Separation of Aluminum Chloride from White Kaolinite by Slime Leaching Process

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ABSTRACT

White kaolinite materials are available raw materials in the western desert in Iraq which exist in Al-Amige region within sediments near the surface. White kaolinite is a high grade raw material which is rich in alumina and its reserve is about 20 million Ton .and because of its locality and its ability of economical investment so the idea of separation of the alumina from it is appeared. The white kaolinite is calcinated at 600^0Cfor one hour .The slime leaching for it was applied using hydrochloric acid at different variable conditions (time, molarity ,and particle sizes) to produce aluminum chloride .The product material can be used as paint manufacturing , antiperspirants ,petroleum refining , product of synthetic rubber and making detergents. The best results were obtained at particle size of-106+75micron, 3 molarity ,3 hour and at 80^0C, 80 r.p.m. and solid: liquid (1:3). The alumina grade in the powder after separation was reduced from 28% to 5.069 %, and the absorption degree of the Aluminum Chloride was 2.91 and the separation percentage was 82.34 %.

Keywords: white kaolinite, calcination,slime leaching, aluminumchloride, hydrochloric acid.

فصل كلوريد الالمنيوم من الكاؤولين الابيض بطريقةالاذابة بالطفو

الخلاصة :

الكاؤولين الابيض هومن الموادالخام المتوفرة في المنطقة الغربية من العراقاذتتواجد في منطقةالعامج ضمن الترسبات القريبة من سطح الارض ويحتوي على رتبة عالية من الالومينا ويبلغ الاحتياطي فيها حوالى 20 مليون طن. وبسبب توفرهذه الخامات محليا وبسبب امكانية استثمارها اقتصاديا , لذابرزت فكرةهذا البحث وذلك بفصل الالومينا منها عن طريق كلسنة الكاؤولين الابيض عند درجةحرارة 600 درجة مئوية لمدة ساعة واحدةوبعدها تم استخدام طريقة الاذابة بالطفوباستعمال حامض الهيدروكلوريك عند ظروف مختلفة من الزمن والمولارية والحجم الحبيبي وذلك لانتاج كلوريدالالمنيوم .ان المادة الناتجة ممكن ان تستخدم في صناعة الاصباغ ومضادات التعرق وتصفية البترول وانتاج المطاط الصناعي وفي صنع المنظفات .ان افضل النتائج التي تم الحصول عليهاهي

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عندحجم حبيبي -106+75 مايكرون ,3 مولاري ,3 ساعة ,وبدرجةحرارة 80 درجة مئوية وبسرعة دورانية 80 دورة بالدقيقة ونسبة الصلب :السائل (3:1) . ان رتبة الالومينا في مسحوق الكاؤولين بعد الفصل قد قلت من 28% الى 5.069% وان درجة الامتصاصية لكلوريد الالمنيوم في المحلول هي 2.91 وان النسبة المئوية للفصل اصبحت82.34 %

INTRODUCTION

Kaolinite is very important group of clay minerals usually white mineral dioctahedralphyllosilicates (sheet silicates). The general formula for it is $Al_4[Si_4O_{10}](OH)_8$. It has a low shrink-swell capacity and a low cation exchange capacity(1-15meq/100g).Kaolinite represents the final product from the chemical weathering of feldspars to give clays[1,2], specific gravity of 2.6–2.7 ,hardness[mohs] 2.0–2.5; monoclinic; white, grayish, or stained a variety of colures[3]. Kaolin-type clays undergo a series of phase transformations upon thermal treatment in air at atmospheric pressure. Endothermic dehydroxylation (or alternatively, dehydration) begins at 550–600 °C to produce disordered metakaolin, $Al_2Si_2O_7$[4].Par Moor and Par, Cornwall [5]and also Alzahranh and Abdul-Majid[6] indicated that kaolinite is calcinated by heating it at (500-600)^oC to get an irregular meta kaolinite($2Al_2Si_2O_7$). It will lose its crystalline water and become crystalline meta kaolinite of dual dimensions as below:

$$2Al_2Si_2O_5(OH) \xrightarrow{\Phi} 2\ Al_2Si_2 + 4H_2O \qquad \ldots(1)$$

The abundance of aluminum in the Earth's crust was estimated to be about 8.8 percent. It occurs in many different minerals. A relatively small amount of aluminum is used to make a large variety of aluminum compounds[7], **Aluminum chloride** ($AlCl_3$) is the main compound of aluminum and chlorine. It is white but samples are often contaminated with iron trichloride, giving it a yellow colour[8] . The solid has a low melting and boiling point. It is mainly produced and consumed in the production of aluminum metal, but large amounts are also used in other areas of chemical industry. The compound is often cited as a Lewis acid[9,10]. It is an example of an inorganic compound that "cracks" at mild temperature, reversibly changing from a polymer to a molecule $AlCl_3$ adopts three different structures, depending on the temperature and the state (solid, liquid and gas). Solid $AlCl_3$ is a sheet-like layered of cubic close packed layers. In this framework, the aluminum centers exhibit octahedral coordination geometry. In the melt, aluminum trichloride exists as the dimmer Al_2Cl_6, with tetra coordinate aluminum . This change in structure is related to the lower density of the liquid phase (1.78 g/cm^3) vs solid aluminum trichloride (2.48 g/cm^3). Al_2Cl_6dimmers are also found in the vapor phase. At higher temperatures, the Al_2Cl_6dimmers dissociate into trigonal planar $AlCl_3$, which is structurally analogous to BF_3. The melt conducts electricity poorly, unlike more ionic halides such as sodium chloride[11,12].

Aluminum chloride is manufactured on a large scale by the exothermic reaction of aluminum metal with chlorine or hydrogen chloride at temperatures between 650 to 750 °C[11]

$$2\ Al + 3\ Cl_2 \rightarrow 2\ AlCl_3 \qquad \ldots (2)$$

$$2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2 \qquad \ldots(3)$$

Hydrated aluminum trichloride is prepared by dissolving aluminum oxides in hydrochloric acid. Heating this solid does not produce anhydrous aluminum trichloride, the hexahydrate decomposes to aluminum oxide when heated to 300 °C[12]

$$2\ AlCl_3 + 3\ H_2O \rightarrow Al_2O_3 + 6\ HCl \qquad \ldots (4)$$

Aluminum chloride is used in petroleumrefining and in the production of synthetic rubber and polymers. Although it has a similar name, aluminum chlorohydrate has fewer and very different applications like as a hardening agent and an antiperspirant. It is an intermediate in the production of aluminum metal[13]

Expermental procedure:

White kaolinite ore isc supplied from Al-Amig region in the western desert inIraq, and is located between wadiamig and wadialhussainiyat [18],and its chemical analysis for it is applied as shown in Table(1) on the other hand the mineral analysis of the ore consiste of (Kaolinite,Quartz,Hematite,Anatase,Goethite,Calsite and Dolomite) as shown in fig (1).It indicates that the grade of alumina in genuine white kaolinite ore was 28%and the reserve is about 20 million Ton[18]. .In order to separate the alumina from it, the ore was crushed using jaw crusher then grinded By ball mill. The ore powder wasclassified to different particle sizes using shaking screen equipment. The obtained particle sizes werec(-250+150,-150+106,-106+75micron).The ore powder of different particle sizes were calcinated to get rid of volatile materials and water vapor[5,6].For calcination process, the carbolite furnace at 600 ^{0}C for one hour was used.

A(25gm) of calcinated ore was used for slime leaching[17].for the slime leaching processa36%hydrochloric acid with different molaritiesof 3,4 and5 were used . The calcinated ore was immersed in the acid molarities asmentioned above in beaker by the
ratio of (1: 3) (solid: liquid) onhot plate magnetic stirrer equipment at (80 r.p.m) &temperature of (80^{0}C) at different times of 1,2 and 3hours.Thenfiltration process was done for each case to separate the solid powder(which contain the silica , iron and the residual of alumina), from the loaded liquid of soluted Alumina as an ($AlCl_3$).The equipment (UV-1100 spectro photometer) was used for the loaded liquid of soluted alumina as an ($AlCl_3$), where the wavelength of aluminum chloride is(450 nm).Drying was applied by using dryer furnace to the solidpowder,and then the chemical analysis was applied for the solid powder to detect the quantity of residual alumina with the rest white solid powder. To calculate the separation percentage, the following formula is used as follow[19]:

$$S\% = \frac{\mathrm{G1} - \mathrm{G2}}{\mathrm{G1}}$$

S%=separation percentage
G1=metal grade in the original ore
G2=metal grade after separation process
The results of separation were explained in Table (2) and (3) and the technical flow chart for the process used in this work was presented in Figure (2)

Results and Discussions

The white kaolinite material is a high grade raw material which is rich in alumina. The experimental procedures were concerned the different parameters effect on the separation process. The purpose of this study is to show the effects of these parameters on the separation process as below:

Effect of the particle size:

The shaking screen for the ore powder produced different particle sizes of (250+150,-150+106,-106+75micron). These particles were calcinated at 600^0C for one hour which gave generally an irregular meta kaolinite .These particleslost their crystalline water as mentioned by Par Moor and Wrnwall and Alzahranh[5, 6].The calcinated particle sizes are immersed in the hydrochloric acid for applying leaching process. The leaching process results were shown in Table (2) and Table(3) .These resultsindicate that the fine particle sizes decreased the alumina grade in the powder after separation as shown in Figure (3) . The lowest alumina grade was observed for particle size of(-106+75 µ), which indicated that the alumina leaching rate in hydrochloric acid increased. The fine particle sizes increased the surface area which exposed to the solvent liquid and increased the leaching rate as explained by Alzahrani and Abdul-Majid [6].

The absorption degree was measured by using UV-1100 spectro photometer equipment to the loaded liquid of soluted alumina, it can be noticed from Table(2) and Fig(4) that the minimum absorption degree was observed at large particle sizes like (-250+150µ) .Therefore the absorption degree was gradually increased with decreasing particle size and at times (1,2and 3,)hours .So that the solubility of alumina in the solution was higher specially atparticle size of (-106+75µ) and the absorption degree was (2.91).Figure (5) shows the leaching quantity of alumina increased and the separation percentage also increased .this explains that the obtained maximum separation percentage was 82.34% at particle size of (-106+75 µ).This also agreed with the work of Fernando G, Colin and O thers[10,17] who explained that in the slime leaching process , the solubility becomes bigger due to the acid attacked the particles from all directions, so that the higher alumina leaching rate or separation percentage was obtained at fine particle sizes.

Effect of leaching time

Figure (6) indicates the effect of leaching time on alumina grade in the powder after separation. This grade is almost big for all particle sizes at leaching time for one hour. Then the alumina grade in the powder decreased due to gradual increase in leaching time to(3 hours) and the minimum grade was obtained with particle size of (106+ 75 µ),while for other particle sizes, the obtained grade was larger and remained constant after (2 hours) .It can be noticed that with fine particles of(-106+ 75 µ),the response of these particles to react with hydrochloric acid was larger which means higher leaching and lower alumina grade from (28%) to(5.69%)in the powder. This can be clearly observed in Figure (7). It illustrates that the absorption degree was generally increased as long as the particle size decreased and this assures that the more leaching of alumina as aluminum chloride occurres especially at (3hours) and the maximum absorption degree was (2.91)at particle size of(-106 +75µ). An increase in leaching time to (3hours) also increased the separation percentage for all particle sizes and the highest percentage of (82.34) %was for particle size of (106+75µ) as shown in Figure(8).

The effect of acid molarity :

The other important parameter that affect the separation process was the molarity of hydrochloric acid .The alumina grade (in the powder) increased with an increase in molarity from(3 to5)hydrochloric acid and the minimum grade was obtained with 3 molarity as shown in Figure (9) and table (3). The leaching rate decreased with an increase in molarity such as(4,5) .

Fig (10) explains that at low molarity such as (3) ,the absorption degree is high , and starting to decrease gradually when the molarity increases specially at (5) molarity, so the optimal molarity was at (3) where the leaching rate increased, this may be due to the presence of the ionic solution at specific pH which increased the leaching rate of alumina in the powder(Ionic decomposition),after that a reaction between the aluminum positive ions with the negative chloride ionsoccured to form $AlCl_3$ which is soluble product in the solution. This agrees with the explanation of Otto Humboldt and others [14] who explained the effect of pH to form important reagent effected the leaching ability of sediments

The increase in acid molarity above the optimal (3) molarity , decreased the separation percentage as shown in Figure (11) . Hamilton Perkins cady[15] explained that on the increasing of ions concentration above the required limit (above3 M in this research) in the solution leads to complex composite formation with the alumina which makes the solublizing process difficult. R.E Dickerson and others[16]explained that some acids have the ability to become more soluble in water ,so in the beginning the range of solubility rate increases ,but with increasing acidity ,the ions concentration increase and the ionizing degree decreases and then the solubility range decreases accordingly like hydrochloric, sulphric and Alcoholic acid. From the above results and discussions it can be concluded that the optimal separation percentage was obtained to be 82.34% at particle size of -106 +75µ achieved ,3hour leaching time and 3molarity of Hydrochloric acid.

CONCLUSIONS

From the chemical analysis for the original white kaolinite ore ,the grade of alumina in it was 28.69%and from the mineral analysis shows that the ore consist of (Kaolinite, Quartz, Hematite, Anatase, Goethite, Calsite and Dolomite).

It was clear from many tests that the best melting time was 3 hours and the best molarity for the hydrochloric acid was 3 molarity and the best particle size -106+75 micron, where the alumina grade reduced from 28% to 5.069 in the Kaolin powder and the absorption degree in the Aluminum Chloride is 2.91,and the separation percentage was increased to produce aluminum chloride at 82.34%

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Table (1) Shows the chemical analysis for original white kaolinite.

Al_2O_3%	SiO_2%	Fe_2O_3%	**TiO_2%**	**Cao%**	**MgO%**	**Na_2O%**	**K_2O%**	**SO_3%**	**L.O.I.**
28	50	1.4	**0.9**	**0.90**	**0.44**	**0.66**	**0.64**	**0.60P**	**16.40**

Table (2) Indicates the results of leaching procces at different times and particle sizes and at 3 acid Molarity .

Separation %	Absorption degree	Grade % for Alumina in solid powder (after separation)	Weight of solidpowder (after separation) (gm)	Time hour	Particle size (micron)
75.54	1.58	7.018	7.148	1hr	-250+150
74.173	2.544	7.41	9.506		-150+106
73.2	2.575	7.69	9.608		-106+75
78.35	1.574	6.21	9.85		-250+150
77.169	2.660	6.55	9.843	2 hr	-150+106
78.94	2.757	6.04	9.065		-106+75
77.69	1.477	6.4	8.573	3hr	-250+150
77.38	2.638	6.49	9.90		-150+106
82.34	2.91	5.069	8.848		-106+75

Table (3) Illustrates the effect of molarity on the grade & absorption and separation%.

Separation%	Absorption degree	Grade % for Alumina in solid powder (after separation)	Weight of solid powder after separation (gm)	Acid molarity (M)
82.34	2.91	6.21	9.85	3
72	2.543	7.98	9.101	4
70	1.49	8.55	8.006	5

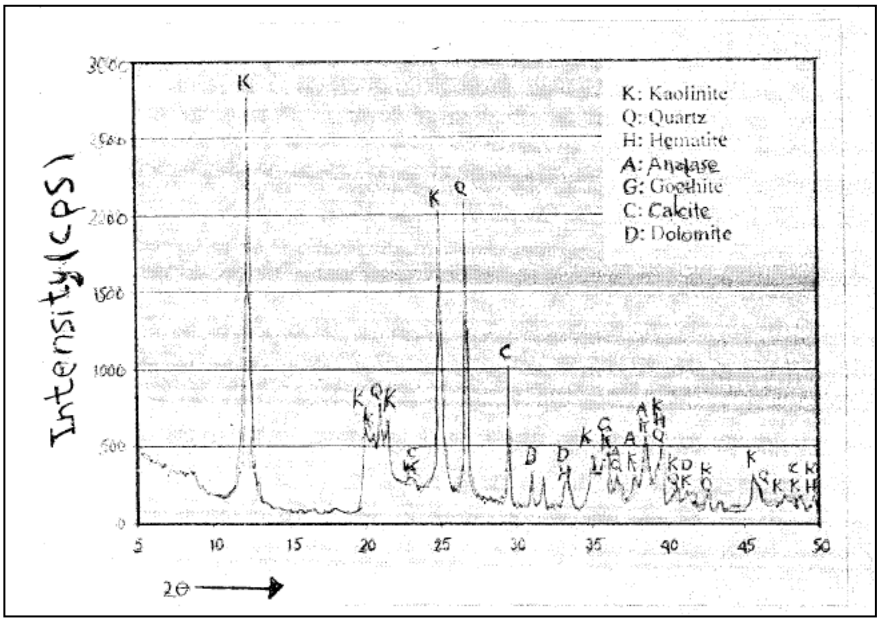

Figure (1) The mineral analysis (XRD) of AL- Amij white kaolinite ore.

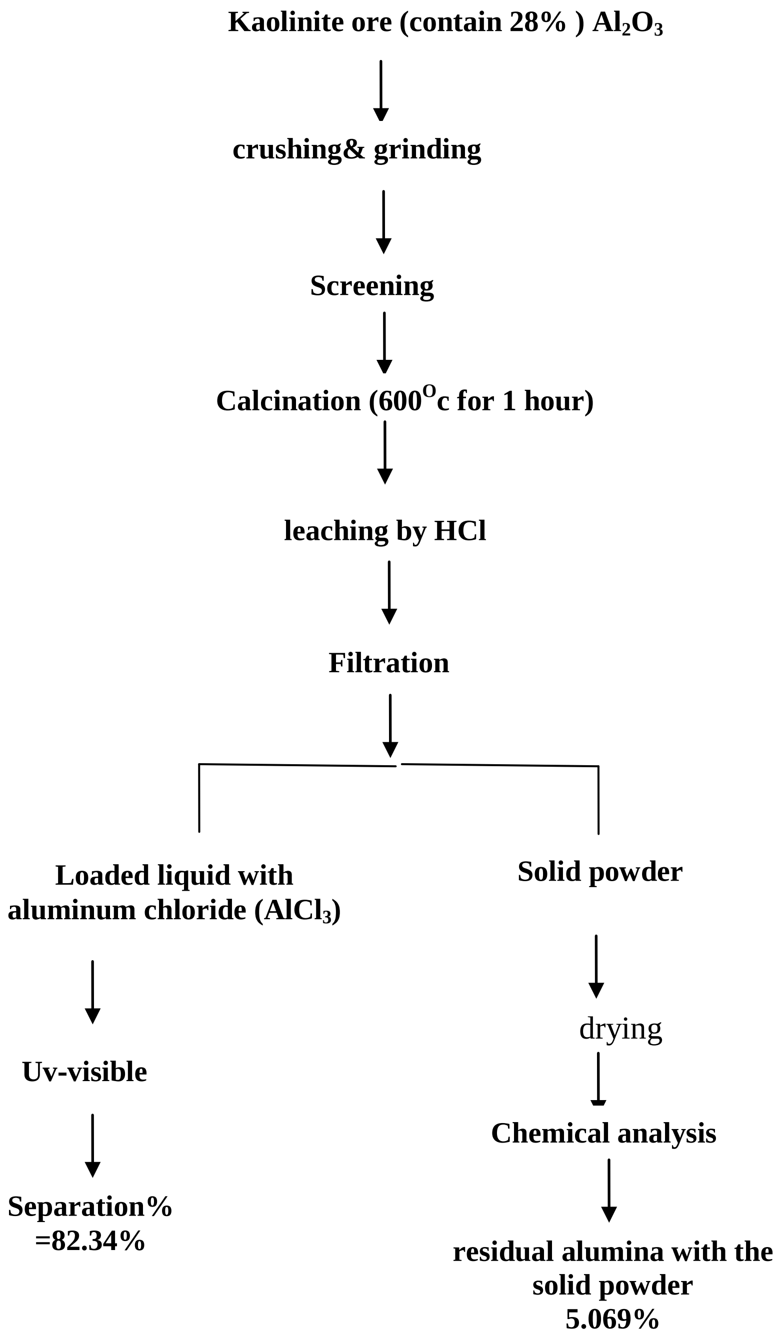

Figure (2) Flow chart for the experimental work used in the study.

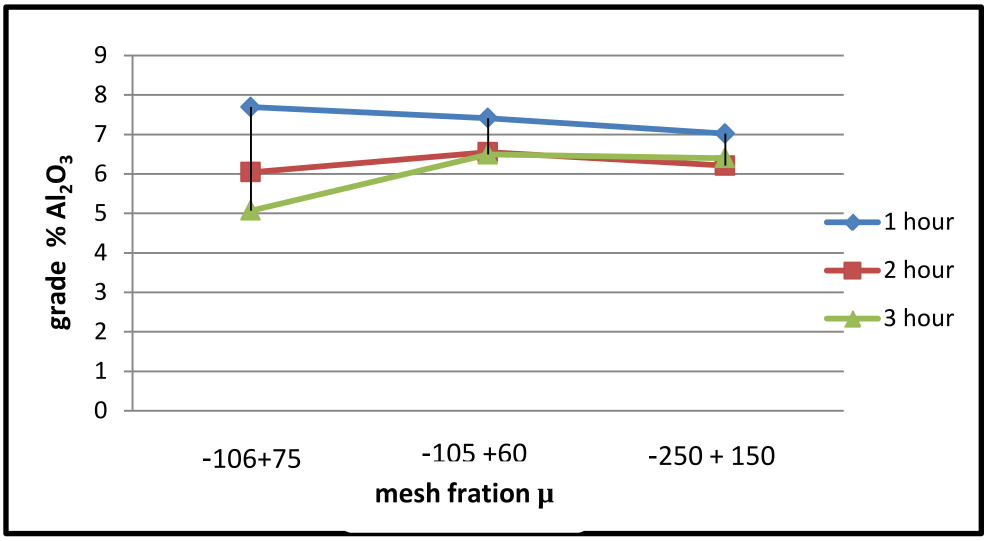

Figure (3) Effect of particle size of ore on the Alumina grade in the residual solid powder.

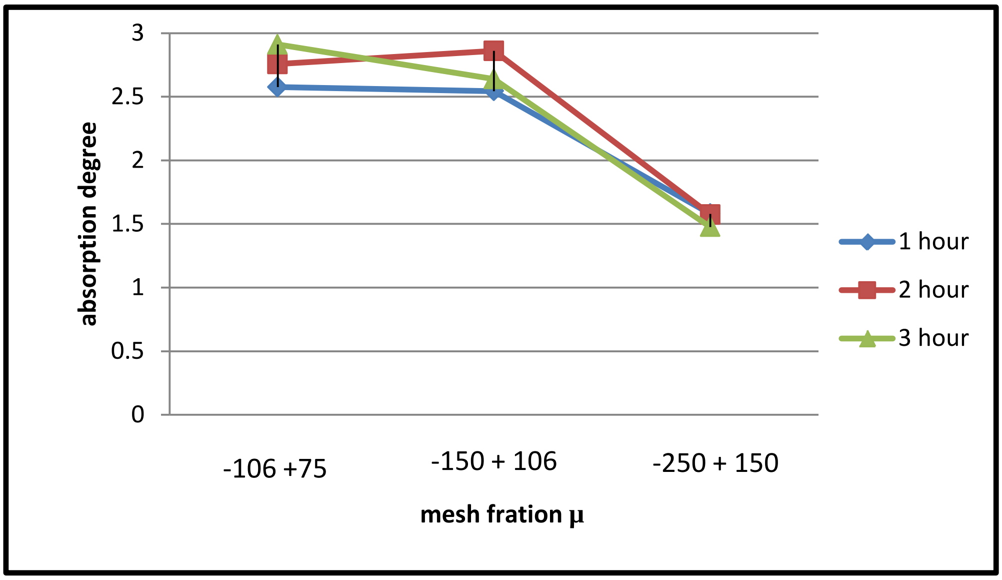

Figure (4) Effect of particle size of ore on the absorption degree of Aluminum in $AlCl_3$ solution.

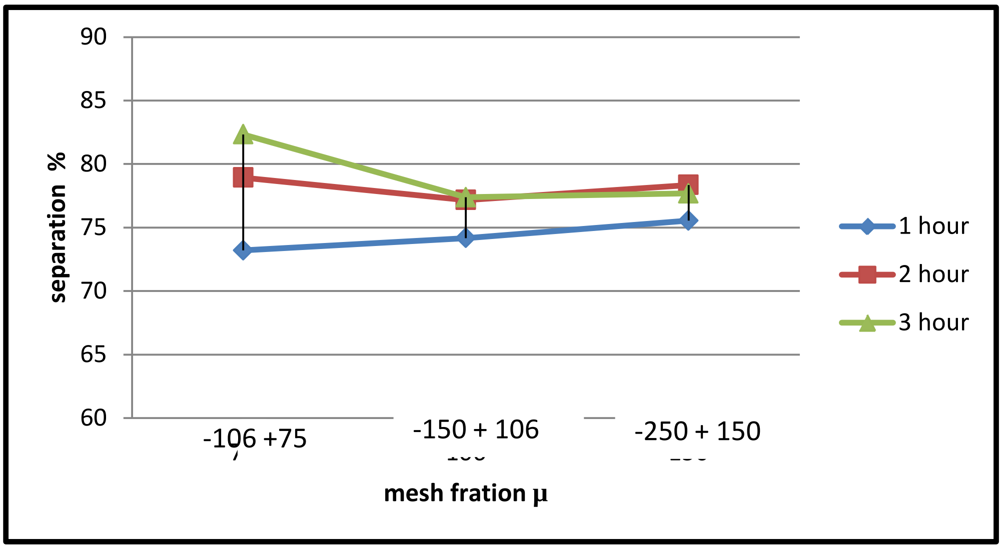

Figure (5) Effect of particle size of ore on the separation percentage of Alumina.

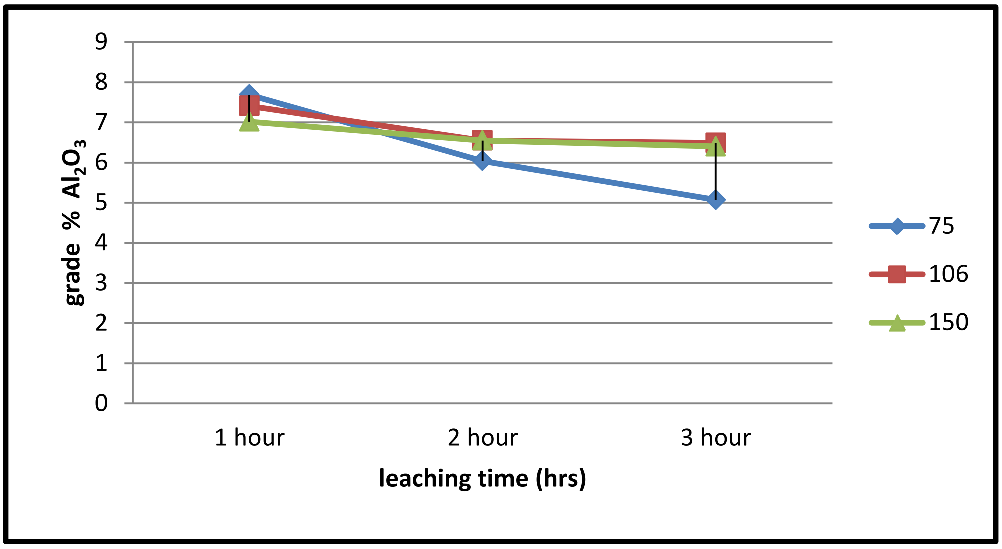

Figure (6) Effect of Leaching time on the grade of Alumina in the residual solid powder.

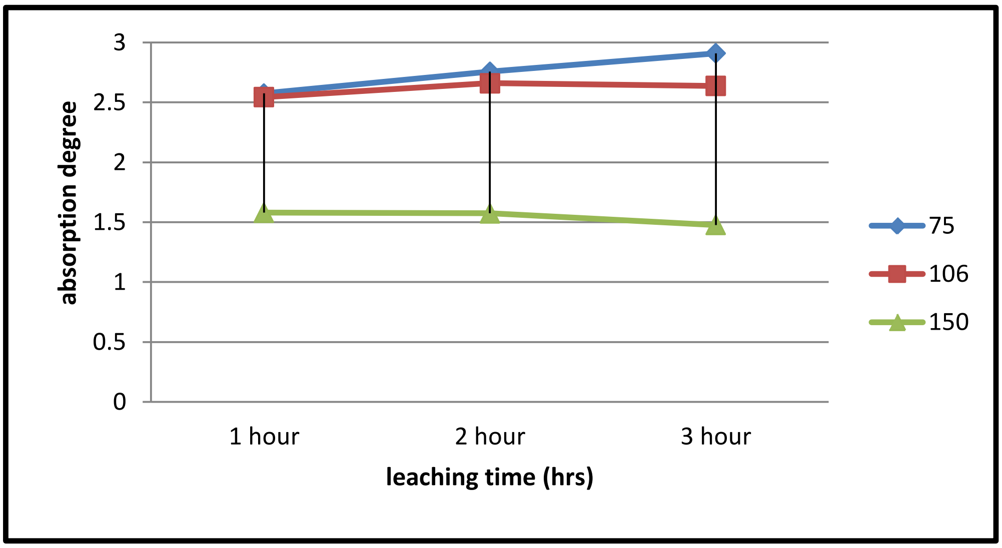

Figure (7)Effect of Leaching time on the absorption degree of alumina in $AlCl_3$ solution.

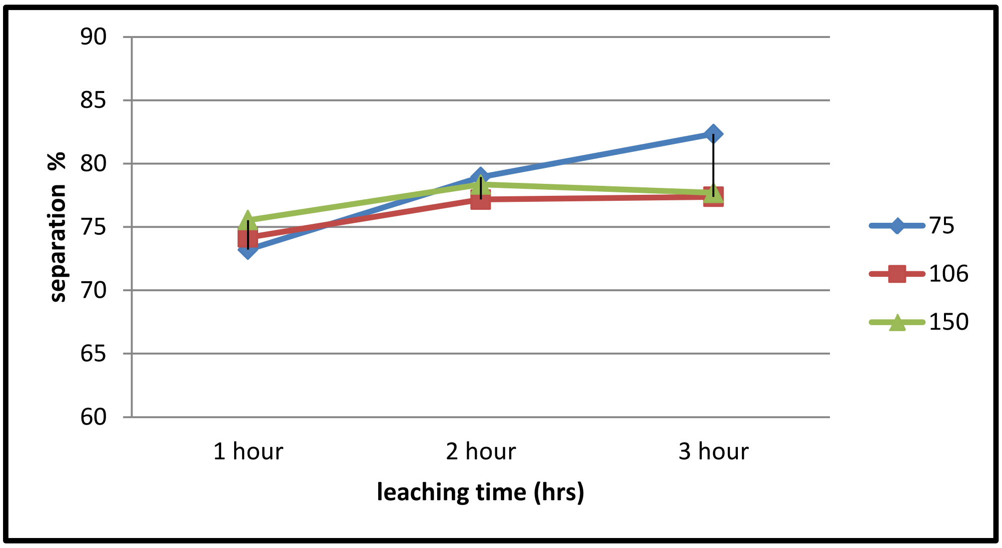

Figure (8) Effect of Leaching time on the separation percentage of Alumina.

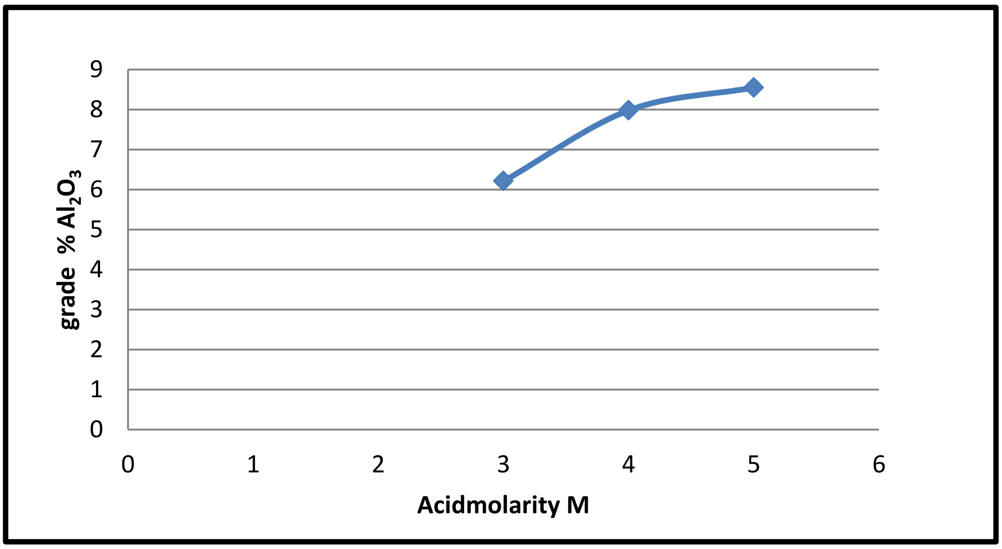

Figure (9)Effect of the molarity on the Alumina grade in the residual solid powder.

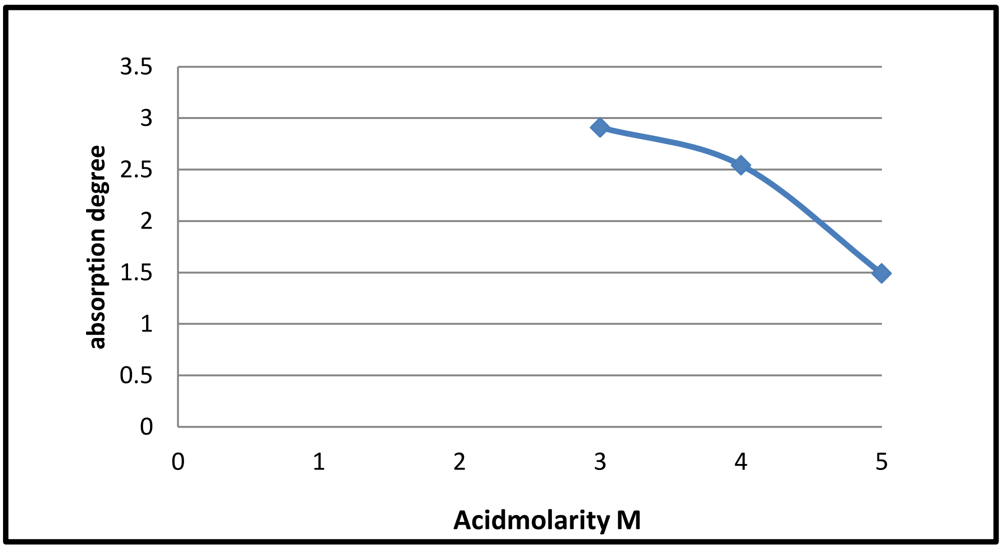

Figure (10) Effect of the acid molarity on the absorption degree in$AlCl_3$ solution.

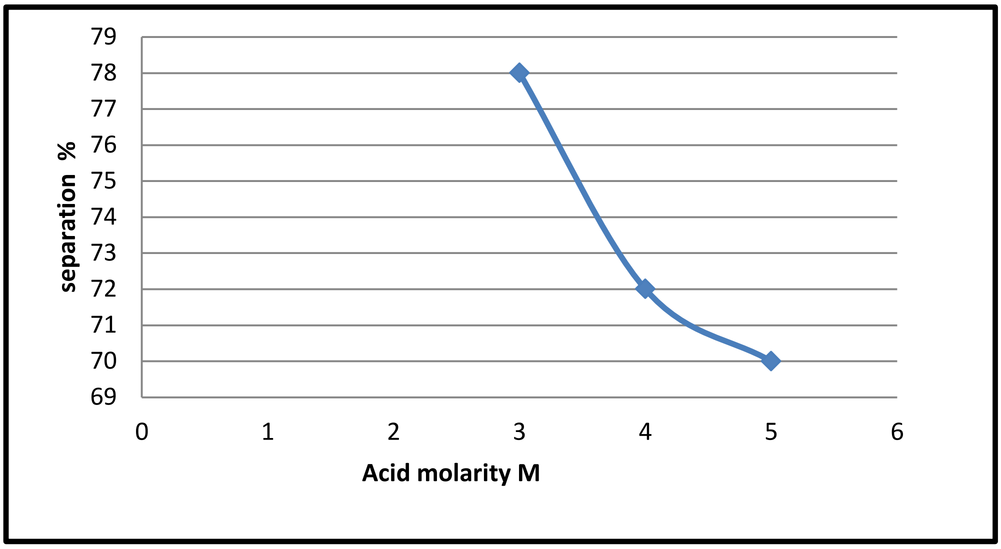

Figure (11) Effect of the acid molarity on the separation percentage of Alumina.