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Extraction of Alumina from Nawan Kaolin by Acid Leaching

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ABSTRACT

This paper describes the production of alumina from Nawan kaolin by acid leaching with sulfuric and hydrochloric acids. Kaolin was calcined at 850°C and was leached with 6 M acid at 90°C, 5M NaOH followed by HCl solutions were added to the leaching liquor and the precipitated aluminum hydroxide was converted to alumina by calcination at 900°C. Materials were characterized by FTIR, XRD, and SEM techniques. The alumina extraction percent was determined at different leaching times (30-180 min) and solid/liquid ratios (0.05-0.15 g/ml). The purity of kaolin is about 95%. The percent of extraction of alumina rapidly increases with the solid/liquid ratio up to 0.1g/ml then decreases thereafter. The percent of extraction of alumina is higher for HCl than H_2SO_4. The size of the chloride and sulfate ions is the key factor that controls the percent of extraction of alumina from calcined kaolin under the studied conditions.

Keywords: Alumina, Kaolin, Acid leaching, FTIR, XRD, SEM.

INTRODUCTION

Alumina that exists as a stable form (α-alumina) and in a variety of meta-stable forms including γ-alumina[1] is an important industrial mineral, which can be used as an abrasive material and as adsorbent[2]. Alumina has been widely used in advanced technological applications including its use for the processing of high-quality insulators[3], semiconductors[4], microelectronics[5], high-strength materials[6], ceramics, refractories[7], biofuel and cell-fuel[8], fireproof plastics[6] and high-grade polishes[9]. Bauxite is the main raw material used in the production of alumina by the Bayer process[10]. But because bauxite is not discovered in Saudi Arabia in economic quantities[11], kaolinitic clay has been processed for the production of alumina alternative to bauxite[12]. Kaolin is widely used in the manufacture of paper, functional filler, fiberglass, and ceramics[13]. Kaolin is a common weathering product of many tropical and sub-tropical soils[14] and consists of kaolinite mineral, $A_{12}Si_2O_5(OH)_4$, in addition to many accessory minerals such as carbonates, feldspars, and hematite. Kaolinite is a member of the two-layer planar hydrous phyllosilicate minerals called the kaolin group[15]. The structural unit of kaolinite consists of single tetrahedral silica and octahedral alumina sheets bonded together by

hydrogen bonding[16]. Leaching process is commonly used in the extractive metallurgy due to its low-cost implication, eco-friendly procedure, low-energy requirement as well as ability to treat low-grade ores[17]. The three processes commonly used for extraction of alumina from clays are; (1) the acid leaching with sulfuric acid, hydrochloric acid or nitric acid to extract the alumina from calcined clay[18,19]. (2) The sulfatization by sintering clay with ammonium sulfate followed by extracting alumina by leaching with hot water[20]. (3) The alkali roasting by sintering clay with lime or soda followed by extracting alumina and silica by leaching with hot water[21,22]. Acids were proved more effective in aluminum extraction, than bases[23]. From an industrial point of view, the leaching of calcined kaolin clay in hydrochloric acid has several significant advantages including; low solubility of silica,[24] the possibility of selective crystallization of $AlCl_3 \bullet 6H_2O$[25] and recovery of hydrochloric acid from the waste products for reuse in the process[26]. There have been a lot of recent research articles has focused on the process extracting alumina from kaolin by acid leaching where the extraction rate did not exceed 90%[27,28]. The alumina could not be efficiently extracted from kaolin by acid leaching because of the existence of the stable structures of Al-O-Si and Si-O-Si[29] as well as the formation of hydrated silica during leaching reaction that would hinder the contact between leaching agent and leaching nucleus[30]. The rate of extraction of alumina can be enhanced by calcination of kaolin in the temperature range 500-750°C prior to leaching to increase the reactivity of the particles by rendering the aluminum in the solid more soluble and removing organic material in the pores[31]. Taking into consideration that the kinetics of the dissolution of aluminum from calcined kaolin by hydrochloric acid is a liquid-film diffusion controlled process[32]. Hence, the rate of extraction of alumina was enhanced by the hydrothermal leaching of calcined kaolin by hydrochloric acid reaching about 98%[33,34]. As the hydrothermal leaching reduces the resistances caused by diffusion in the presence of hydrated silica[35]. The leaching of calcined kaolin in hydrochloric acid in the presence of fluoride ions also makes higher extractions possible at lower roasting and leaching temperatures[36,37]. Generally, the extraction of alumina from calcined kaolin by leaching with hydrochloric acid depends on the many variables including; fineness of kaolin, period and temperature of calcination, the concentration of hydrochloric acid, liquid/solid ratio as well as period and temperature of leaching[15]. A previous work was carried out to extract alumina from the Saudi kaolinitic clay of Riyadh district calcined at 700°C then leached by 3 M hydrochloric acid under boiling reflux conditions with maximum alumina extraction of about 63%11. Another work involves leaching with 40%wt. sulfuric acid under boiling conditions revealed 90.9% extraction of alumina[38]. The objective of this paper is to study the suitability of producing alumina from kaolin deposits located nearby Nawan, Al Baha, KSA by acid leaching with sulfuric and hydrochloric acids.

MATERIALS AND EXPERIMENTAL

Kaolin was provided from the kaolin deposits located about 13 km to the southeast of Nawan city, Al Baha, KSA within coordinates (19o29'10.27" N and 41o15'20.27" E) as illustrated in the location map in Fig. 1. The kaolin deposits cover an area of up to 10 km^2 where kaolin is found in sub-surface layers covered with sand and marl deposits. Kaolin is also shown in the form of a large number of prominent divergent tongues that rise several meters above the earth's surface and extend up to 300 meters. The area contains an enormous stock of whitish kaolin. The kaolin mineral nature varies from hard stone to soft mud depending on the accessory minerals. Kaolin sample was crushed, ground and screened to particles size below 90 µm. Kaolin was calcined in a muffle furnace at 850°C for 2 h and was cooled down in the furnace to the room temperature. Two leaching agents were used, are 6 M sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). 10 g of calcined kaolin was added to 100 ml of the 6 M leaching agent in a 250 mL round flask with condenser previously heated at 90°C (slurry density is 10 g per 100 ml of the leaching agent) and the slurry was stirred at 500 rpm for 3 hours. The slurry was diluted with 100 ml of distilled water as well as was filtered using a Buchner funnel and the dealuminated residue was washed with distilled water and dried at 80°C. The filtrate was heated to near boiling followed by the addition of an excess solution of 5M NaOH, to convert alumina into $NaAlO_2$ to facilitate the separation of the hydroxides of iron and magnesium. After filtration, 6M HCl was added to the $NaAlO_2$ filtrate with stirring to adjust the pH to 7, and the aluminum hydroxide precipitate

was filtered, washed with distilled water and dried at 110°C overnight. Alumina (Al_2O_3) was obtained by the calcination of aluminum hydroxide precipitate in a muffle furnace at 900°C for 2 hours. The leaching procedure was summarized in Fig. 2. The aluminum recovery percent was determined from the weight of alumina. Leaching of Al from calcined kaolin with H_2SO_4 and HCl at different leaching time (30, 60, 90, 120 and 180 min) and solid/liquid ratios (0.05, 0.10 and 0.15 g/ml) using 6 M acid solution at 90°C were studied as the leaching system was illustrated in Figure 3.

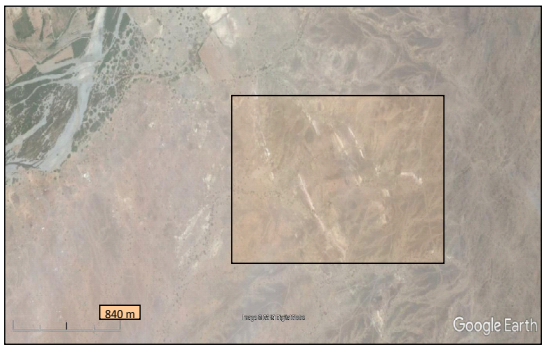

Fig. 1. Kaolin location map

The dehydroxylation of kaolin at 850°C approximately proceeds according to the following equation (1):

$$Al_2O_3.2SiO_2.2H_2O_{(g} \rightarrow Al_2O_3.2SiO_{2(g)}+2H_2O_{(g} \quad (1)$$

The Al_2O_3 recovery was calculated by using Equation (2):

$$\%Al_2O_3 = 100 \times (wt/wt_o) \quad (2)$$

Where: *wt* is the weight of Al_2O_3 obtained in the final step of the procedure; wt_o is the initial weight of Al_2O_3 in calcined kaolin obtained from XRF results (Al_2O_3 equals 42.125 wt%). Hence, wt_o = 4.2125, for 10 g calcined kaolin used in leaching.

The kaolin, calcined kaolin, dealuminated residue, and alumina were analyzed by FTIR, XRD, and SEM techniques. XRF of calcined kaolin was analyzed by Philips PW1606 X-ray fluorescence spectrometer. XRD was analyzed by Philips X-ray diffractometer PW 1370, C_o. with Ni-filtered CuKα radiation (1.5406 Å). Semi-quantitative phase analysis was calculated using the Bruker AXS configuration program. FTIR was traced by spectrometer Perkin Elmer FTIR System Spectrum X in the range 400-4000 cm^{-1}. TGA/DrTGA/DSC was analyzed by Netzsch STA 409 C/CD analyzer with 2°C/min heating rate from room temperature up to 1000°C, under air atmosphere at 50 ml/min flow rate the hold time at the appropriate temperature is zero. SEM was analyzed by Jeol-Dsm 5400 LG apparatus.

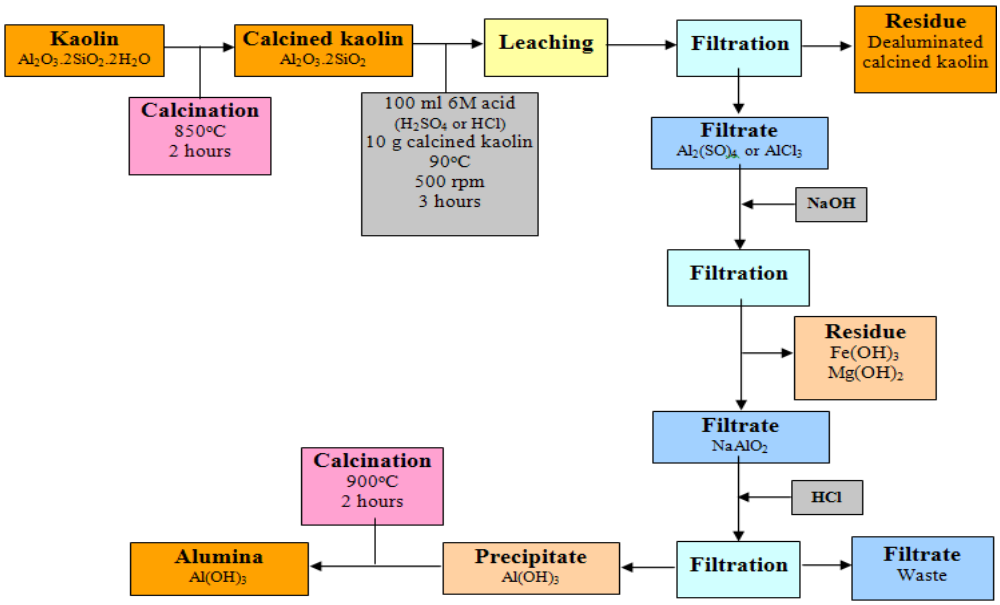

Fig. 2. Flow sheet of the proposed process

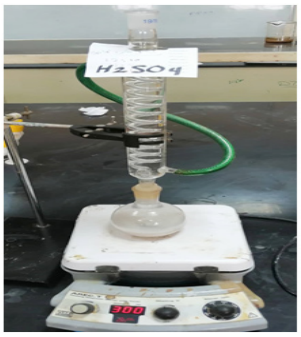

Fig. 3. Leaching system of calcined kaolin

RESULTS AND DISCUSSION

Figure 4 illustrates the thermogravimetric analysis of kaolin. The weight loss below 200°C is due to the loss of physically adsorbed water. The significant weight loss stage within the temperature range (350-700°C) and the corresponding endothermic peak and mass signal peak at 520°C are attributed to the removal of structural water in kaolin[22]. Besides, a sharp exothermic peak at 981°C is assigned to the phase transformation from metakaolinite to Al-Si spinel or the mixture of γ-alumina, amorphous silica, and mullite[39]. Clay materials contain two kinds of structural water molecules. The water molecules present in the first coordination sphere of the interlayer ions dehydroxylate in the range 300-500°C, whereas the structural hydroxyl groups dehydrate in the temperature range of 500-800°C[40].

Table 1 illustrates the XRF analysis of calcined kaolin. The major oxide contents of kaolin are 42.1 wt% Al_2O_3 and 51.3 wt% SiO_2 whereas the minor oxide contents are 1.2 wt% TiO_2 and 1.8 wt% Fe_2O_3.

Figure 5 illustrates the alumina extraction percent from calcined kaolin with HCl and H_2SO_4 as a function of the solid/liquid ratio at different leaching times. The alumina extraction percent rapidly increases with leaching time up to 120 minutes. This is due to that as time passes, the number of acid molecules that interact with the particles of calcined kaolin increases. The alumina extraction percent then increases at a slower rate thereafter. This indicates that the leaching time should not exceed 3 hours. The alumina extraction percent rapidly increases with the solid/liquid ratio up to 0.1 g/ml then decreases thereafter. This might be attributed to that at the lower solid/liquid ratio, the amount of leaching agent is sufficient up to the solid/liquid ratio 0.1 g/ml, thereafter, the amount of leaching agent compensation to every particle decreases with increasing the amount of solid in the leaching liquor[41]. The alumina extraction percent from calcined kaolin is higher for HCl than H_2SO_4. It can be concluded that the size of the chloride and sulfate ions is the key factor that controls the alumina extraction percent from calcined kaolin under the same leaching conditions. According to the literature, the radius of the ion, R_{ion}, can be defined as:

$$R_{ion} = d_{ion\text{-}water} - R_{water} \quad (3)$$

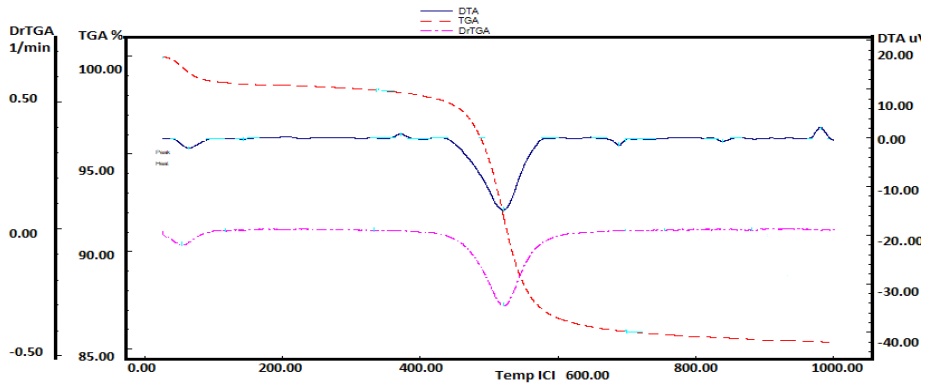

Fig. 4. TGA/DTA/Dr TGA of kaolin

Table 1: XRF analysis of calcined kaolin

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	Cl
Wt %	0.222	0.303	42.125	51.330	0.066	0.228	0.502	0.574	1.268	0.026	1.820	0.069

Where R_{water} is an appropriate distance that characterizes the radius of a water molecule, (the average of the reported value is R_{water}= 0.1420 ± 0.0005 nm), and dion-water is the mean

intermolecular distance between the ion and water molecule[42]. Several authors determined the ionic radii in aqueous solutions by using X-ray, electron, and neutron diffraction and Monte Carlo and molecular dynamics computer simulation methods[43,44].

The reported values of the Cl-(O water) internuclear distance is of the average 0.318 ± 0.006 nm, whereas that of S-(O water) is 0.381 ± 0.007 nm[42]. Hence, as the chloride ion is smaller in size compared to the sulfate ion, the attack of HCl molecules is more aggressive than H_2SO_4 on the calcined kaolin particles under the similar conditions and gives the higher alumina extraction percent. This indicates that the optimum solid/liquid ratio is 0.1 g/ml.

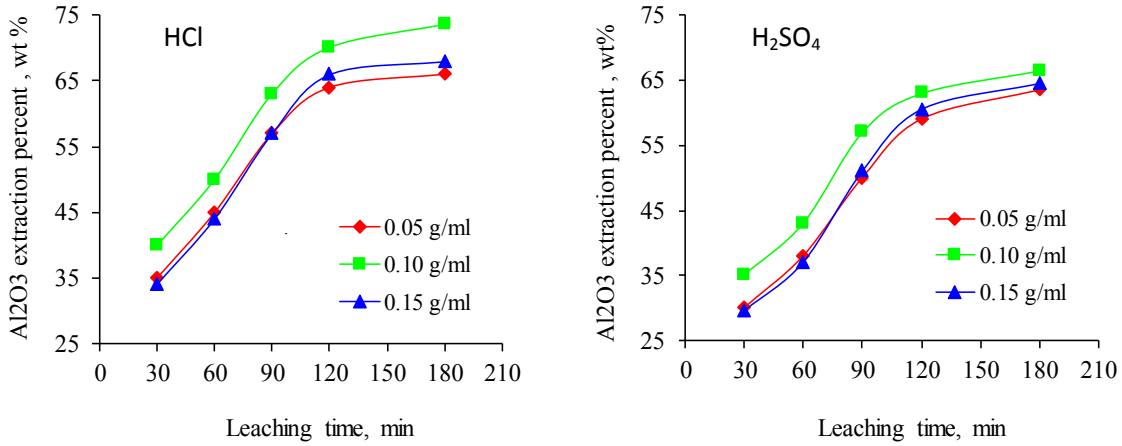

Fig. 5. Alumina extraction percent from calcined kaolin with HCl and H_2SO_4 as a function of solid/liquid ratio at different leaching times

Figure 6 illustrates the XRD patterns of kaolin, calcined kaolin, dealuminated residue, and Al_2O_3. Kaolin consists of 67.0 wt% kaolinite and 29.5 wt% quartz and traces of anatase (TiO_2). The calcination of kaolin, leads to the dehydroxylation of the kaolinite mineral, resulting in the formation of amorphous dehydroxylated aluminosilicate phases with the survival of quartz. The acid leaching of calcined kaolin by H_2SO_4 or HCl selectively dissolves alumina without dissolving silica from the amorphous dehydroxylated aluminosilicate phases. The XRD pattern of alumina shows that the two peaks at 2θ=37.8° and 45.7° are assigned to (311) and (400) diffractions of γ-Al_2O_3[45].

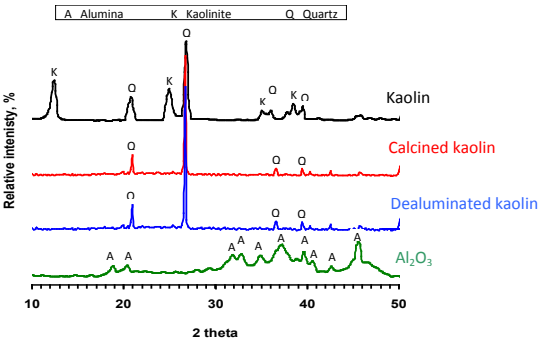

Fig. 6. XRD patterns of kaolin, calcined kaolin, delauminated kaolin and Al_2O_3

Figure 7 illustrates the FTIR spectra of kaolin, calcined kaolin, dealuminated residue, and Al_2O_3. In the FTIR spectrum of kaolin, the band at 1105 cm^{-1} is attributed to the asymmetric stretching vibrations of Si-O-Si, the band at 1025 cm^{-1} is due to the alternating stretching vibrations of Si-O-Si and Al-O-Al[46]. The band at 908 cm^{-1} is attributed to the bending Al-O-H vibrations (hydroxyl groups sitting on the alumina faces)[46]. The band at 683 cm^{-1} corresponds to the symmetric Si-O-Si stretching vibration[47].

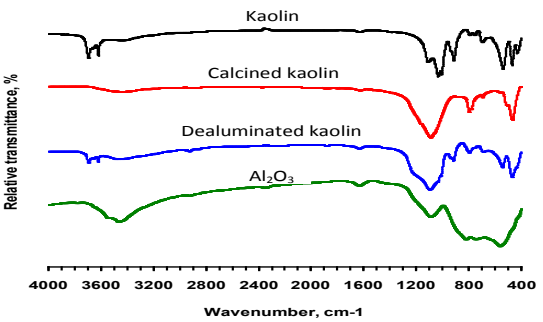

Fig. 7. FTIR spectra of kaolin, calcined kaolin, delauminated kaolin and Al_2O_3

The band at 532 cm^{-1} is due to Al^{4+}-O-Si vibrations, where Al^{4+} is in octahedral coordination[46]. The band at 465 cm^{-1} is responsible for the bending O-Si-O vibration[48]. The bands at 3700 and 3621 cm^{-1} are due to elongation vibrations of OH- groups sitting at the edges of the kaolin platelets[49]. The band at 3618 cm^{-1} is connected with the internal OH- groups[49]. The bands at 1610 and 3691 cm^{-1} are responsible for the bending HO-H vibrations of adsorbed water molecules49. In the FTIR spectrum of calcined kaolin, the bands at 792, 686 and 459 cm^{-1} are characteristic for quartz and attribute to the Si-O-Si symmetric stretching vibration and O-Si-O bending vibrations[50]. The bands at 3407 and 1610 cm^{-1} are attributed to stretching and bending vibrations of OH- groups of absorbed water[51]. The formation of the band at 1090 cm^{-1} is attributed to the Si-O stretching vibrations of amorphous SiO_2[51] proves the formation of metakaolinite structure[52]. In the FTIR spectrum of dealuminated residue, the band at 536 cm^{-1} is due to Al^{4+}-O-Si vibrations in the octahedral coordination[50]. The bands at 779, 671 and 459 cm^{-1} are characteristic for quartz due to the symmetric Si–O–Si stretching vibration and O-Si-O bending vibrations[46,50]. The new absorption band at 910 cm^{-1} is due to the Si-O-H bending vibrations of the hydrated silica formed in a leaching process that involves the replacement of Al of Al-O-Si structure with H^+ [53]. The band at 3616 cm^{-1} is attributed to the internal OH- groups[49]. The bands at 1620 and 3685 cm^{-1} are responsible for the bending HO-H vibrations of adsorbed water molecules[49]. The band at 1086 cm^{-1} is attributed to Si-O-Si asymmetric stretching vibrations[54]. This band is shifted to a lower frequency as an indication for lowering the degree of polymerization of the silica network[55] may be due to the influence of acid leaching. The FTIR spectrum of alumina, the large broadband at 400-1000 cm^{-1} is attributed to Al-O-Al stretching vibration arising from the distribution of alumina among the octahedral and tetrahedral sites[56]. The bands at 808, 722, and 562 cm^{-1} are attributed to vibration of the Al-O bonds of pseudo-boehmite structure[57]. The band at 1080 cm^{-1} corresponds to the Al-O-H mode of boehmite[57]. The very large band centered at 3440 and 3540 cm^{-1} ascribed to stretching vibration of bonded OH- groups, isolated OH- groups, and stretching vibrations of adsorbed water molecules. The band at 1614 cm^{-1} is due to bending of adsorbed water molecules[58].

Figure 8 illustrates the SEM micrographs of kaolin, calcined kaolin and Al_2O_3. The SEM micrograph of the kaolin shows hexagonal platelets of kaolinite mineral in addition to a small proportion of halloysite tubular crystals[59]. After being thermally treated, metakaolin attains its original shape. Therefore, the thermal treatment does not drastically modify the morphology[60]. The SEM micrograph of kaolin illustrates the existence of flat plate particles with sizes of around 1 µm was observed, where the flat particles stacked together. Although kaolin was calcined no changes can be observed by microscopic examination. SEM micrograph of the alumina illustrates the appearance of octahedral alumina crystals[61].

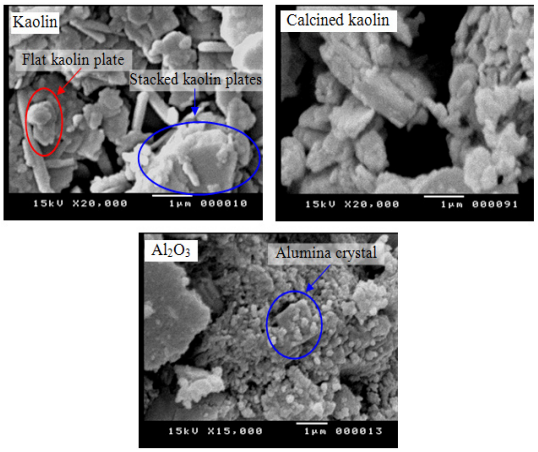

Fig. 8. SEM photographs of kaolin, calcined kaolin and Al_2O_3

CONCLUSION

This paper studied the suitability of kaolin deposits located nearby Nawan, Al Baha, KSA for the production of alumina by acid leaching with 6 M sulfuric acid or hydrochloric acid for 30-180 min and solid/liquid ratios 0.05-0.15 g/ml. The optimum conditions for the Al recovery from the studied kaolin include the grinding and screening of kaolin to particles size below 90 µm, calcination of kaolin at 850°C for 2 h leaching with 6 M HCl with the solid/liquid ratio of 0.1 g/ml for 3 h at 90°C and 500 rpm in a reflux system. The percent of aluminum recovery from calcined kaolin under the studied conditions reaches about 75 wt%.

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Confilicts of Interest

The authors declare no confilict of interest.

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