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A comparative study of the super cooling and carbonization processes of the gibbsitic Ghanaian Bauxite

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Abstract: A comparative study of the super cooling and carbonization processes of the gibbsitic Ghanaian Bauxite was investigated. Carbonization of the sodium aluminate solution ($\text{NaAl}(\text{OH})_4$) was carried out by introducing CO_2 at atmospheric pressure into the solution to obtain aluminate trihydrate gel precipitate which was calcined at a temperature of 550°C to produce gamma-alumina. In the super-cooling process, fresh alumina seed was used to precipitate the pregnant solution ($\text{NaAl}(\text{OH})_4$). The effect of Lime in desilicisation, precipitating time, lime addition and alumina yield were determined. The percentage yield of aluminum obtained at the end of experiment for carbonization and super cooling were 92% and 62% at 6 hours and 100 hours respectively. The desilicisation of 0.0008-0.001g/l of SiO_2 was effectively achieved by the addition of varied concentration of lime. The average particle size of 0.105 and 0.193 mm for both super cooling and carbonization process were obtained from the products respectively.

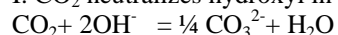
Keywords: super cooling, carbonization, sodium aluminate, carbon dioxide and Alumina.

I. INTRODUCTION

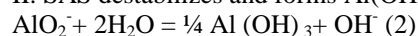
Alumina is widely used in a variety of engineering fields such as electrical insulating, microelectronic, and structural fields, because of their excellent chemical stability, electric properties and good mechanical properties besides relatively low cost in the manufacturing process. Alumina powders for sintering are, in general, prepared by calcination of mother salts such as aluminum hydroxide, ammonium alum, and ammonium dawsonite at high temperature.

The most common industrial process for alumina production from bauxite is the Bayer process. Seed precipitation is the key stage which has a significant effect on the yield and specification of product [1–3]. Supersaturated sodium aluminate (NaAlO_2) solution is obtained by dissolving aluminous ore, bauxite, in a hot solution of sodium hydroxide (NaOH). The gibbsite, $\text{Al}(\text{OH})_3$, and boehmite in the bauxite react with the caustic solution to form soluble aluminate ions, $\text{Al}(\text{OH})_4^-$. After the removal of the insoluble impurities, the supersaturated solution is cooled to the desired crystallization temperature, and supplied with gibbsite seed particles, so that the dehydroxylation of $\text{Al}(\text{OH})_4^-$ ions into $\text{Al}(\text{OH})_3$ may occur in precipitation. This hydroxide is then calcined or dehydrated to alumina for further processing and production of aluminium [4–7]. Lots of works have been done on precipitation process for enhancing precipitation ratio of sodium aluminate liquor and getting qualified products [8]. The used of carbonization to precipitate the alumina by enforced decomposition of aluminate ions by sparging CO_2 gas into desilicated sodium aluminate solution (SAS) followed by aiding with mechanical stirring is one of the alternate ways for precipitating of Aluminum liquor. Generally, carbonization can be expressed as [9].

I. CO_2 neutralizes hydroxyl in the solution because SAS is strongly alkaline.



II. SAS destabilizes and forms $\text{Al}(\text{OH})_3$ precipitate due to the neutralization of CO_2 .



During the decomposition, several physicochemical sub-processes such as mass transfer through the gas-film, reaction in the liquid film and crystallization of aluminate ions become the rate determining step at certain conditions, respectively. However, because of the complexity of the coupled process, the mechanism of carbonization is still poorly understood [10, 11] hence need for more research and more data in order to compare

with other processes. Awaso, a suburb of Ghana has large deposit of gibbsitic bauxite. In this paper the carbonization of aluminates liquor from Ghanaian gibbsitic bauxite which contains about 42w/w% of alumina was investigated. This was achieved by using CO₂ to precipitate the aluminum liquor and comparing the result with seeding or the supercooling process. The effect of precipitating time, lime addition and alumina yield were determined.

This work will therefore present a study to identify the differences that occurs in precipitation in relation to supercooling (Bayer process) and carbonization. Carbonization of the sodium aluminate solution (NaAl(OH)₄) was carried out by introducing CO₂ at atmospheric pressure into the solution to obtain aluminate trihydrate gel precipitate which was calcined at a temperature of 550°C to produce gamma-alumina. Also, for the Bayer process, fresh alumina was used as a seed to precipitate the pregnant solution. The effect of Lime in desilicisation will be monitored.

II. MATERIALS AND EXPERIMENTAL WORK

A. Materials used

NaOH (99.99%) pellets were obtained from Mina Chemical, Takoradi, Pure Powdered alumina (Aluminium oxide 60 HF254, basic Type E), Lime from Air Liquide, Tema, 25Kg of CO₂ from Air Liquide (99.99%), Tema. Table 1 shows elemental analysis of the bauxite while Fig. 1 shows an image of gibbsitic ore (thank to Ghana atomic energy commission).

Table 1: elemental analysis of bauxite

Element	Na	Fe	Si	Al
Composition w/w%	0.022	36.4	0.03	42.42

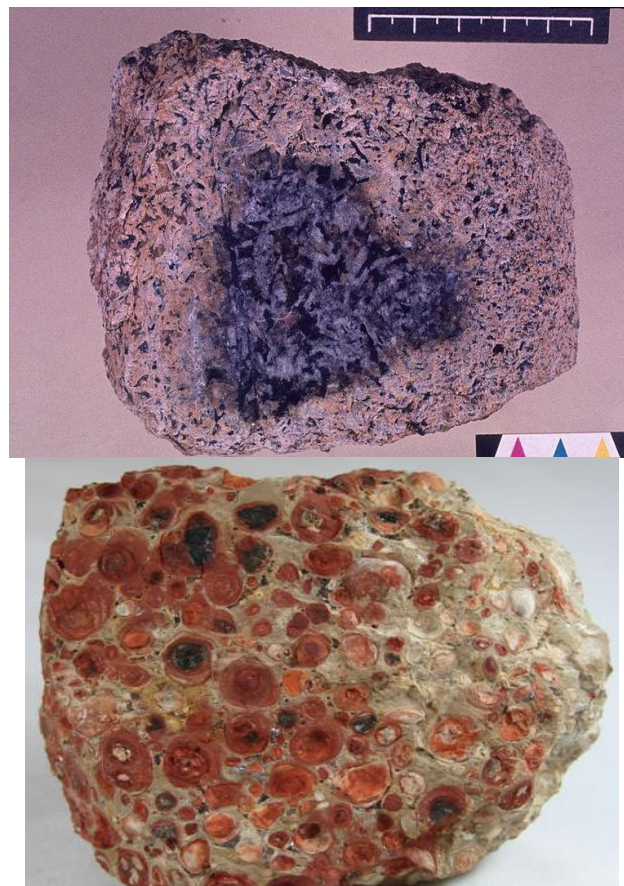


Fig.1 Image of gibbsitic ore [12]



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B. Experimental work

A composite sample made up of laterite from Awaso bauxite mines of composition 42% Al_2O_3 , 3% SiO_2 , 15-20% FeO_3 and others was washed and dried. The sample (bauxite) was crushed and milled in order to reducing the particle size and increasing the available surface area for digestion. A mesh/size analysis of 100 micron mesh of which 70% passed through and 30% retained was used. A weighed amount of ore was leached at a caustic ratio of 3.4 in an autoclave at 150°C in one and half hours. The same procedure was repeated for the addition of 3%, 6%, 9% and 12% lime (CaO). The digested pulp was cooled and diluted with distilled water at ratio of 20:1. The diluted liquor was decanted and filtered by vacuum filtration and the red mud was washed with distilled water. The washed water was used for further dilution. The pregnant liquor was precipitated by supercooling and carbonization. Fig.2 shows the process flow chat for the procedure for the experiment.

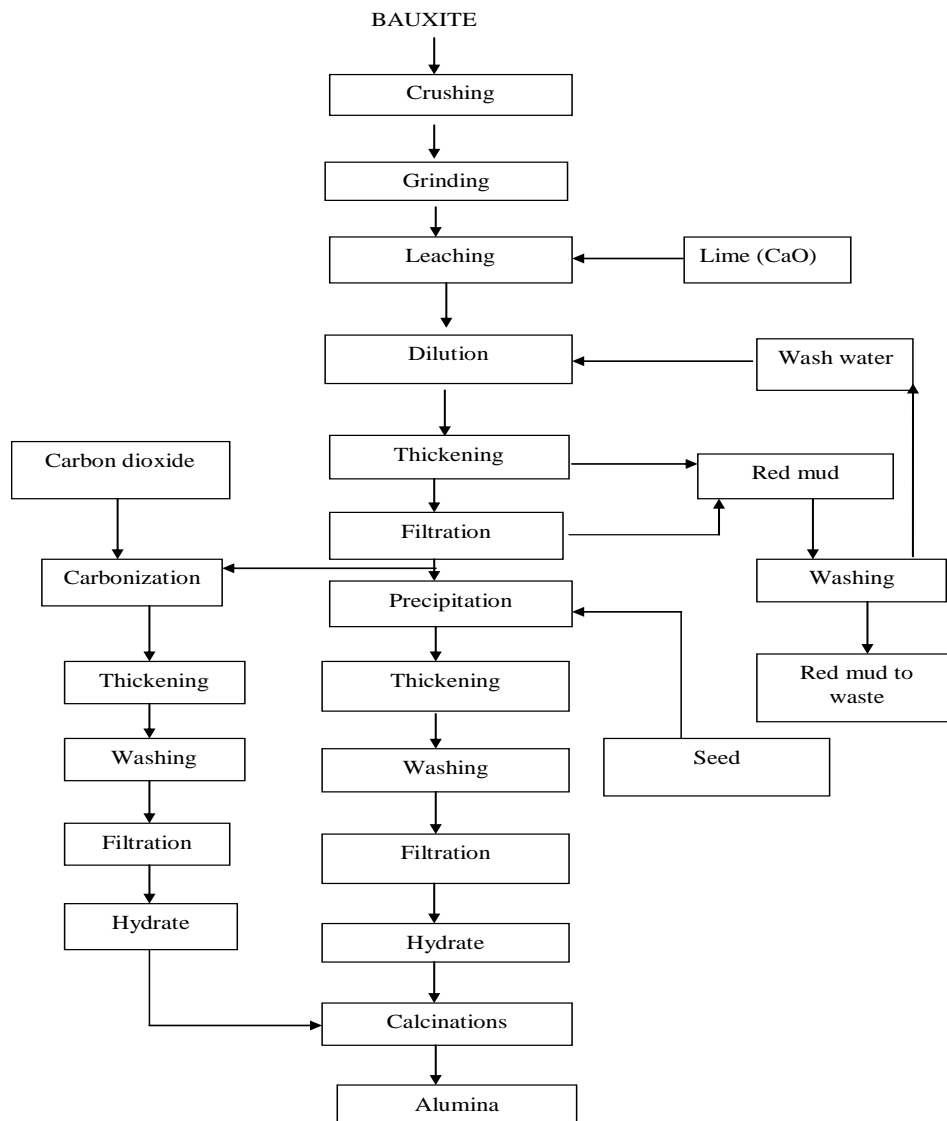


Fig. 2 Schematic representation of the overall process flow sheet.

The following steps explain both the super cooling and carbonization process; In the Super cooling process, two litres of the filtrate was heated to 80°C in five litres stainless steel container. The heated solution was seeded with pure alumina at a seed ratio of one and super cooled with persistent stirring for 6 hours. This was achieved by using ice blocks which forces the temperature from 70°C to 20°C and then from 20°C to 5°C . The resulting mixture was allowed to stand for 100 hours where the aluminate liquor decomposes.



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Likewise, in carbonization process, two litres of the filtrates were measured into flat bottom flasks and carbon dioxide gas was dispersed continuously through the solutions at atmospheric pressure for 6 hours.

Aluminium hydroxide products from super cooling and carbonization were washed vigorously with hot water to reduce the amount of Sodium Hydroxide in the products. Both washed Aluminium hydroxide $Al(OH)_3$ from super cooling and carbonization were dried in an oven at $400^\circ C$ in 1 hour. The dried products were further calcined to $550^\circ C$ in the furnace (kiln) to obtain gamma alumina within 1 hour thirty minutes.

The calcined product (alumina) was then analysed to obtain the composition of aluminium, sodium, iron and silicon in the product. The iron in the calcined product was analysed using Atomic Absorption Spectrometer 240fs while sodium, silicon and aluminium were analysed using Instrumental Neutron Activation Analysis (INAA) (again, thank to Ghana atomic energy commission). The irradiation was categorized according to the half-life of the element of interest. Table 2 below show the result of irradiation scheme analysis.

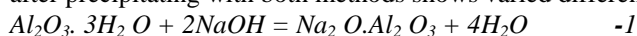
Table 2 Summary of irradiation scheme

	Element	Isotopes	Half Life	Gamma Ray Energies (keV)	Irradiation Time	Counting Time
Short Lived Radio-nuclides	Al	^{28}Al	2.24 min	1778.9	120 s	600 s
	Si	^{14}Si	2.58 h	1-100.01		

After the irradiation, radioactivity measurement of induced radionuclide was performed by a PC-based γ -ray spectrometry set-up. It consists of an n-type HPGe detector coupled to a computer based multi-channel analyser (MCA) via electronic modules. The relative efficiency of detector is 25% and its energy resolution of 1.8 keV at a γ -ray energy of 1332keV belonging to ^{60}Co . Through appropriate choice of cooling-time, detector's dead time was controlled to be less than 10%. Identification of γ -ray product radionuclide was identified through the energies and quantitative analysis of the concentration was achieved using the γ -ray spectrum analysis software, ORTEC.

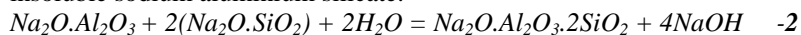
III. RESULTS AND DISCUSSION

The production of alumina from bauxite is influenced by precipitating condition. The super-cooling method of precipitating crystals from sodium aluminate solution is compared with carbonization at the presence of lime, varied time of precipitating and role of desiliconization. From reaction 1 the product of digestion without lime after precipitating with both methods shows varied differences.

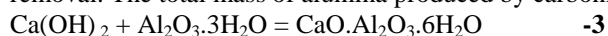


However, effective desiliconisation by lime (CaO) addition affected the mass of alumina produced. As shown in Fig. 3 the product from carbonization increased as lime also increased but obtained an optimum at 9% lime added.

At over $100^\circ C$ Aluminium Hydroxide forms a solution of Sodium Aluminates. The ferric oxide of the bauxite is unaffected by the NaOH and it is left in the residue called red mud. Part of the Silica reacted with NaOH to form insoluble sodium aluminium silicate.



As a result no impurity from the silica was left in the Sodium Aluminate solution but some NaOH and dissolved Al_2O_3 was lost. However, the presence of lime displaced the sodium ion thereby freeing the lixiviant to increased leaching in both methods as shown in reaction 2 but reaction 4 proved the role of lime in silicon removal. The total mass of alumina produced by carbonization was higher.



This phenomenon can be explained by the reaction in which $CaO \cdot Al_2O_3 \cdot 6H_2O$ is adsorbed on the surface of Calcium Hydroxide and Silica in the ore diffuse onto and reacts to form hydro garnet ($CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) [13].





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Hence, the NaOH is displaced by the lime allowing the expensive caustic to leach the alumina from the ore with little interference from the silica. The solubility of Sodium Aluminium silicate in the aluminate solution decreases by decreasing the concentration of aluminate liquor (desilicisation).

Also, for the metallurgical purpose the purity of alumina is more importance. As seen from the Fig. 4 and 5, the purity of alumina is high in both super cooling and carbonization. The increased of SiO₂ in the solution would subsequently be removed in the desilicisation stage. The pH of the pregnant liquor increases gradually with increasing solid/liquid ratio up to about 12.5.

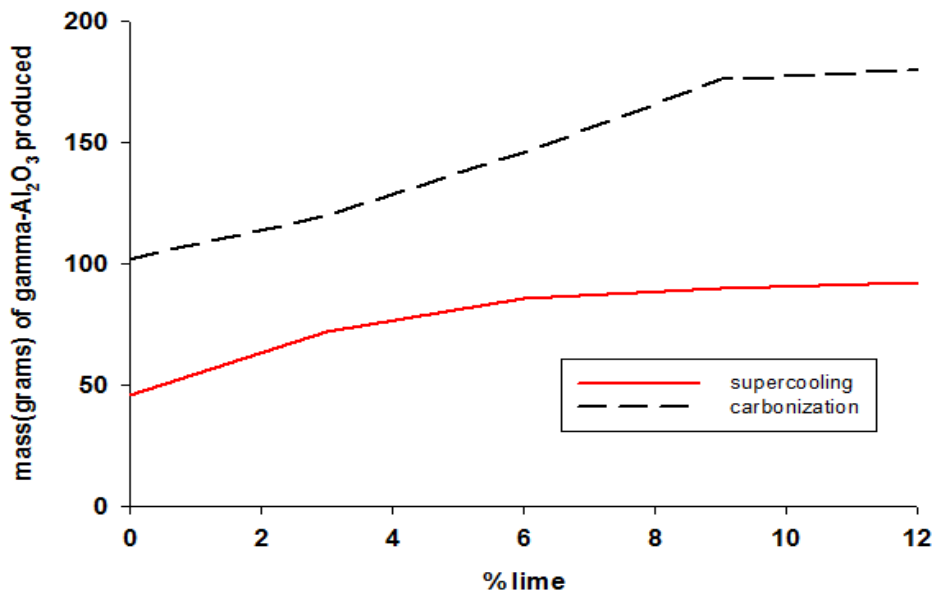


Fig. 3 mass of gamma alumina produced at varied lime concentration

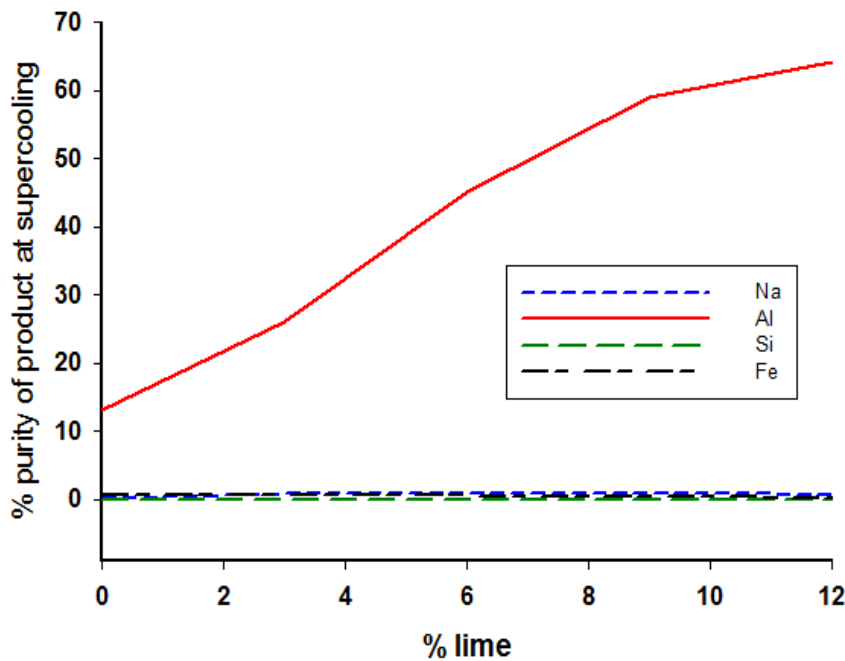


Fig.4 purity of the gamma alumina produced



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The sodium aluminate solution produced in desilicisation at room temperature contained 0.0008 to 0.001g/l silica. Hayashi [14] reported that the obtained silica concentrations are less than 0.04 g/l. The amount of silica precipitation during carbonization depends upon the amount of alumina precipitated; consequently, control of this parameter yield high purity alumina with the silica content below the maximum level for electrolytic reduction of alumina given as 0.012 to 0.020 SiO₂.

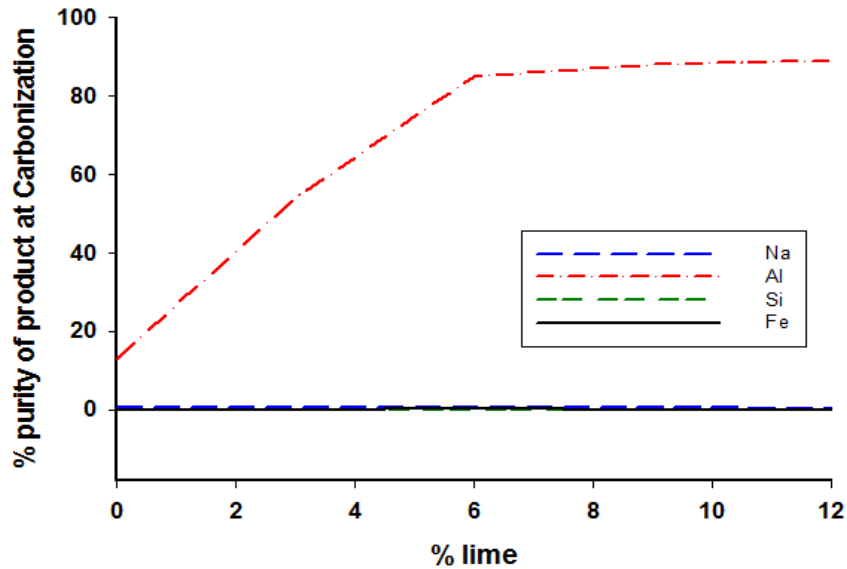
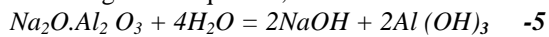


Fig.5 percentage purity of product at carbonization

The impurities such as Si, Na, and Fe were successfully removed by thorough hot water washing and as such makes the carbonized processes more suitable for metallurgical purpose.

Again, decomposition of aluminate liquor is based on the property of Sodium Aluminate to be hydrolysed according to the equation;



The sodium aluminate liquor is decomposed in two stages; the aluminate liquor is hydrolysed; particles of aluminium hydroxide form crystallizing nuclei and the crystals of aluminium hydroxide grow as shown in Fig.5 and 6. The aluminium metal concentration increased in carbonization as compared to the supercooling method.

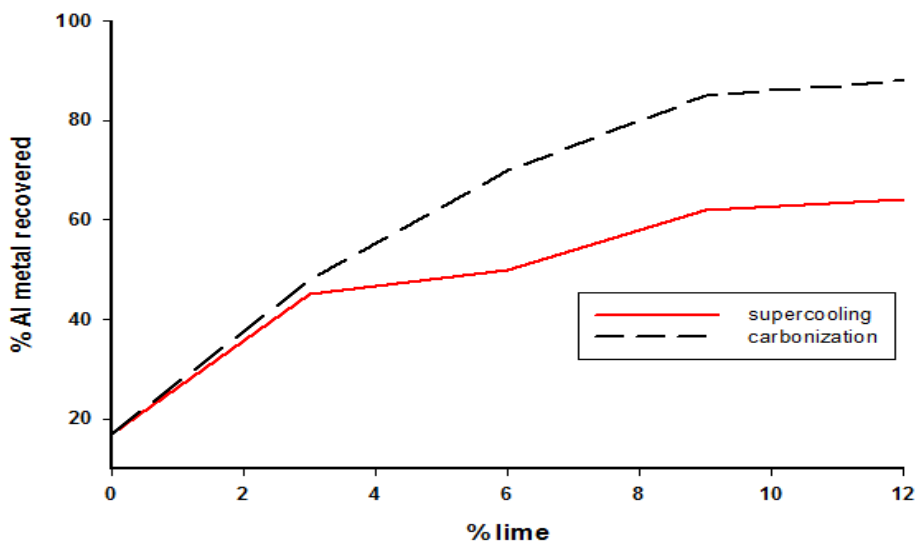
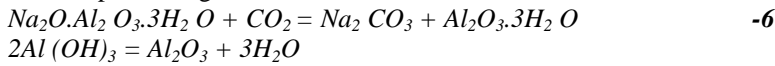


Fig.6 percentage of aluminium metal recovered at varied lime concentration

Carbonization involves the following chemical reactions and the neutralization of the leached liquor which is strongly alkaline. The acidic gas stabilizes the liquor and leads to vigorous precipitation of crystals as compared to the supercooling.



The reaction 6 epitomizes this concept and the XRD spectrum in Fig.7 of the product dried at room temperature for X-ray diffraction analysis, shows that the precipitate was amorphous with poorly crystallized alumina monohydrate.

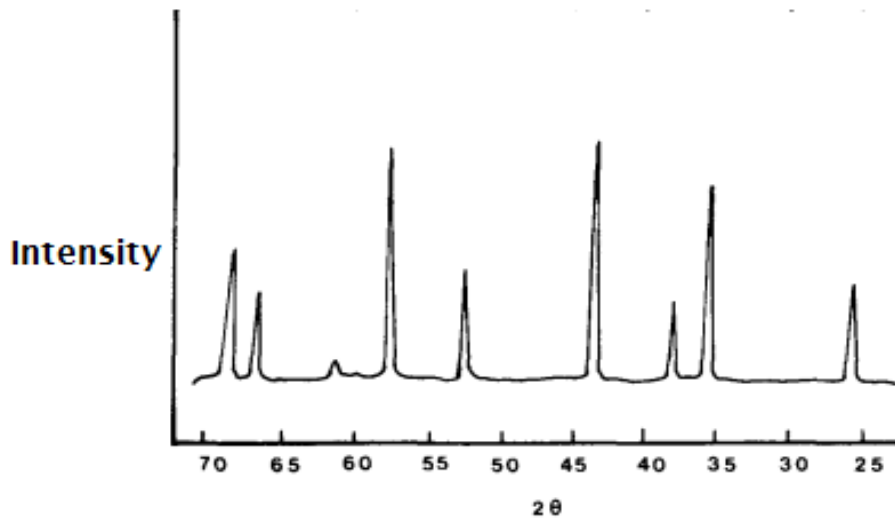


Fig.7 XRD spectrum of the carbonized gamma-alumina

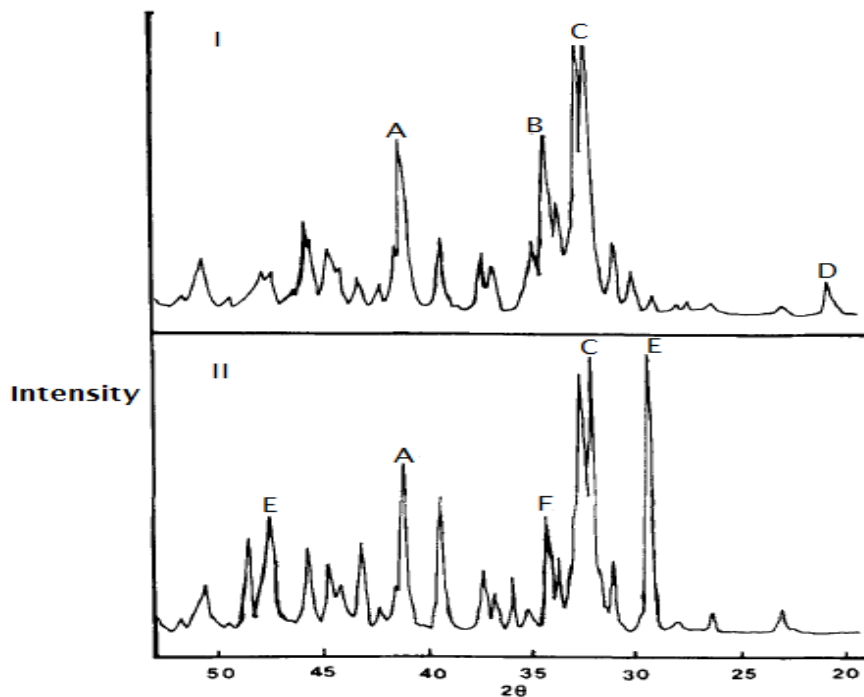


Fig.8 XRD patterns of a carbonized product of the leach residue showing hydrated

compounds; (A= $2CaOSiO_3 \cdot H_2O$; B= $Na_2O \cdot 3CaO \cdot SiO_2$; C= $\beta\text{-}2CaOSiO_2$; D= $Na_2O \cdot Al_2O_3$; E= $2CaOSiO_3$; F= $3CaO \cdot SiO_2$)

Again, Fig. 8 shows another XRD pattern of the solids after the leaching (II) and before (I). The main diffraction lines indicate the lines of unhydrolyzed dicalcium silicate and hydrolysed dicalcium silicate. The $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ compound was not detected in the pattern because of the calcium-aluminate content in the carbonized product. The predominate peaks were hydrolysed and unhydrolyzed dicalcium silicate.

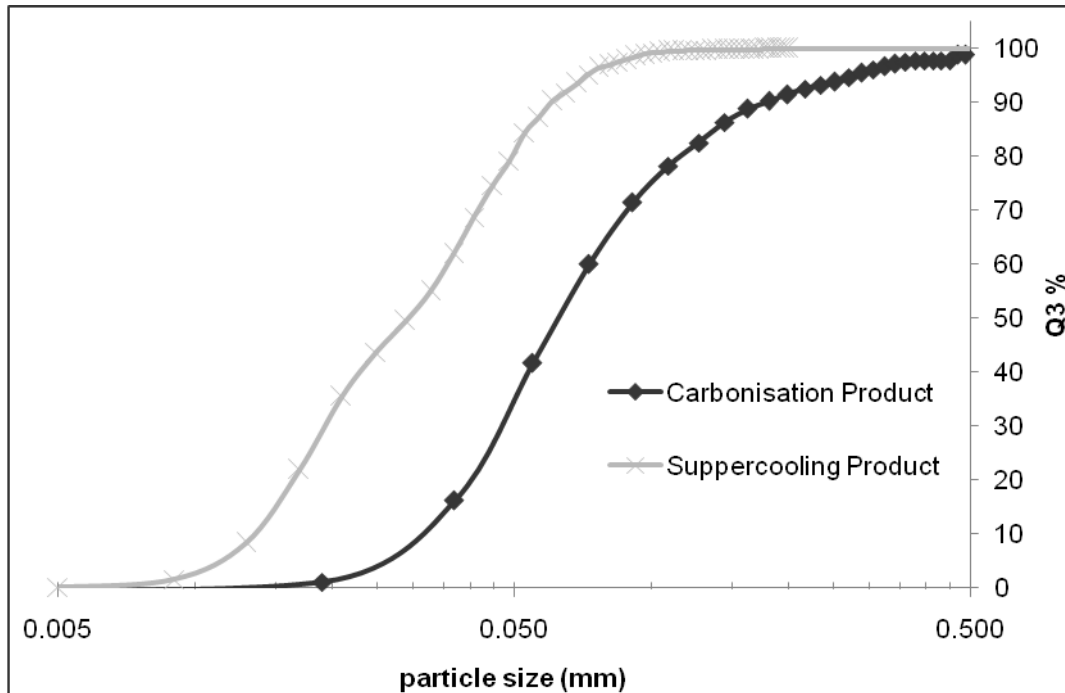


Fig. 9 particle size distribution of both suppercooling and carbonization product

On the other hand, Fig. 9 above shows the particles size distribution of both product from carbonization and supercooling. It shows that, the product from supercooling is finer than that of carbonization with an average particles size of 0.105 and 0.193mm respectively. This could be as a result of the time used for crystallization as well as smooth growth kinetic of seeding against carbonization. In the supercooling process more time was used for example 100 hours in order to produce alumina, so due this fine alumina was able to form, while in the case of carbonization process which used only 6 hour for the crystallization, even though the alumina produced has high purity. The carbonization process is more efficient but the alumina produces was coarser compare to the alumina produced from supercooling process.

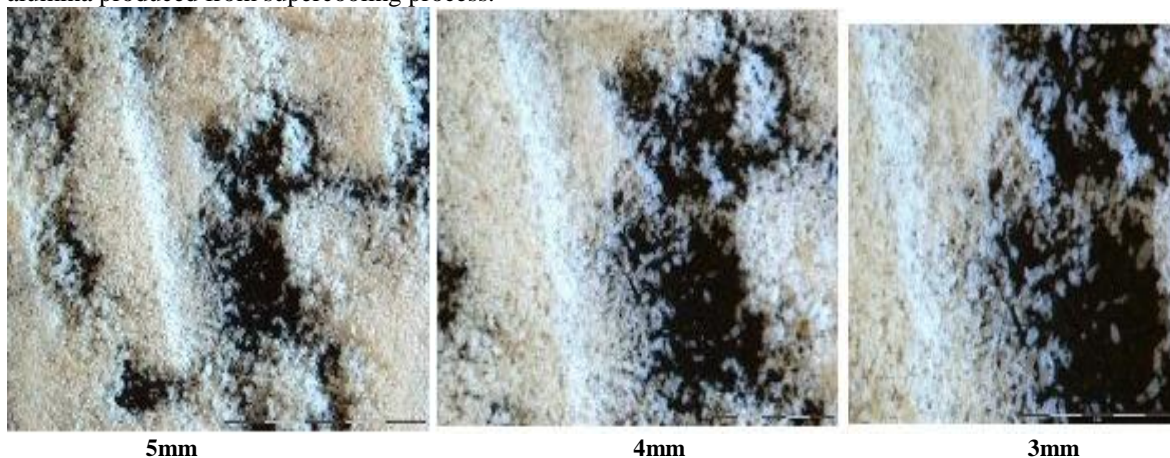


Fig. 10 SEM (microscope) for product from supercooling at different magnifications

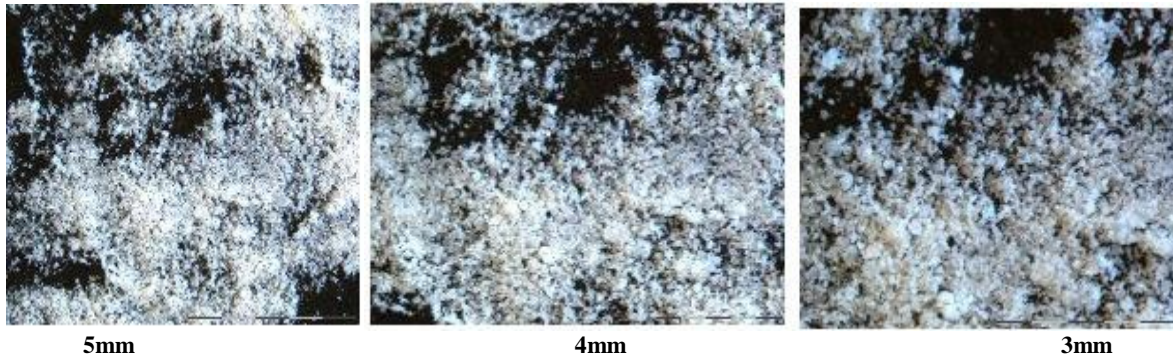


Fig. 11 SEM (microscope) for product from carbonization at different magnifications

Again, Fig. 10 and 11 shows the microscopic image of both products from supercooling and carbonization process with different magnification respectively. Even though high resolution magnification in micro range could not be obtained, but the results so far indicate that the products from supercooling have uniform morphology while the product of carbonization without seeds consists of large aggregates.

IV. CONCLUSION

From the experimental result, it could be concluded that; the percentage yield of alumina obtained at the end of experiment for both carbonization and super cooling were 92% and 65% at 6 and 100 hours respectively. The desilicisation was effectively achieved by the addition of varied concentration of lime which could be concluded that the higher rate of lime addition gave higher results of the product due to the chemical significant of lime in the process. Again, alumina from supercooling is finer than that of carbonization process with an average particle size of 0.105 and 0.193mm of supercooling and carbonization process respectively. Furthermore, the products from supercooling have uniform morphology while the product of carbonization without seeds consists of large aggregates. Hence it can be concluded that the carbonization process is more effective than the super cooling in terms of yield, production time and purity.

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