particle size of (-75) μ. Separating the proper size was carried out using mechanical sieve shaking. The ground raw material samples of kaolinite clay and limestone in addition to soda ash were mixed in predetermined proportion using drum for well mixing. The prepared mixture was made into a paste by adding distal water and mixing, after which the material is formed into ball with 20 mm diameter.

Table 2: The chemical composition of the raw materials.

Material	**Chemical Composition(% weight)**								
	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	TiO_2 %	CaO %	MgO%	Na_2O %	L.O.I %	Total %
Kaolinite	43.46	1.12	38.69	2. 3	0.15	0.2	0.31	13.66	99.89
Limestone	0.4	0.03	0.13	n.a	54.8	0.6	0.03	43.36	99.35

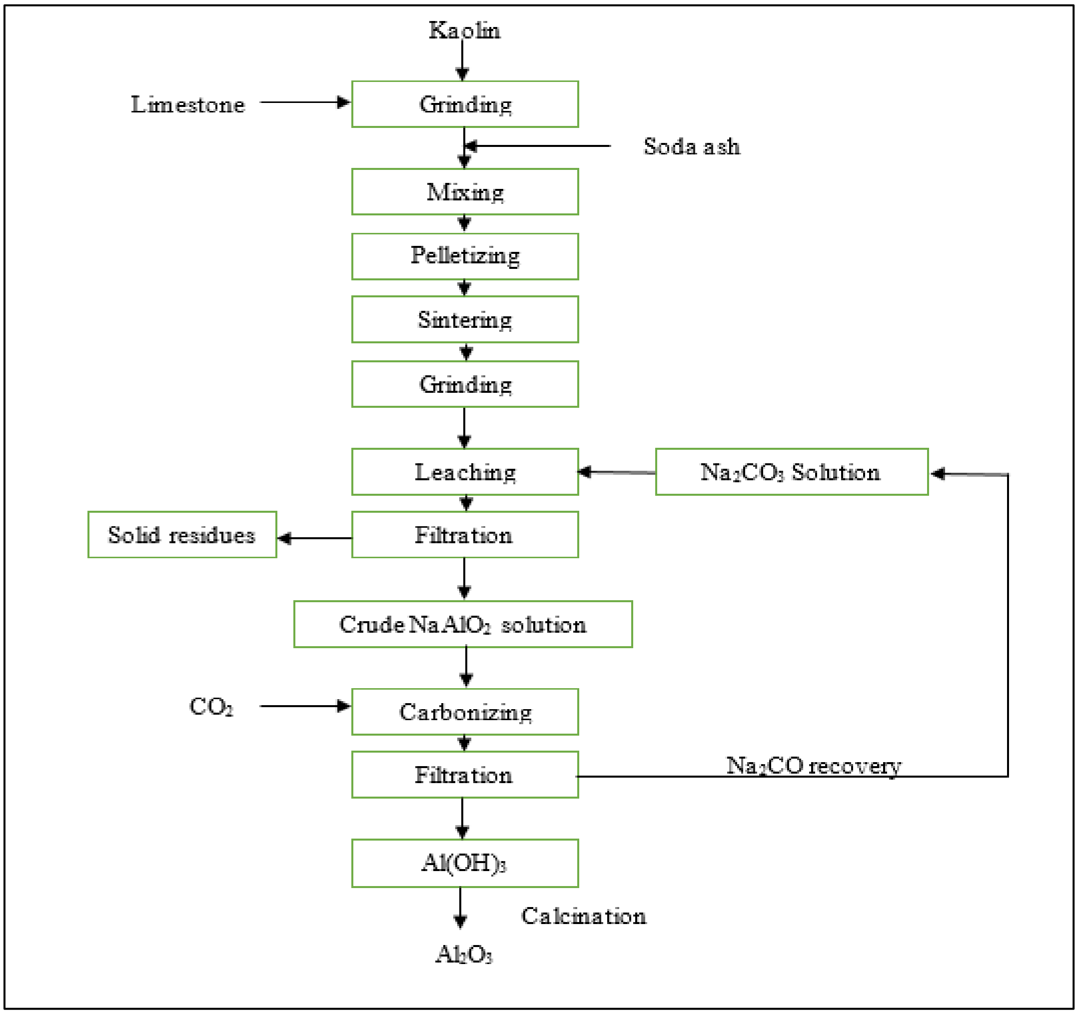

Figure 1: Flowchart of lime/soda sinter process for alumina production [12].

These balls were left to dry in air, and then dried in oven at a temperature of 150 °C for 2 hrs, to eliminate the moisture and prevent cracking inside the furnace during sintering. The sintering tests were carried out in a laboratory electrical furnace. After sintering, the samples were ground to -75µ and analyzed for Al_2O_3content.In each sintering test three parameters were studied: temperature, time and molar ratio of Na_2O/Al_2O_3. The effect of different sintering parameter of the sintering efficiency was investigated using factorial experimental design technique that helps to achieve the best combination of process variables for optimum control results. This method also helps to try various combinations of factors settings to establish the best way to run the operation [14]. In addition, a series of steps were followed in order to collect data or information required and was prepared in a suitable tables for analyzing statically and reach conclusions that can be generalized and utilized. The program used was (Minitab 16) factorial technique to study the individual and combined effect for the variables of the process during the sintering in statistical way. Table 3, below showed the maximum and minimum value for each parameter. For the leaching stage, the optimum sintered mixture was prepared. The leaching experiments were done in 50 ml three neck fat bottom flask, with stirring by electrical stirrer at 600 rpm. The leaching experiments were performed at constant conditions, which were chosen according to previous study that include: Particle size -75 μ, temperature of 70 ºC, time of 30 min, and sodium carbonate solution with concentration of 70 g/l and solid to liquid ratio of 1/4. The resulted pregnant solution, which has been prepared from the leaching, was subjected to carbon dioxide gas at 3 l/min flow rate for 60 min at 70 °C to precipitate aluminum hydroxide.

Table 3: Variables selected for the sintering process with their limits

Parameters	Max.	Min.
Temperature (°C)	1300	1125
Time(min)	90	45
Na_2O/Al_2O_3	1.4	1

7. Results and Dissections

I. Analysis Model of Sintering

After the preparation of Kaolin, limestone, and soda ash, it can be seen from Table 4, the alumina (Al_2O_3) content in the sinter feed for molar ratioof Na_2O/Al_2O_3. Knowing the chemical analysis for the mix materials before sintering process in order to recognize the increase in the alumina that would happen after the sintering. Table 4, shows the chemical composition of raw mix depending on the molar ratio before sintering. The obtained results of the alumina percentage (Al_2O_3 %) and leachability after sintering are given in Table 5. Depending on the level of significance (0.05), and using the test (F- test) the regression model that the value of probability (P value) is less than 5 % was found. It is noticeable that the results of regression analysis that gave the adjusted R-squared ((R-Sq (Adjusted)) equal to (82. 46 %). This means that the independent variables X_1, X_2 and X_3 (which are temperature, time and molar ratio) explain (82.46 %) of the changes that occur in the dependent variable Y (Al_2O_3 extraction %) and the rest is due to other factors such as the random error. It outputs the value of the coefficient of the determination (R-Sq) equal to (90.77 %). It can be noted that, the difference between R-squared and adjusted R-squared rate is relatively low which is preferred to be close to one. Therefore, the obtained results are satisfied. It indicates that the linear model provides a good fit over the ranges of process parameters.

$$Y = -24.8365 + 0.0537297X_1 + 0.164332X_2 + 17.2532X_3 \quad (1)$$

The (X_1, X_2 and X_3) represent the temperature, time and molar ratio which affect the (Y) Al_2O_3 extraction %. From the equation, it can be seen that the X_3 is the most effective parameters on the Al_2O_3 extraction %.

II. Response Surface Analysis

The response surface analysis includes a surface response analysis of three-dimensional diagrams (Three-Dimensional Plots) and contour diagrams (Contour Plots) and through these schemes the impact of variables (temperature, time and molar ratio) on alumina extraction %. The Figure 2, represented a three-dimensional plot of the effect of temperature and time on the alumina extraction %. It has been shown that the X-axis was defined as the temperature while the Y-axis was defined as the time and the Z-axis represented the alumina extraction %. It can be noted that both variables (temperature and time) have a clear impact on the alumina extraction %. It can be seen that the temperature is increased to a certain value (1212 °C) and then decreased, while the time increasing in a proportional way with the alumina extraction %. Figure 3, represents the contour plot for the values of temperature and time with the alumina extraction %. It can be observed, there is no intersection between the two factors at low levels. While there is an interaction between them at intermediate to high levels where the alumina extraction % increases with increased values of time but for the temperature it was in the range of (1200 - 1260) °C.

Table 4: Chemical composition of raw materials mix in (wt. %).

Molar ratio (Na_2O/Al_2O_3)	SiO_2%	TiO_2 %	Al_2O_3 %	CaO %	Na_2O %	L.O.I %	Total %
1	15.09	1.20	13.47	30.22	7.5	32.34	99.82
1.08	14.95	1.17	13.34	30.00	7.93	32.29	99.68
1.2	14.74	1.09	13.16	29.46	8.97	32.13	99.55
1.3	14.57	1.05	13.01	29.09	9.34	32.00	99.06
1.4	14.39	1.03	12.94	28.99	9.99	31.99	99.33

Table 5: Alumina % and alumina extraction % from sintering.

No	Temperature (ºC)	Time (min)	Na_2O/Al2O_3	Al_2O_3 %	Al_2O_3 Extraction %
1	1160	54.1	1.08	17.08	63.04
2	1264.5	54.1	1.08	17.47	70.32
3	1160	80.9	1.08	18.23	65.79
4	1264.5	80.9	1.08	18.36	72.82
5	1160	54.1	1.3	18.0	69.85
6	1264.5	54.1	1.3	18.23	75.19
7	1160	80.9	1.3	18.11	71.29
8	1264.5	80.9	1.3	18.74	77.89
9	1125	67.5	1.2	17.56	59.96
10	1300	67.5	1.2	16.72	67.00
11	1212.5	45	1.2	16.63	67.72
12	1212.5	90	1.2	19.95	80.00
13	1212.5	67.5	1	17.38	65.86
14	1212.5	67.5	1.4	17.85	68.41
15	1212.5	67.5	1.2	18.74	76.97
16	1212.5	67.5	1.2	18.74	77.96
17	1212.5	67.5	1.2	18.73	77.89
18	1212.5	67.5	1.2	18.72	77.98
19	1212.5	67.5	1.2	18.73	77.98
20	1212.5	67.5	1.2	18.73	77.93

III. Response Surface Analysis

The response surface analysis includes a surface response analysis of three-dimensional diagrams (Three-Dimensional Plots) and contour diagrams (Contour Plots), and through these schemes the impact of variables (temperature, time and molar ratio) on alumina extraction %. The Figure 2, represented a three-dimensional plot of the effect of temperature and time on the alumina extraction %. It has been shown that the X-axis was defined as the temperature while the Y-axis was defined as the time and the Z-axis represented the alumina extraction %. It can be noted that both variables (temperature and time) have a clear impact on the alumina extraction%. It can be seen that the temperature is increased to a certain value (1212 °C) and then decreased, while the time increasing in a proportional way with the alumina extraction %. Figure 3, represents the contour plot for the values of temperature and time with the alumina extraction %. It can be observed, there is no intersection between the two factors at low levels. While there is an interaction between them at intermediate to high levels, where the alumina extraction % increases with increased values of time but for the temperature it was in the range of (1200 - 1260) °C. The effect of temperature and molar ratio on the alumina extraction% can be seen with the three-dimensional plot as shown in Figure 4. The X-axis was defined as the temperature while the Y-axis was defined as the molar ratio and the Z-axis represented the alumina extraction %. The both variables (temperature and molar ratio) have almost similar effecting role on the alumina extraction %, whereas the increase is up to a specific value and then it decreases, with the notice that the effect of molar ratio is less than the effect of temperature. Figure 5, is the contour plot for the values of temperature and molar ratio on the alumina extraction %. It has been shown that the highest alumina extraction % lies with middle range of both variables of temperature and molar ratio which shown an intersection between them at intermediate levels. For the combination effect of the time and molar ratio, it was represented in a three- dimensional plot as shown in Figure 6. The X-axis was defined as the time while the Y-axis was defined as the molar ratio and the Z-axis represented the alumina extraction %. It can be seen that the highest alumina extraction %, is in a proportional relationship with the time but with the molar ratio it is more likely a convex curve. Figure 7, is the contour plot for the time and molar ratio, which shows that the heist alumina extraction %, lies with the increase of time and molar ratio. The intersection is within the intermediate levels range for both variables (time and molar ratio).

IV. Optimal design for sintering

Optimal design in short is a method to select the best combination experimental trials (runs). For the sintering process, it was with three variables: temperature, time and molar ratio where by five levels for each have been experimented in 20 runs factorial matrix. The optimal design, figure 8, which gave the highest alumina extraction percentage of 80.00 %, was with the following conditions:

- Temperature 1212.5 °C.
- Time 90 min
- Na_2O/Al_2O_3 1.2

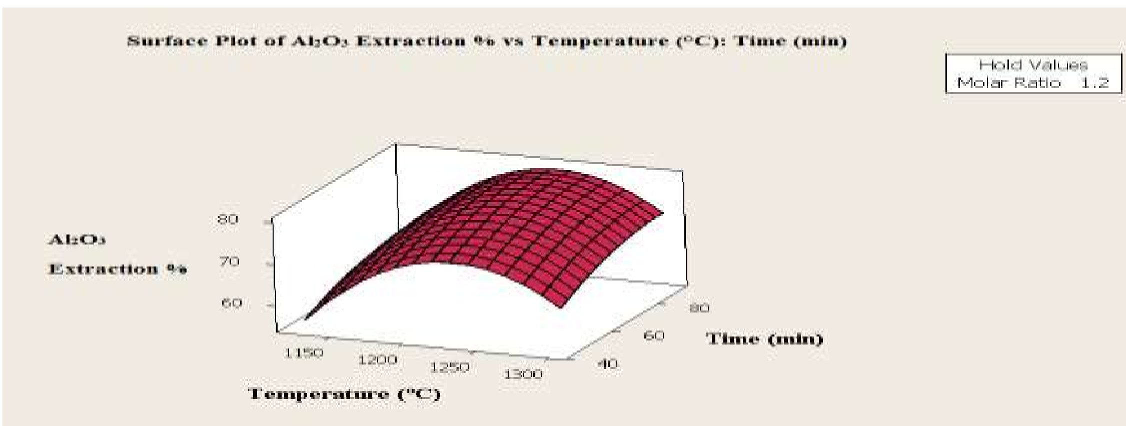

Figure 2: Surface plot diagram illustrates the effect of temperature and time on the alumina extraction %

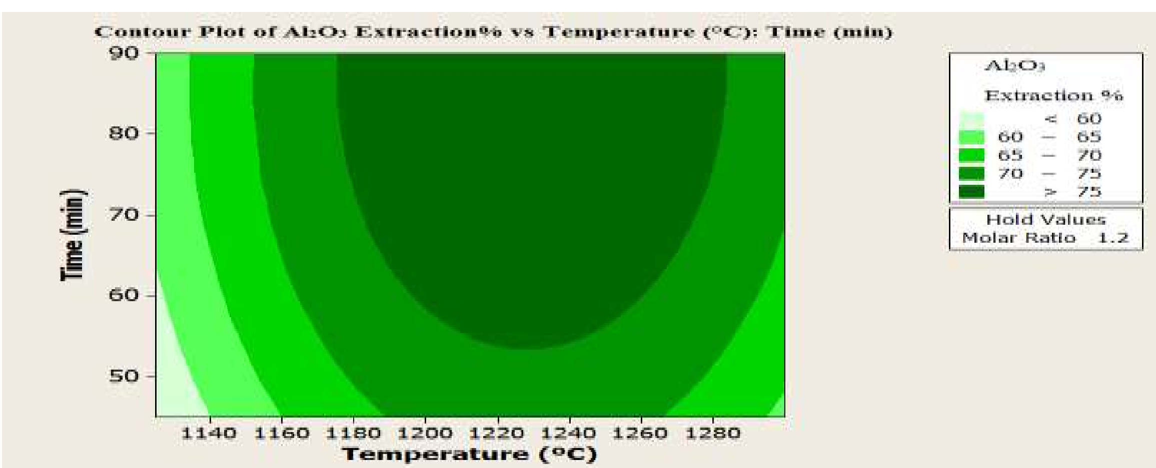

Figure 3: Contour plot diagram illustrates the effect of temperature and time on the alumina extraction %

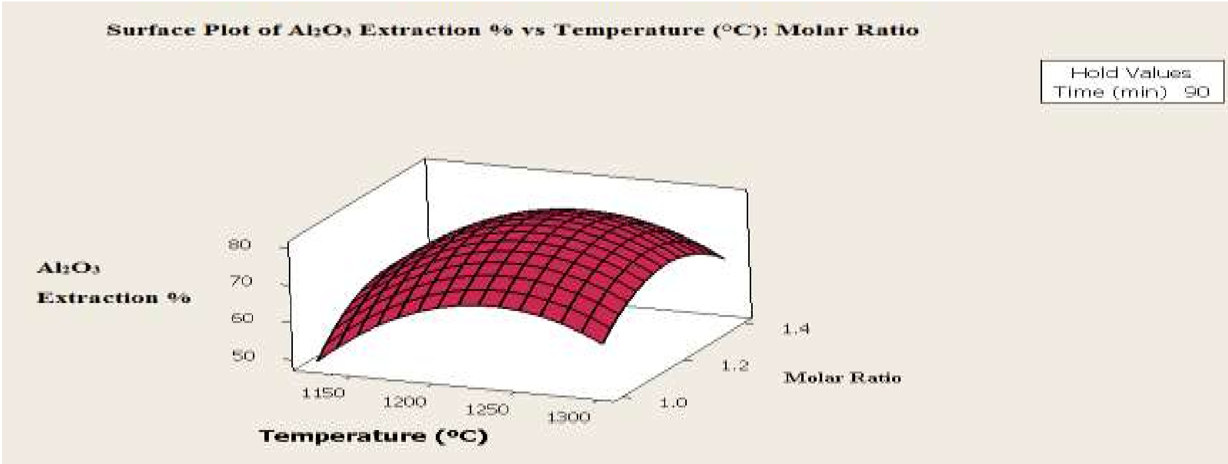

Figure 4: Surface plot diagram illustrates the effect of temperature and molar ratio on the alumina extraction %

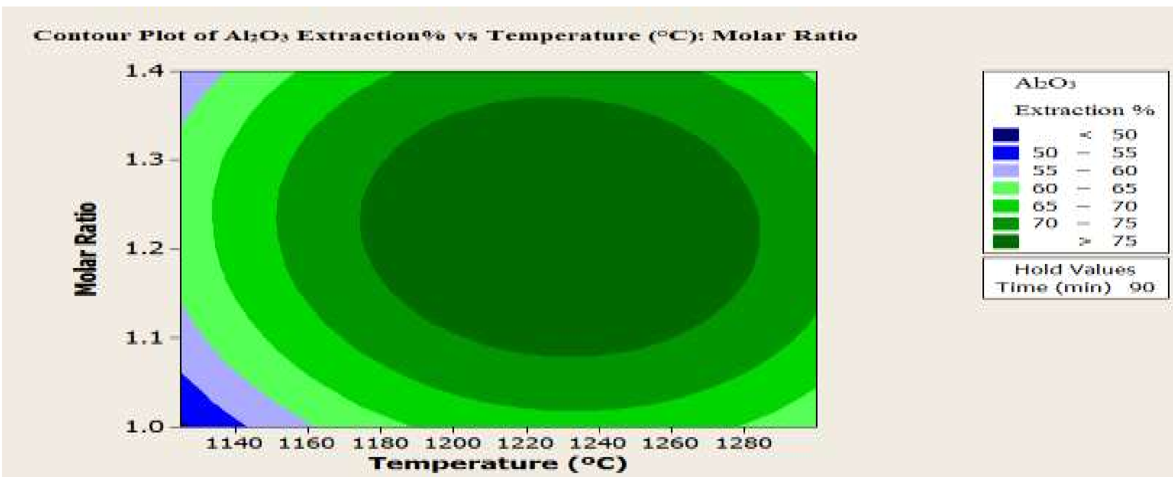

Figure 5: Contour plot diagram illustrates the effect of temperature and molar ratio on the alumina extraction %

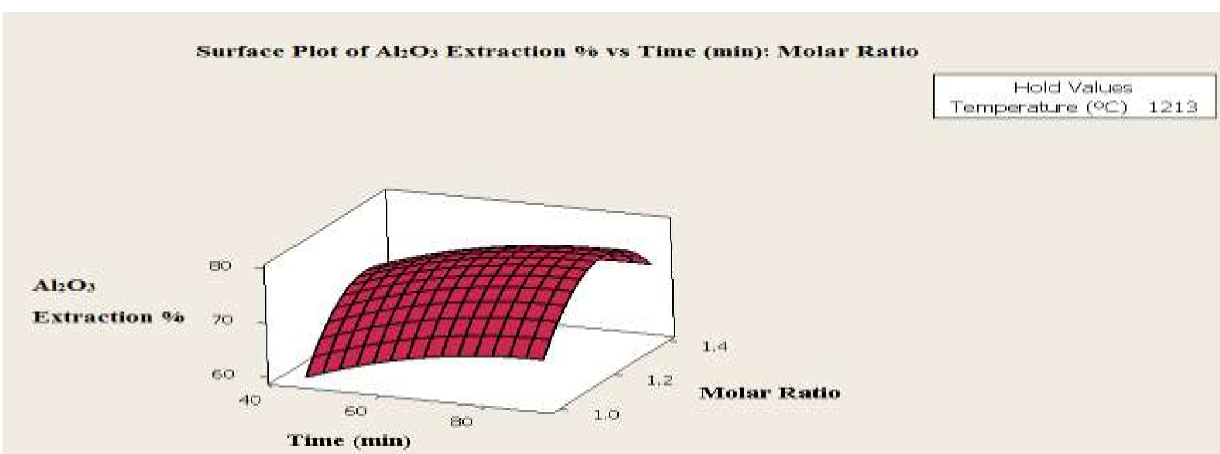

Figure 6: Surface plot diagram illustrates the effect of time and molar ratio on the alumina extraction %

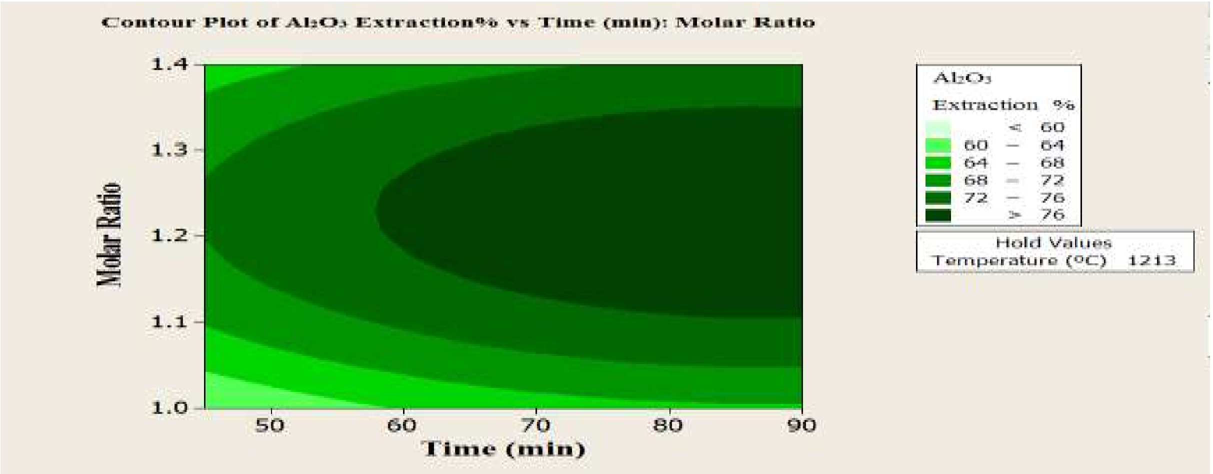

Figure 7: Contour plot diagram illustrates the effect of time and molar ratio on the alumina extraction %

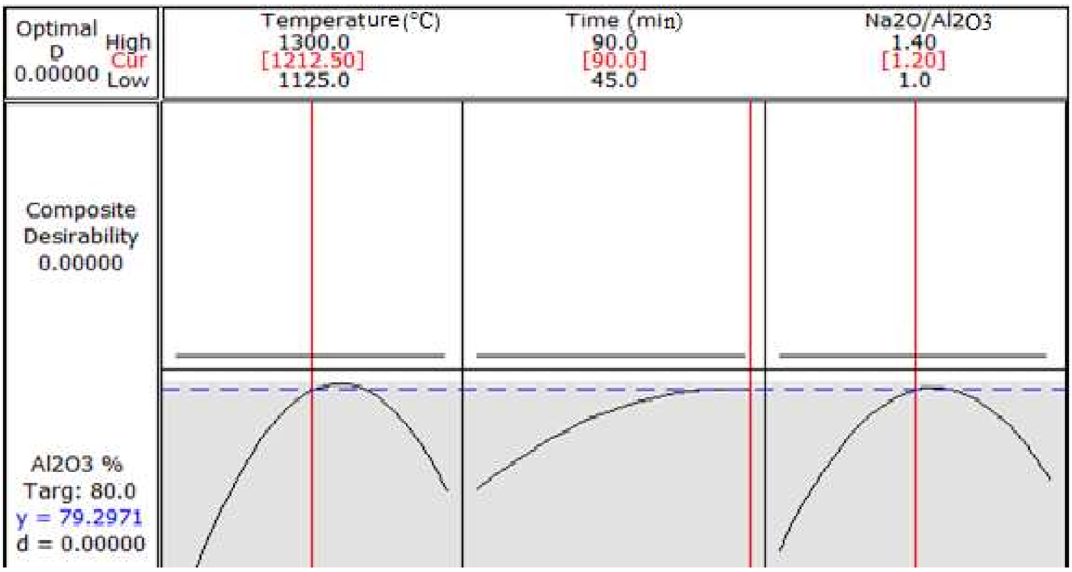

Figure 8: The optimal design for sintering process

8. Conclusions

From the chemical analysis for alumina % before and after sintering by lime-soda, it can be concluded the following optimal results using statistical program (Minitab16).

1) It can be noted that, the sintering operation is assumed that the most effective stage in achieving high alumina extraction. The highest alumina extraction percentage of 80.00%, was with the following conditions:

- Temperature 1212.5 °C.
- Time 90 min.
- Na_2O/Al_2O_3 1.2.

2) The extraction % of alumina increases with increasing temperature, time and molar ratio, but the molar ratio was observed to be the most significant parameter affecting the extraction of alumina as shown in the following mathematical prediction model which determined by the statistical software program (Minitab 16):

$$Y = -24.8365 + 0.0537297X_1 + 0.164332X_2 + 17.2532X_3 \quad (1)$$

The (X_1, X_2 and X_3) represent the temperature, time and molar ratio which effect the (Y) Al_2O_3 extraction %.

3) The contour analysis and factor profiling show the optimal response point and the variables impact on the alumina recovery rate. With the increase of reaction temperature and molar ratio, the alumina recovery rate constantly increases; the maximum of alumina recovery rate was predicted and verified.

4) in order to complete the lime-soda sinter process for extraction of alumina from colored kaolinite ores, leaching process has been done with sodium carbonate solution after sintering at constant conditions which include: Particle size -

75 µ, temperature of 70 ºC, time of 30 min, and sodium carbonate solution with concentration of 70 g/l and solid to liquid ratio of 1/4. The resulted pregnant solution was subjected to carbon dioxide gas at 3 l/min flow rate for 60 min at 70 °C to precipitate aluminum hydroxide, which has been calcined to 1200 °C for 2 hrs, to obtain alpha alumina (α-Al_2O_3) with purity of 98.5 %.

Recommendations

This work can be extended in the future and developed to take into account the following suggestions:

- Bench scale followed by pilot plant tests are recommended to conform the results gained in this work, and study of the economic feasibility of the process.
- Use of other statistical software programs or methods such as Taguchi.

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