

INFLUENCE OF PROCESS CONDITIONS ON REDUCTION OF SILICON AND CALCIUM IMPURITIES IN ALUMINUM SOLUTION

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:

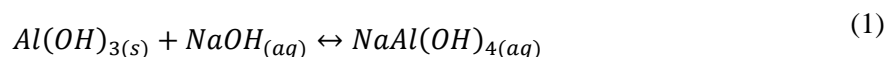
As it is known, during regular conditions Bayer's process is used for production of alumina of a 99.0 % grade of purity. In order to obtain high-purity alumina which can then be used for special purposes, additional purification is performed in relation to the application of impurities, and, in the first hand removal of silica (Si) and calcium (Ca). One of the most effective ways of removing these compounds is the process of desilication. The method consists of treating an aluminate solution with lime that binds silica and calcium to tricalcium-aluminate (TCA) which is insoluble and therefore easily separated of the solution. The experimental research examined the impact of process parameters (temperature, time, concentration of added lime) on the efficacy of purifying aluminate solution from Si and Ca, which has a practical and theoretical contribution to aluminate solution research. Synthetic aluminate from non-metallurgic alumina and pure sodium-alkaline (NaOH) is used, in the caustic ratio in the range of 1.45-1.55. Classic volume analysis and analysis using optical emission spectroscopy (ICP-OES) were used to determine the contents of aluminum and impurities. The experimental research found that short intervals are adverse because soluted compounds $\text{Ca}(\text{OH})_2$ and tetra-calcium aluminum are formed. Also, during longer reaction time and higher temperatures there was an increase in the contents of Si and Ca in the aluminum, because some components from the limestone were dissolved. Small amounts of lime are adverse because there is an increase in calcium content in the solution since part of the lime dissolved, without interacting with the present impurities, while large quantities led to large aluminum loss due to the formation of TCA.

KEYWORDS: aluminate solution, high purity alumina, lime

INTRODUCTION

The mentioned process of Al_2O_3 production is based on the precipitation of aluminum hydroxide crystals, as polymorphs of gibbsite from caustic solu-

tions of sodium aluminate [1]. The chemical basis of the Bayer process can be summarized via the following reversible chemical equation:

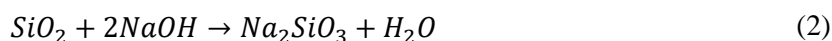


A solution of sodium aluminate was obtained by leaching the hydrated alumina from bauxite with a hot NaOH solution [2,3]. In the second part of the Bayer process, aluminum hydroxide is added to the sodium aluminate solution to act as a crystallization germ. As a result, $\text{Al}(\text{OH})_3$ crystals are segregated, which are converted into anhydrous Al_2O_3 by calcination, while the regenerated alkali is returned to the process [4,5].

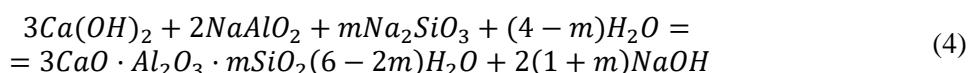
Minerals in bauxite such as rutile (TiO_2), hematite (Fe_2O_3), magnetite (Fe_3O_4), organic bitumens are

insoluble in NaOH and as such can be removed as waste sediment, known as "red mud" [6]. In addition to aluminum oxide, other minerals present in bauxite react with NaOH solution to form a soluble compound, e.g. compounds of silicon, phosphorus (P_2O_5), vanadium (V_2O_5), gallium (Ga_2O_3), sulfides (FeS_2), minerals magnesite (MgCO_3), siderite (FeCO_3)... [7]. Due to their nature, they represent a technological problem because they can be found in the final product. The most common compounds in bauxite are silicon compounds, which can be free as quartz

(SiO₂) or bound in kaolinite (Al₂O₃•2SiO₂•2H₂O) or other aluminosilicates. Their removal is the most common problem in Bayer's production process [8].



The formed sodium silicate reacts with sodium aluminate to form permutite (Na₂O • Al₂O₃ • 2SiO₂ • 2H₂O), which is insoluble and precipitates [2]. Although the solution is purified from silicon in this way, the basic problem lies in the fact that binding



This compound does not contain NaOH, which allows it to be reused in the process [6]. In addition to the basic role of purification of silicon solution, the addition of lime increases the leaching rate and the degree of alumina utilization [9]. The mechanism of action is such that it destroys the insoluble membranes of sodium titanate that envelop Al(OH)₃ parti-

They react with the alkali to form a solution of sodium silicate:

Na₂O and Al₂O₃ also occurs, which represents a pure loss of alkali and aluminum.

By adding lime, one part of the dissolved silicon will bind into a low soluble hydrogranate:

cles, thus enabling their contact with the alkali [10,11,12].

Despite the process of purification of bauxite by the Bayer process, the corresponding impurities remain in the solution and later crystallize together with aluminum hydroxide. **Table 1** shows the content of non-metallurgical and metallurgical alumina.

Table 1. Composition of metallurgical and non-metallurgical alumina [13]

Component	Metallurgical alumina		Non-metallurgical alumina	
	Typical values [%]	The limit values [%]	Typical values [%]	The limit values [%]
Al ₂ O ₃	98.8-99.0	98.7	98.8-99.0	98.7
SiO ₂	0.005-0.010	0.015 max	0.005-0.010	0.015 max
Fe ₂ O ₃	0.008-0.012	0.018 max	0.008-0.012	0.018 max
Na ₂ O _{total}	0.30-0.35	0.42 max	0.15-0.20	0.25 max
CaO	0.018-0.025	0.030 max	0.018-0.025	0.030 max
P ₂ O ₅	0.0002-0.0005	0.0009 max	0.0002-0.0005	0.0009 max
TiO ₂	0.0020-0.0027	0.003 max	0.0020-0.0027	0.003 max
ZnO	0.017-0.020	0.022 max	0.017-0.020	0.022 max

As can be seen from **Table 1**, 1-1.3 % of impurities can be found in the final product, where SiO₂, CaO, Fe₂O₃, ZnO and Na₂O make up the largest part. As mentioned, silicon and calcium compounds are removed by desilicization by adding calcium compounds to the solution (mainly lime is used) which has the role of binding the present silicon to the insoluble compound [14]. Fe₂O₃ and ZnO are removed by the addition of finely precipitated hydroxide which acts as a crystallization germ, while Na₂O is removed by the hydrothermal washing method [15,16,17].

Silicon dioxide (SiO₂) aggravates most of the industrially important properties of alumina, and is undesirable (but usually unavoidable) in the product.

First, silicon is a harmful pollutant in aluminum metal, and especially in industrial alumina powder [4]. A bigger problem occurs with the application of alumina in special processes. Thus, a very important question is what is the composition of the alumina used as a raw material for the production of alumina-based ceramics, given that silicon contamination is a problem in all advanced applications of ceramics. Silicon is harmful in the high-quality ceramic industry because it concentrates on grain boundaries and makes alumina sensitive to static fatigue caused by moisture; it is a serious problem if it occurs in dental or orthopedic implants, reduces refractoriness when alumina is used as a refractory material, reduces hardness [18,19,20].

The subject of this research is the removal of silicon and calcium from the aluminate solution by the addition of calcium oxide in order to obtain special (advanced) types of high purity alumina. For this purpose, the aluminate solution was treated with lime during the experiment because it is the most industrially and commercially acceptable, most efficient, does not change the caustic ratio and does not contaminate the solution. This paper also investigates the influence of process parameters (desilicization time, temperature and amount of added lime) on the process of silicon and calcium removal.

EXPERIMENTAL

MATERIALS AND METHODS

Non-metallurgical hydrate obtained in the factory "Alumina" d.o.o. Zvornik and alkali NaOH were used as raw materials for obtaining ultra-pure aluminum hydroxide.

The leaching rate of aluminum hydroxide is optimized by the addition of lime ($CaO_{active} = 90.93\%$).

SYNTHESIS OF SYNTHETIC ALUMINATE

To obtain a volume of 1 l of synthetic aluminate with caustic modulus $\alpha_k=1.50$ (tolerance 1.45 - 1.55), 204 g of sodium hydroxide and 260 g of dry non-metallurgical hydrate were weighed on an analytical scale. The measured NaOH was transferred to a 2 l beaker and then was added water up to 350 ml. This solution was first heated and then dry non-

metallurgical hydrate was added moderately. The resulting solution was further heated and allowed to boil for 15 min.

After that, the obtained aluminate solution was cooled to room temperature and transferred to a 1 l Erlenmeyer flask, with water addition to the line marked on the neck of the flask. Volume (100 ml) of the solution was taken to determine Al_2O_3 , Na_2O_k , Ca and Si in the initial sample, while the rest was transferred to a beaker and heated to the synthesis temperature. Finally, a given amount of lime is added to that synthetic solution.

Upon completion of the synthesis, the solution was filtered using a Büchner flask and funnel (a white filter strip was used). The filtrate as well as the initial sample was subjected to classic volumetric analysis and analysis using optical emigration spectroscopy to determine the content of Al_2O_3 , Na_2O_k , Ca and Si. The precipitate left on the strip was washed with 1 l of hot distilled water and then dried for 2 h at 105°C to remove a coarse moisture.

RESULTS AND DISCUSSION

INFLUENCE OF TIME ON THE PROCESS OF PURIFICATION OF ALUMINATE SOLUTION

Determination of the influence of time on the purification of silicon and calcium was performed at a temperature of $t = 65$ °C, the amount of additional lime of 20 g/l for different times of 10 - 50 min. **Table 2** shows the results.

Table 2. Influence of time as a process parameter on the purification of aluminate solution

Method of analysis	Time [τ]					
	Initial sample	10 min.	20 min.	30 min.	40 min.	50 min.
Classic volumetric analysis						
	Na_2O_k [g/dm ³]	156.55	156.55	156.55	156.55	156.55
	Al_2O_3 [g/dm ³]	169.83	168.30	164.73	163.88	163.26
	α_k	1.52	1.53	1.56	1.57	1.58
ICP-OES						
	Ca [ppm]	9.08	1.36	2.28	1.72	0.96
	Si [ppm]	78.16	30.8	23.68	23.44	20.08
Granulation TCA						
	ds50% [μ m]		6.18	7.47	6.19	8.06
					9.08	

The concentration of Na_2O_k remained the same even after 50 min., which confirms the fact that the hydrogranate was formed by addition of lime, which does not bind alkali. The amount of Al_2O_3 in the solution decreases from 169.83 g/dm³ in the initial sample to 161.97 g/dm³ after 50 min. of reactions, with a corresponding increase in the caustic module.

The Si content decreases over time, while the Ca content is the lowest after 40 min. The reason for that is that insoluble tricalcium aluminate was formed. A further increase in time leads to an increase in the Ca content in the solution because certain components from the industrial lime have dissolved. From the previous table, it is clear that at a temperature of

65°C and at amount of 20 g/l of lime, the time after process should be stopped is 50 min. Although there was a slight increase in the calcium content of the solution, at that time the silicon content was the lowest.

INFLUENCE OF TEMPERATURE ON THE PROCESS OF PURIFICATION OF ALUMINATE SOLUTION

Figures 1 and 2 show the influence of temperature on the content of aluminate solution by the addition of 20 g/l of lime and after 120 min. of reaction.

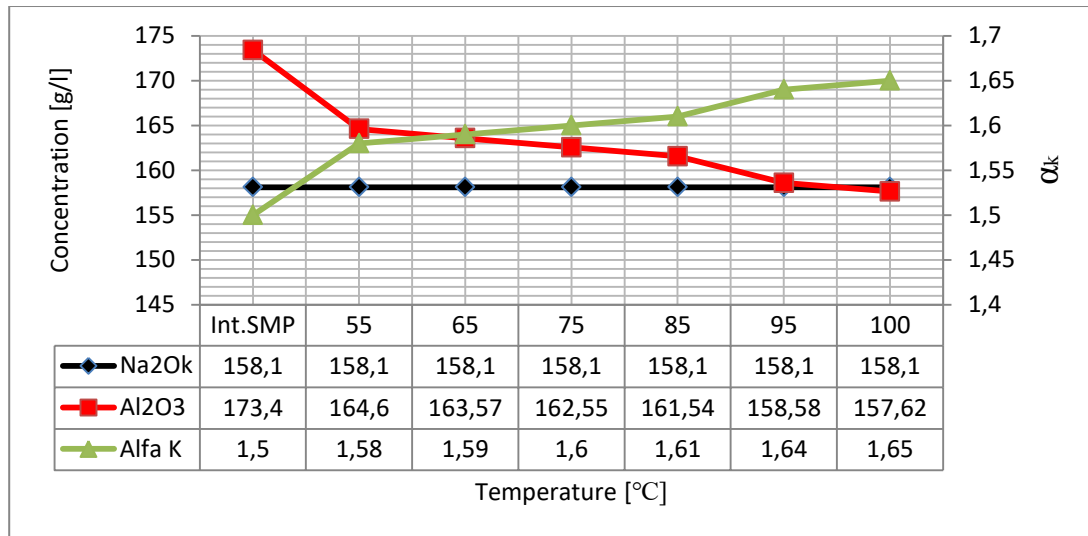


Figure 1. Dependence of caustic ratio and concentration of Na₂O_k and Al₂O₃ on temperature

As with the influence of time as a process parameter, even with a change in temperature there is no significant change in the content of caustic soda. The

aluminum content decreases with increasing temperature, which is followed by an increase in the caustic module.

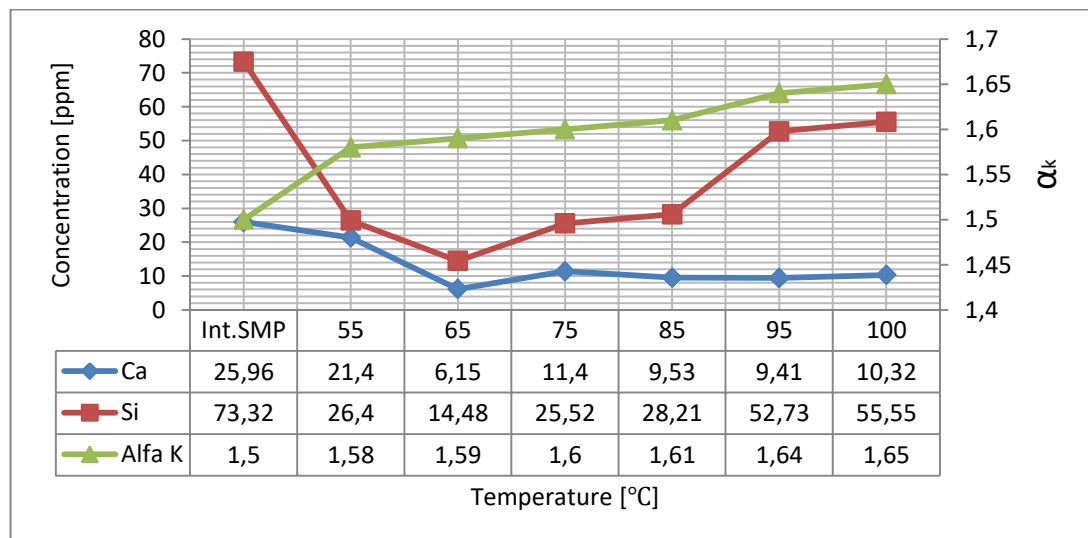


Figure 2. Dependence of Si and Ca contents on temperature

At temperatures below 55°C, calcium removal is very slow, and only 17 % of the starting amount is removed. From the previous diagram it can be seen that the concentration of calcium is the lowest at 65°C, at which its concentration is 6.15 ppm. Unlike calcium, the removal of silicon is more intensive at

lower temperatures (removed even 65 % Si at $t = 55^\circ\text{C}$), while at a temperature of 65°C, similar to calcium, the maximum amount of silicon is removed. At this temperature, the minimum concentration of Si and Ca is observed on the graph of the dependence of concentration on temperature (Figure 2). At higher

temperatures, there was an increase in the solubility of the components present in the lime, which in total increases the concentration of impurities in the final aluminate. Therefore, this temperature is adopted as optimal and future industrial processes of obtaining high purity alumina can take place on it.

INFLUENCE OF THE AMOUNT OF ADDED LIME ON THE PROCESS OF PURIFICATION OF ALUMINATE SOLUTION

Determination of the influence of the concentration of added lime was performed at the following process parameters:

$t = 65 \text{ }^\circ\text{C}$
 $\tau = 120 \text{ min.}$
 $c_{\text{lime}} = 7.5 - 50 \text{ g/l}$

Even at different concentrations of added lime, the amount of sodium present in the solution will not change and will remain the same as in the starting sample. As the amount of added lime increases, the Al_2O_3 content in the solution decreases. Increasing the concentration of calcium present leads to a larger number of collisions with aluminum molecules from the aluminate, which results in the formation of insoluble tricalcium aluminate (**Figure 3**).

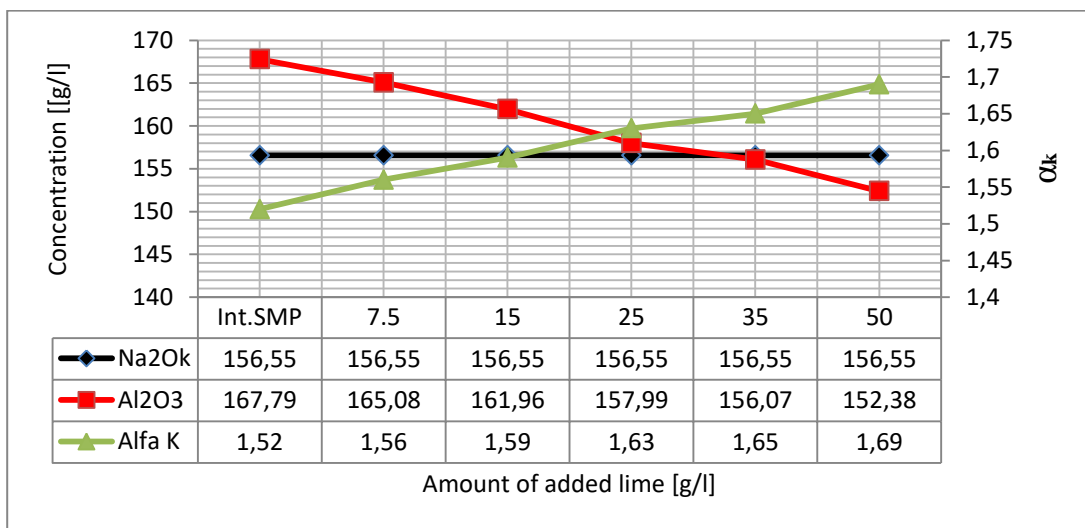


Figure 3. Dependence of the caustic ratio and concentration of Na_2O_k and Al_2O_3 on the amount of added lime.

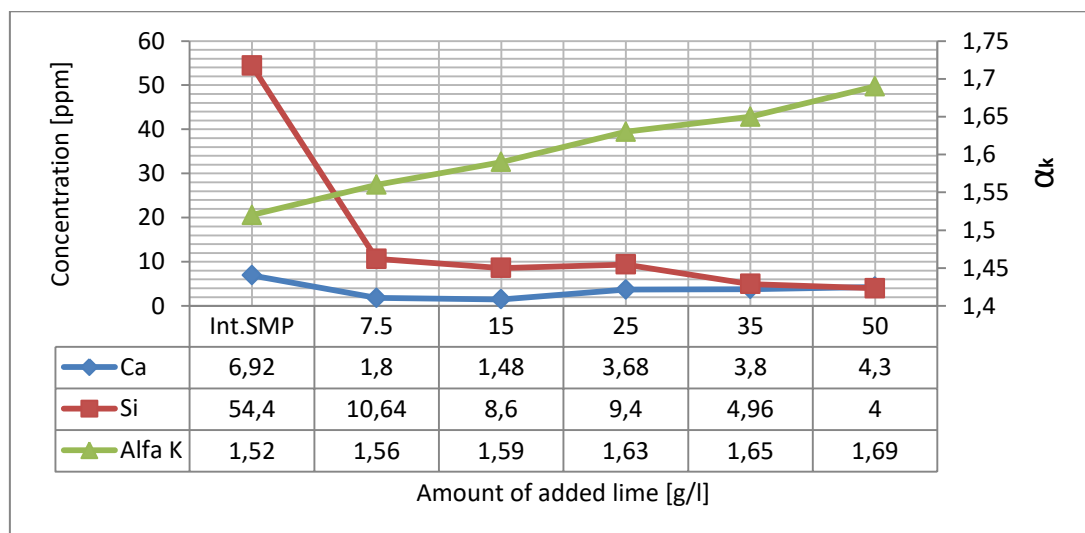


Figure 4. Dependence of Si and Ca content on the amount of added lime

Figure 4 shows the dependence of the content of Si and Ca in the solution on the amount of added lime. The addition of relatively small amounts of lime is advantageous because there is a pronounced

removal of calcium and silicon in the solution. The addition of 15 g/l of lime removes most of the calcium and it lagged only 1.48 ppm. With further addition of lime, the value of silicon constantly decreases,

while the content of calcium in the solution increases. After 120 min. of reactions and at a temperature of 65°C, depending on whether it is desired to remove more calcium or silicon, two different optimal amounts of added lime are adopted: 15 g/l and 50 g/l of added lime. The addition of 50 g/l of lime removes most of the silicon due to the formation of insoluble hydrogranate, but in some cases this is not desirable because larger amounts of impurities pass from industrial lime into solution and because the Al_2O_3 content decreases due to insoluble tricalcium aluminate. Therefore, the process can take place with the addition of 15 g/l of lime, whereby larger amounts of calcium are removed with significantly lower losses of aluminum.

CONCLUSION

The aim of this study was to determine the influence of process parameters on the removal of silicon and calcium from non-metallurgical hydrate, which can then be used as a precursor for obtaining special types of alumina. Unlike the Bayer process where bauxite is the starting material, in this case the non-metallurgical hydrate was converted to a soluble form by the addition of alkali and then treated with lime to remove Si and Ca. In order to determine the parameters at which the largest amount of impurities will be removed, the optimal temperature, reaction time and the amount of added lime during the desilication process were determined.

In the process carried out at a temperature of 65°C and the amount of additional lime of 20 g/l, the optimal duration of the desilication process is 50 min. During this time, most of the silicon is removed because an insoluble compound of hydrogranate, which contain Ca and Si, is formed, which purifies the solution. The desilication process, which was carried out at $\tau = 120$ min., $c_{CaO} = 20$ g/l and temperatures in the range of 55 - 100°C, determined the mechanism of removing impurities from the solution. Calcium and silicon had the lowest value at a temperature of 65°C, why is this temperature considered as optimal on which future processes could be based. Higher temperatures led to the dissolution of individual components from the lime, which resulted in an increase in the impurity content in the final solution. Finally, the influence of the amount of added lime on the desilication process was determined. The addition of 50 g/l of lime removes most of the silicon, but due to the formation of insoluble hydrogranate, large losses of aluminum are expressed. Therefore, in special cases, 15 g/l of lime is added, removing most of the calcium with negligible alumina losses.

During future research, additional optimization is needed to determine the concentration of lime and its full effect on calcium removal. For that purpose, research should be performed by adding lime in the range $c_{CaO} = 7.5 - 15$ g/l. The next round of optimization should be performed at the recommended value of the amount of lime addition and temperature, while the time range will be extended in relation to this research and will be in the range of 10 - 130 min. Also, in order to obtain high purity alumina, in addition to desilication as a method of removing Si and Ca, it is necessary to include a method based on the addition of crystallization initiators which remove zinc (Zn) and iron (Fe), and a method of hydrothermal washing which removes sodium (Na). By optimizing the parameters from the purification procedures, high-purity aluminum hydroxide was synthesized, which can be used for special purposes due to its physical and chemical properties.

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