

De-soda Process Using Silica for Fabrication of Low Soda Alumina Powder

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ABSTRACT

Low soda alumina powder was fabricated using silica (α -quartz) as an agent for removing soda components in the alumina. Quartz powder 2 mm in size was added to aluminum hydroxide obtained through the Bayer process, and then the mixture was heated at various temperatures. Finally, the heat-treated powders were sieved for classification. In this study, the effects of the quartz amount and heating temperature on the mechanism of removing soda were examined. A minimum soda content of 0.005 wt% was observed at the conditions of 15 wt% quartz (based on $\text{Al}(\text{OH})_3$ amount) heat-treated at 1600°C for 8 h. The soda components, such as Na_2O , NaOH , and Na_2CO_3 , in alumina were ionized and activated at high temperature, and this facilitated the reaction with quartz silica and alumina producing nepheline. The advantages of using quartz include low iron content and low cost in comparison with the conventional de-soda process using chamotte, another silicate mineral.

Key words : Low soda alumina, Quartz, Chamotte, Bayer process, Aluminum hydroxide

1. Introduction

Alumina is one of the most general oxide ceramic materials, while being chemically stable and having a high melting point with excellent physical properties such as electrical insulation, mechanical strength, hardness, etc. Based on such properties, it is widely used in various industry areas such as refractory, abrasives, adsorbents, etc. Recent application to precision electrical, electronic areas is requiring a high electrical insulation, according to which high purification of alumina is a requisite.¹⁾

General alumina powders are fabricated by Bayer process. Aluminum hydroxide obtained from bauxite is dissolved in an aqueous solution of sodium aluminate by application of a thermal decomposition process and a chemical treatment process using caustic soda (NaOH) after which aluminum hydroxide is produced according to precipitation conditions, followed by firing to fabricate alumina powders.²⁾ Under this fabrication process, about 0.2 ~ 0.8 wt% of soda (Na_2O or Na_2CO_3) is present as an impurity in aluminum hydroxide, causing Na component to be included inside primary particle crystals or between secondary particles, which results in degradation of insulation of alumina.³⁾ Low-soda alumina is a ceramic material with increased alumina purity through controlling the contents of soda (Na_2O) in alumina. By controlling the soda contents below 0.05%, it

is applied to products such as AM (Alumina Metallizing), PCB substrate, glass-reinforcing raw material for OLED, etc., and is used particularly for structural ceramics to obtain a high sintered density at lower temperatures by grain refining.

While there are Cl_2 gas reduction method as a removal method by forming Na salt for easy volatilization through firing after adding NH_4Cl or HCl ,⁴⁾ method for removing soda through heat treatment and water cleaning of aluminum hydroxide,⁵⁾ and method for removing soda by using an inorganic acid such as dilute chloric acid solution for solvent,^{6,7)} etc. as the methods to remove soda contained in alumina, many problems exist such as occurrence of corrosion in processes, inefficiency, environmental problems and degradation in breakability and grindability as well as sintering characteristics due to large growth of alumina crystals, etc. For such reasons, low-soda alumina is obtained by using a reaction method with silicate addition in most commercial equipment and a production method by adding chamotte as a general additive is being employed.⁸⁾ In the case of this method where chamotte is used as an additive, however, domestic production is inadequate, causing problems of decreasing an overall alumina purity by increasing iron contents in the low-soda alumina products as the final product due to the high iron contents contained in chamotte. In addition, since chamotte composition remains even after sieving to cause a decrease in alumina purity, quality values are lowered by overall degradation of various characteristics.

In the present study, a fabrication method for low-soda alumina has been considered where the soda contents are controlled by employing thermal decomposition process of

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aluminum hydroxide and reaction method with silica (SiO_2 , α -quartz) addition.⁹ To such method, the principle is applied where the soda composition in alumina is decreased by removing the reactants after reacting the component in the form of soda (Na_2O , NaOH , Na_2CO_3) exposed at interfaces of aluminum hydroxide particles with SiO_2 component during the process where transition-type active alumina (or amorphous alumina) obtained through thermal decomposition process of aluminum oxide is fired to become alpha particle alumina.¹⁰ Also, in comparison with the existing chamotte method^{8,11}, the reaction method with silica addition is also a method which remarkably lowers contamination by iron contents, and reduces production costs due to the low prices as compared with chamotte. In the present article, discussion has been made with focus on what effects several process variables such as particle sizes and added amounts of silica, firing temperatures, etc. have on a change in Na_2O contents of alumina for such reaction method with silica addition. According to previous results, a decrease in soda composition has been observed as a result of particle size control for the added de-soda agent.¹² Also, fabrication of low-soda alumina has been attempted by using chamotte instead of silica, and the results have been compared and analyzed.

2. Experimental Procedure

2.1. Starting raw material for alumina

For the alumina raw material used in de-soda experiments, aluminum hydroxide (WH83, KC Co. Ltd, Korea) of 60 μm in average particle size obtained by Bayer process has been employed, with the analysis result for chemical compositions according to XRF shown in Table 1. Also, a SEM micrograph of the aluminum hydroxide employed is shown in Fig. 1.¹³ It mostly takes a form of agglomerated

Table 1. Chemical Composition of Aluminum Hydroxide (wt%)

Al_2O_3	Fe_2O_3	SiO_2	Na_2O	L.O.I.*
63.3	0.01	0.01	0.18	36.5

*Loss on Ignition

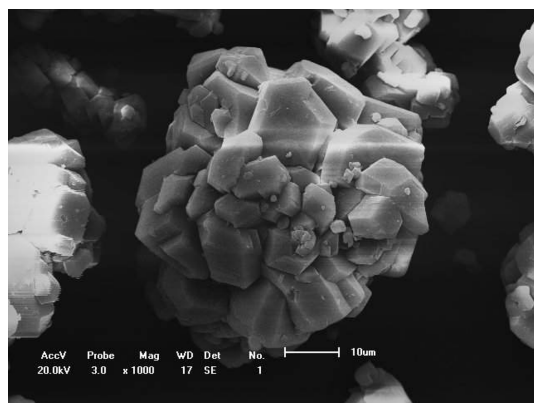


Fig. 1. SEM micrograph of aluminum hydroxide.

particles due to interposition of crystal water, etc., and primary particles show a mosaic form while taking a particle form of hexagonal plate.¹⁴ The aluminum hydroxide used for the present experiments undergoes phase transformation into α - Al_2O_3 which is stable at firing temperatures above about 1150°C after going through intermediate crystal phases such as gamma (γ), theta (θ), delta (δ), etc.¹⁵

2.2. Experiments as a function of sizes of de-soda agent

Removal rates of soda in alumina are affected by contact areas between alumina powder and additive, and hence the sizes of de-soda agent powder act as an important factor. Also, de-soda agent should be easily separated from alumina powder after being mixed with aluminum hydroxide and subsequently fired. In the present study, after silica as a de-soda agent was classified into 5 kinds of sizes by being divided through the meshes No. 4 ~ 30 (4.75 mm ~ 0.60 mm), experiments were conducted by addition of 10 wt% each based on 2 kg of aluminum hydroxide.

2.3. Experiments as a function of silica contents

Mixed with 2 kg of aluminum hydroxide was silica powder as a de-soda agent in the ratios of 15 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, and 100 wt%. Raw material and additive were mixed by dry ball-mill method for 30 min without balls placed inside, and the mixed powder was then placed in a square alumina crucible for heat treatment at the temperature of 1350°C in an air atmosphere, while being held for 1 h at the maximum temperature. Silica powder and reaction products remaining in a coarse condition within the heat-treated powder have been removed by sieving. For comparative analysis, experiments were conducted by mixing chamotte with de-soda agent by the same method. Shown in Table 2 and Table 3 are compositions of silica as a de-soda agent and chamotte employed in the experiments.

For a quantitative analysis of chemical compositions of each sample after firing, Na_2O , Fe_2O_3 , SiO_2 components were quantitatively analyzed using Standard Reference Material (699, NIST Co. USA) and XRF (XRF-1800, Shimadzu, Japan), while the scanning electron microscope (SS-550, Shimadzu, Japan) was used for observation of particle shapes of low-soda alumina samples after firing. Also, the specific surface area analyzer (TRYSTRA II 3020, Micromeritics, USA) was used for measurement of specific surface areas of the samples.

Table 2. Chemical Composition of Silica (α -Quartz) (wt%)

SiO_2	Fe_2O_3	Al_2O_3	K_2O	TiO_2	CaO/MgO
99.5	0.22	0.15	0.11	0.01	0.02

Table 3. Chemical Composition of Chamotte (wt%)

Al_2O_3	SiO_2	Fe_2O_3	$\text{Na}_2\text{O/K}_2\text{O}$	TiO_2	CaO/MgO
≥ 40.61	≥ 57.00	≤ 1.38	≤ 0.21	≤ 0.75	≤ 0.61

2.4. Experiments as a function of change in firing temperatures

After silica was added to 2 kg of aluminum hydroxide in the ratio of 15 wt%, the mixed powder was heat-treated in the temperature range of 1300°C ~ 1600°C, followed by cooling after each temperature was held for 1 h. Composition analysis was conducted for each sample of alumina obtained by sieving after firing.

2.5. Experiments as a function of holding times per firing temperature

After silica was added to 2 kg of aluminum hydrogen oxide in the ratio of 15 wt%, the mixed powder was fired at 1300°C and 1600°C while holding times were varied from 1 h to 8 h. Composition analysis was conducted for each sample of alumina obtained by sieving after firing.

3. Results and Discussion

To study the effects of particle sizes of silica used as a de-soda agent, de-soda effects were experimented by using silica classified by size. Composition analysis results of the samples with silica powder after heat treatment in air at 1350°C for 1 h are given in Table 4. Whereas Na₂O contents were decreased as the silica particle sizes were reduced, SiO₂ contents were drastically increased in the case of powder which passed through the meshes 10~18 being smaller than 1 ~ 2 mm. While separation of alumina powder and silica powder is realized through sieving after heat treatment reaction in the fabrication process, the residual amount was shown to be increased, the smaller the silica particle sizes in this case. Based on the above experimental results, it could be affirmed that the sizes of silica powder which could be most efficiently used were in the range of 1 ~ 2 mm, and hence silica powder of about 2 mm in size was employed for all subsequent experiments.

Composition analysis results of each sample as a function of added amounts of silica powder having a particle size of 2 mm are shown in Table 5. Although Fe₂O₃ contents did not show any particular change as the added amounts of silica were increased, Na₂O contents were gradually decreased down to 0.015 wt% upon addition of 100 wt% of silica, i.e., addition of the same amount of silica based on Al(OH)₃ content of the sample. On the other hand, silica composition showed a tendency of continuous increase. While general low-soda alumina is meant for products having a soda con-

Table 4. Change in Chemical Composition of Alumina Powder Fired at 1350°C as a function of Silica Sizes (wt%)

Silica size (mm)	Na ₂ O (wt%)	SiO ₂ (wt%)
0.7	0.028	0.076
0.9	0.045	0.058
1.5	0.054	0.023
3.0	0.077	0.022
4.4	0.091	0.021

tent of less than 0.05 wt%, 0.05 wt% of soda content and 15 wt% of silica content as the condition for allowing minimization of silica contamination were selected as the experimental conditions, since not only fabrication costs were raised commercially but also silica contents remaining in alumina powder were increased if the added amounts of silica de-soda agent were increased. While contamination of silica in firing processes is caused by grain refining of silica due to thermal action as the firing temperatures are raised, cracking occurs on particle surfaces by volume changes due to phase transition upon temperature rise, and particle surfaces fall off by continuous temperature rise so as not to be separated even by sieving.⁹⁾

Composition analysis results for the samples as a function of firing temperatures are shown in Table 6. A decrease in Na₂O composition with an increase in firing temperatures has been clearly observed. Na₂O composition was decreased by a given ratio up to 1500°C, after which the tendency toward a gradual decrease was indicated. Neither Fe₂O₃ nor silica composition showed any particular difference as firing temperatures were increased. Unlike volatilization method where Na is removed through production of volatilized salts by using acids such as HCl and H₃BO₃⁷⁾, the soda removal mechanism by addition of a silica de-soda agent is considered to operate by production of nepheline as a Na-Si-Al compound in a stable condition from the reaction of silica

Table 5. Change in Chemical Composition of Alumina Powder Fired at 1350°C in Various Silica Amount (wt%)

SiO ₂ Amount*	Fe ₂ O ₃	Na ₂ O	SiO ₂
0	0.013	0.253	0.018
5	0.013	0.108	0.019
10	0.014	0.057	0.022
15	0.015	0.051	0.025
20	0.015	0.049	0.033
25	0.015	0.048	0.041
30	0.015	0.033	0.057
40	0.016	0.029	0.067
50	0.016	0.024	0.075
100	0.018	0.015	0.098

*wt% based on Al(OH)₃ amount

Table 6. Change in Chemical Composition of Alumina Powder with 15 wt% Silica Additive at Various Firing Temperature

Temperature (°C)	Fe ₂ O ₃ (wt%)	Na ₂ O (wt%)	SiO ₂ (wt%)	SSA [#] (m ² /g)
1300°C	0.014	0.058	0.022	3.6
1400°C	0.015	0.039	0.024	2.8
1500°C	0.017	0.018	0.025	1.8
1600°C	0.019	0.012	0.026	0.8

[#]specific surface area

and alumina with Na. Although there are some differences depending on compositions, nepheline is being reported to be produced by 3 components of $\text{Na}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3$ at $800^\circ\text{C} \sim 1300^\circ\text{C}$, and the soda contents are presumed to be decreased by production of the compound of nepheline through ionization of soda component in alumina due to a high thermal energy and its binding with Si, Al ions.⁹⁾ For such reasons, a better efficiency of soda removal appears to have been exhibited at elevated temperatures. However, since agglomeration and grain growth of alumina powders are unavoidable upon firing at temperatures above an optimum temperature, control for appropriate firing temperatures is essential. As expected, specific surface area (SSA) of the powder has been decreased along with grain growth of alumina as a result of temperature rise.

Microstructural changes of the powder as a function of firing temperatures using the reaction method with silica addition are shown in Fig. 2. While no particular changes in microstructures were observed up to 1400°C , drastic growth of primary particles was observed above 1500°C . Further increased particle sizes were observed at 1600°C for the primary particles showing a size of about $2.0 \mu\text{m}$. Upon calcination of aluminum hydroxide mentioned earlier, the tendency toward degradation in grindability and sintering characteristics of powders was exhibited due to a large crystal growth of alumina at a given temperature in the case of volatilization method with addition of a volatilization aid for soda.^{7,16)}

Composition analysis results for each sample as a function of holding times upon firing process are shown in Table 7. At 1300°C , only a decrease in Na_2O composition was observed with an increase in holding times, while no large changes were indicated for other compositions. At 1600°C , similar results were exhibited, and Na_2O contents could be decreased to 0.005 wt% upon holding for 8 h. Specific surface area of alumina powder was shown to be reduced due to the effects of grain growth, the higher the temperatures and

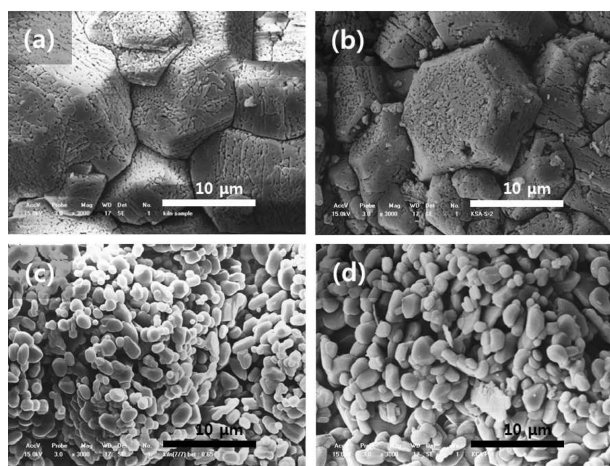


Fig. 2. SEM micrographs of alumina powder with silica additive fired at (a) 1300°C , (b) 1400°C , (c) 1500°C and (d) 1600°C .

Table 7. Change in Chemical Composition of Alumina Powder with 15 wt% Silica Additive at Various Firing Temperature and Holding Time

Temperature ($^\circ\text{C}$)	Holding Time (hr)	Fe_2O_3 (wt%)	Na_2O (wt%)	SiO_2 (wt%)	SSA (m^2/g)
1300	1	0.014	0.057	0.022	3.6
	2	0.014	0.046	0.023	2.8
	4	0.014	0.025	0.025	1.5
	8	0.015	0.017	0.025	0.8
1600	1	0.018	0.012	0.026	0.8
	2	0.018	0.010	0.026	0.5
	4	0.019	0.009	0.028	0.4
	8	0.021	0.005	0.029	0.4

Table 8. Change in Chemical Composition of Alumina Powder with 15 wt% Chamotte Additive at Various Firing Temperature

Temperature ($^\circ\text{C}$)	Fe_2O_3 (wt%)	Na_2O (wt%)	SiO_2 (wt%)
1300°C	0.023	0.055	0.033
1400°C	0.026	0.050	0.057
1500°C	0.029	0.032	0.067
1600°C	0.033	0.022	0.080

the longer the holding times.

In Table 8, the results are given after implementation of soda removal experiments with addition of 15 wt% of chamotte having a size of 2 mm as a de-soda agent. When compared with the case of adding silica (Table 6), greater contents of Na_2O were detected at high temperatures in the case of adding chamotte, and the contents of Fe_2O_3 were also increased. When chamotte was employed as a de-soda agent, more SiO_2 was observed at all temperatures. The reason for occurrence of such results despite chamotte having relatively lower SiO_2 contents compared with silica is attributed to occurrence of the decomposition as a result of temperature rise and along with existence as smaller SiO_2 particles within alumina due to non-dense structures in the case of chamotte prepared by synthesis in comparison with the single substance of silica.

4. Conclusions

By mixing silica in quartz phase as a de-soda agent with alumina and subsequent heat treatment to fabricate low-soda alumina, Na_2O contents could be decreased to a minimum of 0.005 wt%. To minimize the contents of silica included as a de-soda agent for final alumina, use of silica

particles of about 1~2 mm in size was efficient, and the economic effects as a de-soda agent could be obtained when about 15 wt% of silica was added based on the amount of aluminum hydroxide. Upon addition of silica, Na component in alumina is considered to be removed from alumina by reaction with silica and alumina components in the heat treatment process at a high temperature. By using such silica as a de-soda agent, it is considered that iron contamination can be decreased as compared with the case of fabricating low-soda alumina by using chamotte, and a cost increase for fabricating low-soda alumina powder can be reduced thereby.

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